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# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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# Chiral Schiff Base Ruthenium(II) Carbonyl Complexes: Synthesis, Characterization, Catalytic and Antibacterial Studies

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# Chiral Schiff Base Ruthenium(II) Carbonyl Complexes: Synthesis, Characterization, Catalytic and Antibacterial Studies

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Chiral Schiff base ruthenium(II) carbonyl complexes of the type [Ru(CO)(L')(B)] (L'= tetradentate Schiff bases; B = PPh<sub>3</sub>, pyridine (py), piperidine (pip) or morpholine (morph)) has been synthesised by the reactions of  $[RuHCl(CO)(PPh_3)_2(B)]$  (B = PPh<sub>3</sub> or py or pip or morph) with appropriate Schiff bases having the donor groups (O,N) viz., bis[3(1'-naphthyl)salicylidene-cyclohexanediimine] (L1) or bis[3(1'-naphthyl)salicylidenepropylenediimine] (L2) or bis[3(1'-naphthyl)salicylidenediphenyldii mine] (L3) in 1 : 1 molar ratio. Complexes have been characterized by elemental analyses and spectral (IR, electronic, <sup>1</sup>H- and <sup>31</sup>P-NMR) data. An octahedral structure has been tentatively proposed for all the new complexes. The catalytic and antibacterial activities have also been carried out for these new complexes.

Keywords chiral ligand, ruthenium(II), deprotonation, steric effect, chelation

## INTRODUCTION

During the past decades, there has been a great deal of interest in the synthesis and characterization of transition metal Schiff base chelates because of their importance as catalysts in many reactions.<sup>[1-4]</sup> Recently, Kureshy et al. reported, enantioselective epoxidation of non functionalised olefins, *viz.* cis-stilbene, trans-3-nonene and trans-4-octene with iodosyl benzene as oxidant was demonstrated in the presence of catalytic amounts of chiral Schiff base metal complexes.<sup>[5]</sup> Furthermore, tetradentate Schiff base complexes are important in

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designing metal complexes related to synthetic and natural oxygen carriers.<sup>[6]</sup> Extensive information is available on the chemistry of transition metal complexes containing Schiff bases, related mostly to first row transition metals, relatively little work has been done on ruthenium complexes containing Schiff bases.<sup>[7]</sup> Ruthenium complexes, by virtue of their wide range of reversible and accessible oxidation states, have proved to be useful catalysts in many reactions such as hydrogenation, oxidation, carbonylation, hydroformylation, etc.<sup>[8-10]</sup> In addition, some ruthenium carbonyl complexes play an important role in homogeneous catalysis.<sup>[11]</sup> In view of not only to investigate the coordination behavior of chiral Schiff bases containing N2O2 chromophores, but also to assess the catalytic and biological activity of new complexes, we report the synthesis, spectral, catalytic and antibacterial studies of ruthenium(II) carbonyl complexes of the type [Ru(CO)(L')(B)] (L' = chiral Schiff bases; B = PPh<sub>3</sub>, pyridine (py), piperidine (pip) or morpholine (morph)). The general structure of chiral Schiff base ligands used in this study is shown in Figure 1.

# **EXPERIMENTAL**

Commercially available RuCl<sub>3</sub>.3H<sub>2</sub>O was used without further purification. The solvents were purified and dried according to the standard procedures.<sup>[12]</sup> Elemental analyses were carried out by using Carlo Erba 1106 elemental analyzer. IR spectra were recorded with Nexus FTIR spectrophotometer in the range  $4000-500 \text{ cm}^{-1}$ . Electronic spectra were recorded in CH<sub>2</sub>Cl<sub>2</sub> on Hitachi-Elmer Model 20/200 spectrophotometer. Melting points were recorded on Micro heating table and are uncorrected. <sup>1</sup>H-NMR and <sup>31</sup>P-NMR spectra were recorded on a Brucker 400 MHz instrument using TMS and *o*-phosphoric acid as an internal reference, respectively. The starting complexes<sup>[13]</sup> and Schiff base

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$$\mathbf{L1} \qquad \mathbf{R}_1 = \mathbf{R}_2 = (\mathbf{CH}_2)_4$$

L2 
$$R_1 = H, R_2 = CH_3$$

L3 
$$R_1 = R_2 = C_6 H_5$$

FIG. 1. Structure of chiral Schiff base ligands.

ligands<sup>[14]</sup> have been prepared by the procedures available in literature.

