



# Ruthenium(II) hydrazone Schiff base complexes: Synthesis, spectral study and catalytic applications

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## ABSTRACT

Ruthenium(II) hydrazone Schiff base complexes of the type  $[\text{RuCl}(\text{CO})(\text{B})(\text{L})]$  (where  $\text{B} = \text{PPh}_3, \text{AsPh}_3$  or  $\text{Py}$ ;  $\text{L} =$  hydrazone Schiff base ligands) were synthesized from the reactions of hydrazone Schiff base ligand (obtained from isonicotinoylhydrazide and different hydroxy aldehydes) with  $[\text{RuHCl}(\text{CO})(\text{EPh}_3)_2(