## General Procedure for Preparation of [Ru(CO)(L')(B)](L' = dibasic chiral Schiff base ligand; B = PPh<sub>3</sub> or py or pip or morph)

To a benzene (20 mL) solution of  $[RuHCl(CO)(PPh_3)_3]$  or  $[RuHCl(CO)(PPh_3)_2(B)]$  (B = py or pip or morph) (0.077–0.095 g, 0.01 mmol), added the appropriate Schiff base ligands (0.060–0.087 g, 0.01 mmol) (molar ratio of the ruthenium complex:ligand = 1:1). The resulting mixture was heated under reflux for 5 h. The completion of the reaction was checked by TLC, concentrated on rotavapor to 3 mL and precipitated by petroleum ether (60–80°C). The complexes were filtered, washed with petroleum ether and recrystallised from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (60–80°C) and its purity was checked by TLC (yield: 75–85%).

#### **Catalytic Studies**

The catalytic activity of ruthenium(II) carbonyl complexes in aerial oxidation of cinnamaldehyde was followed by spectrometrically monitoring the increase in the cinnamic acid absorbance as a function of time. A chloroform solution of the ruthenium(II) complex (2 mL,  $1 \times 10^{-4}$  M) and 2 mL of  $1 \times 10^{-3}$  M freshly distilled cinnamaldehyde in chloroform was mixed in 1 cm quartz cell at room temperature (24°C) and the absorbance change at 280 nm was recorded.

#### **Antibacterial Studies**

Two pathogenic microbials were used to test the biological activity of the ligands and their ruthenium(II) carbonyl complexes, namely, *S. aureus* and *S. typhi*. The nutrient agar (NA) medium was prepared<sup>[15]</sup> and a quantity of 10 mL of the medium was poured into the sterilized Petri plates and allowed to solidify. The plates were inoculated with spore

suspensions of pathogenic bacteriocides. By using the sterilized cork borer, wells were dug in the center of the culture plates. The test complex solution (0.5 mL) in DMSO was added to these wells, and the plates were incubated at  $26 \pm 2^{\circ}$ C for 24 h. Then the inhibition zone appeared around the wells in each plate was measured and recorded as the cytotoxic effect of the appropriate complexes. The solvent only treated plate was maintained separately in order to avoid the activity due to solvent, if any. *Streptomycin sulfate* was used as a standard.

#### **RESULTS AND DISCUSSION**

Chiral Schiff base ligands react with  $[RuHCl(CO)(PPh_3)_2(B)]$  (B = PPh<sub>3</sub> or py or pip or morph) in 1 : 1 molar ratio in benzene to afford stable chelated ruthenium(II) carbonyl complexes as shown below (Scheme 1). The new complexes are soluble in most of the common organic solvents. Molecular weight determination (Rast method) and elemental analysis data (Table 1) confirm the complexes to be a hexa-coordinated.

#### **Infrared Spectra**

The IR spectra of the Schiff base ligands were compared with that of the ruthenium complexes to obtain the information about the binding mode of the ligands to ruthenium metal in the complexes (Table 2). A strong band was observed at 1640– 1620 cm<sup>-1</sup> in the spectra of the free Schiff bases, which is the characteristic of the azomethine (-HC=N) group. It is expected that coordination of the nitrogen to the metal atom would reduce the electron density in the azomethine group and thus lower the -HC=N absorption. In the IR spectra of the complexes, this band is shifted to the region at 1615– 1595 cm<sup>-1</sup>, indicating the coordination of the Schiff bases



( $R_1$  and  $R_2$  groups are as previously described;  $B = PPh_3$  or py or pip or morph)

SCH. 1. Preparation of chiral Schiff base Ruthenium(II) complexes.

S. No	Complex	Color	M. Pt. °C	Found (Calcd.) %		
				С	Н	Ν
(1)	$[Ru(CO)(L1)(PPh_3)]$	Green	135	76.10(76.48)	5.70(5.61)	2.79(2.83)
(2)	[Ru(CO)(L1)(py)]	Green	120	80.92(81.89)	5.75(6.09)	5.61(5.62)
(3)	[Ru(CO)(L1)(pip)]	Green	125	80.70(81.08)	6.70(6.76)	5.59(5.68)
(4)	[Ru(CO)(L1)(morph)]	Green	130	79.00(78.57)	6.40(6.46)	6.29(6.41)
(5)	$[Ru(CO)(L2)(PPh_3)]$	Green	127	72.80(72.78)	4.60(4.69)	3.10(3.03)
(6)	[Ru(CO)(L2)(py)]	Green	140	68.20(68.76)	5.90(5.78)	5.68(5.60)
(7)	[Ru(CO)(L2)(pip)]	Green	155	65.90(65.70)	5.03(4.88)	5.36(5.35)
(8)	[Ru(CO)(L2)(morph)]	Green	135	67.30(67.35)	4.97(4.98)	5.60(5.61)
(9)	$[Ru(CO)(L3)(PPh_3)]$	Green	155	75.80(75.75)	4.79(4.65)	2.60(2.64)
(10)	[Ru(CO)(L3)(py)]	Green	151	73.73(73.77)	4.60(4.48)	4.90(4.78)
(11)	[Ru(CO)(L3)(pip)]	Green	130	73.20(73.23)	5.10(5.02)	4.91(4.85)
(12)	[Ru(CO)(L3)(morph)]	Green	140	70.95(71.78)	5.01(4.96)	4.81(4.74)

TABLE 1 Analytical data of Schiff base ruthenium(II) carbonyl complexes

through azomethine nitrogen.<sup>[16]</sup> A strong band was obtained at  $1290-1270 \,\mathrm{cm}^{-1}$  in the free Schiff bases, which has been assigned to phenolic C-O absorption. On complexation, this band was shifted to a higher frequency range 1320- $1300 \,\mathrm{cm}^{-1}$ , indicating the other coordination of Schiff bases through the phenolic oxygen atom.<sup>[17]</sup> This has been further supported by the disappearence of the broad band at  $\sim$  3000 cm<sup>-1</sup>  $\nu$ (OH) in the complexes indicating the deprotonation occurs prior to coordination. The spectra of all the complexes showed a very strong absorption around  $\sim 1950 \,\mathrm{cm}^{-1}$ due to the coordinated carbonyl group. The complexes contain coordinated nitrogen bases, a medium intensity band was observed in the  $1020-1000 \,\mathrm{cm}^{-1}$  region, corresponding to the coordinated pyridine, piperidine and morpholine.<sup>[18]</sup> Thus, the IR spectral data reveal the dibasic tetradentate behavior of chiral Schiff base moiety in all the ruthenium complexes.

#### **Electronic Spectra**

All the ruthenium(II) complexes are diamagnetic, indicating the presence of ruthenium in +2 oxidation state. The ground state of ruthenium(II)  $(t_{2g}^{6} \text{ configuration})$  in an octahedral environment is  ${}^{1}A_{1g}$  and the excited states corresponding to the  $t_{2g}^{5}$   $e_{g}^{1}$  configuration are  ${}^{3}T_{1g}$ ,  ${}^{3}T_{2g}$ ,  ${}^{1}T_{1g}$  and  ${}^{1}T_{2g}$ . Hence, four bands corresponding to the transitions  ${}^{1}A_{1g} \rightarrow {}^{3}T_{1g}$ ,  ${}^{1}A_{1g} \rightarrow {}^{3}T_{2g}$ ,  ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$  and  ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$  are possible in the order of increasing energy. The electronic spectra of all these complexes in dichloromethane showed one or two bands in the 550–320 nm region. The bands in the 550–495 nm range were assigned to the spin-allowed  ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$  transition based on the low extinction coefficient values ( $\in$ ) as compared to charge transfer bands.<sup>[19]</sup> The other high intensity bands in the 375–320 nm region were assigned to the charge transfer transitions.<sup>[20]</sup> The nature of the electronic spectra of all the complexes indicates that an octahedral geometry around ruthenium ion in the complexes and the spectra are very similar to the ones observed for the other ruthenium(II) complexes.<sup>[21]</sup>

# <sup>1</sup>H and <sup>31</sup>P-NMR Spectra

The <sup>1</sup>H-NMR spectra of the complexes were recorded to confirm the presence of coordinated chiral Schiff bases in the ruthenium(II) complexes and are presented in Table 2. In complexes (1-4), multiplets observed in the regions  $\delta$  1.86–2.06 and 2.60-2.75 ppm has been assigned to methylene group protons and methine proton, respectively. The presence of doublets and a multiplet in the regions  $\delta$  1.20–1.23, 2.10– 2.13 and 2.35-2.40 ppm in complexes (5-8), has been assigned to methyl protons, methylene protons and methine proton, respectively. The presence of a sharp singlet at  $\delta$ 2.55-2.60 ppm in the spectra of complexes (9-12), has been assigned as due to the methine proton. In all the complexes, a multiplet observed in the region  $\delta$  7.20–8.20 ppm has assigned to the protons in triphenyl phosphine, heterocyclic nitrogen bases and naphthyl. A sharp singlet at  $\delta$  8.90-10.00 ppm in the spectra of all the complexes has assigned to azomethine proton signal. The above spectral observations are in good agreement with the values reported for similar chiral Schiff base complexes.<sup>[14]</sup>

The <sup>31</sup>P-NMR spectra were recorded for few complexes to confirm the presence of triphenylphosphine group or heterocyclic nitrogen base in the complexes. The signal appeared at  $\delta$  26.05, 26.10 and 25.99 ppm in the spectrum of (1), (5) and (9) respectively, confirmed the presence of triphenylphosphine group in these complexes. However, complexes (2), (7) and (10) exhibited no such signal confirming the absence of

Cpx. No	$\nu_{(C \equiv O)}a$	$\nu_{(C-O)}a$	$\nu_{(C=N)}a$	$\lambda_{max}b$	(∈)	<sup>1</sup> H-NMR	<sup>31</sup> P-NMR
(1)	1940 vs	1310 s	1595 vs	500	(878)	1.86–2.01 (m, 4(CH <sub>2</sub> )), 2.60–2.69 (m, CH),	26.05
				340	(3099)	7.20-8.00 (m, aromatic), 8.90 (s, N=CH)	
(2)	1945 vs	1310 s	1600 vs	495	(729)	1.88–2.05 (m, 4(CH <sub>2</sub> )), 2.63–2.74 (m, CH),	no signal
				325	(4294)	7.22-8.03 (m, aromatic), 9.00 (s, N=CH)	
(3)	1945 vs	1300 s	1600 vs	320	(4038)	1.89–2.04 (m, 4(CH <sub>2</sub> )), 2.63–2.75 (m, CH),	a
						7.23-8.10 (m, aromatic), 8.90 (s, N=CH)	
(4)	1950 vs	1310 s	1615 vs	550	(979)	1.86-2.06 (m, 4(CH <sub>2</sub> )), 264-2.72 (m, CH),	a
				375	(5415)	7.21-8.00 (m, aromatic), 9.00 (s. N=CH)	
(5)	1950 vs	1315 s	1595 vs	340	(4312)	1.20–1.22 (d, CH <sub>3</sub> ), 210–211 (d, CH <sub>2</sub> ),	26.10
						2.35-2.39 (m, CH), 7.20-8.00	
						(m, aromatic), 8.90 (s, N=CH)	
(6)	1960 vs	1310 s	1610 vs	500	(747)	1.20–1.23 (d, CH <sub>3</sub> ), 2.10–2.13 (d, CH <sub>2</sub> ),	а
				360	(4011)	2.35-2.40 (m, CH), 7.20-8.20	
						(m, aromatic), 8.93 (s, N=CH)	
(7)	1955 vs	1320 s	1605 vs	365	(5067)	1.20–1.23 (d, CH <sub>3</sub> ), 2.10–2.12 (d, CH <sub>2</sub> ),	no signal
						2.35-2.39 (m, CH), 7.20-8.00	-
						(m, aromatic), 9.00 (s, N=CH)	
(8)	1940 vs	1315 s	1600 vs	495	(887)	1.20–1.23 (d, CH <sub>3</sub> ), 2.10–2.11 (d, CH <sub>2</sub> ),	а
				370	(5567)	2.35-2.39 (m, CH), 7.20-8.00	
						(m, aromatic), 8.96 (s, N=CH)	
(9)	1945 vs	1310 s	1595 vs	330	(4987)	2.55 (s, CH), 7.20-7.90 (m, aromatic),	25.99
						9.97 (s, N=CH)	
(10)	1960 vs	1300 s	1610 vs	505	(937)	2.58 (s, CH), 7.20-8.00 (m, aromatic),	no signal
				325	(4576)	9.99 (s, N=CH)	-
(11)	1950 vs	1300 s	1615 vs	370	(4847)	2.55 (s, CH), 7.20-7.90 (m, aromatic),	а
						9.98 (s, N=CH)	
(12)	1960 vs	1320 s	1610 vs	320	(5978)	2.60 (s, CH), 7.20-8.00 (m, aromatic),	а
						9.97 (s, N=CH)	

 TABLE 2

 IR, Electronic and NMR spectral data of ruthenium (II) carbonyl complexes

 $a = cm^{-1}$ ; b = nm; s-strong; vs- very strong;  $\in -dm^3 mol^{-1} cm^{-1}$ ; s-singlet; d-doublet; m-multiplet; a-not recorded.

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triphenylphosphine group. This observation indicates the retention of coordinated pyridine or piperidine or morpholine in the complexes even after the coordination of tetradentate Schiff bases. The <sup>31</sup>P-NMR spectral studies clearly indicate a more labile Ru-P bond compared to Ru-N bond in these complexes, which is a reflection of better  $\sigma$ -donating ability of the nitrogen bases compared to that of phosphorus in triphenylphosphine.<sup>[19]</sup>

# **Catalytic Studies**

The catalytic activitiy of complexes (1), (3), (5), (7), (9) and (11) was investigated for aerial oxidation of cinnamaldehyde to cinnamic acid. The course of the reaction was followed spectrometrically by monitoring the increase in benzoic acid absorbance at 280 nm as a function of time. Plots of the absorbance versus time were linear. The slope of the line is equal to the reaction rate constant K, the observed K values are given in Table 3. There is no change in absorbance at 280 nm in the absence of complex, indicating the catalytic activity of new complexes. The catalytic activity was found to decrease with increase in size of the diamino group.<sup>[22]</sup> This may be due to possibility of steric effect which hindered the formation of activated complex and thus reduced the rate of oxidation.<sup>[23]</sup> Based on the low extinction coefficient values ( $\in = 24,987$ ) as compared to trans-isomer, the product was assigned to be a cis- isomer (Table 4).

# **Antibacterial Studies**

The antibacterial activities of the complexes were studied by Agar-Well diffusion method.<sup>[24]</sup> Seven days old cultures of *S. aureus* and *S. typhi* were used as a test organisms which were grown on nutrient agar (NA) medium. Then, 1% and 2% solutions of the complexes in DMSO were used for the studies. From the results it is concluded that the ruthenium(II) carbonyl complexes possess more activity than their parent ligand and the toxicity increases with increase in concentration of the test solution containing new complexes (Table 4). It has also been observed from the antibacterial screening studies that the ruthenium chelates have higher activity than the corresponding free ligands against the same microorganism under

TABLE 3 Catalytic activity of ruthenium(II) carbonyl complexes

Cpx. No.	$K (M^{-1} s^{-1})$
(1)	$1.316 \times 10^{-3}$
(3)	$1.161 \times 10^{-3}$
(5)	$2.718 \times 10^{-3}$
(7)	$3.008 \times 10^{-4}$
(9)	$3.871 \times 10^{-5}$
(11)	$4.113 \times 10^{-5}$

TABLE 4
Antibacterial activity data of Schiff base ligands and
ruthenium(II) carbonyl complexes

	Diameter of inhibition zone (mm) <sup>a</sup>				
	S. aureus		S. typhi		
Compound	1%	2%	1%	2%	
Streptomycin sulfate (standard antibiotic)	7	9	6	9	
(L1)	3	5	1	4	
(1)	7	8	4	7	
(2)	5	6	4	6	
(L2)	1	2	1	2	
(5)	3	5	2	4	
(6)	3	5	3	5	
(L3)	2	5	3	5	
(10)	4	6	5	7	
(12)	3	7	4	8	

 $^{a}$ 1% and 2% indicate 1 g and 2 g of the compound in 100 mL of test solution.

identical experimental conditions, which is consistent with earlier reports.<sup>[25]</sup> This can be attributed to the Tweedy's chelation theory, according to which the chelation reduces the polarity of the metal atom mainly because of the partial sharing of its positive charge with donor group and possible  $\pi$ -electron delocalisation over the whole ring.<sup>[26,27]</sup> This increases the lipophilic character of the metal chelate which favours its permeation through lipid layers of the bacterial membranes. Furthermore, the mode of action of the compounds may involve the hydrogen bond through the >C==N group with active centres of cell constituents resulting in the interference with normal cell process.<sup>[28]</sup> Though the complexes possess activity, it could not reach the effectiveness of the standard drug (*Streptomycin sulfate*). The variation in the



(R<sub>1</sub>, R<sub>2</sub> and B groups are as previously described)

FIG. 2. General structure of the ruthenium(II) carbonyl complexes.

effectiveness of different compounds against different organisms depends either on the impermeability of the cells of the microbes or differences in ribosomes of microbial cells.<sup>[29]</sup>

The following octahedral structure has been tentatively proposed for all the new ruthenium(II) carbonyl complexes based on the analytical and spectral (IR, electronic, <sup>1</sup>H- and <sup>31</sup>P-NMR) data (Figure 2).

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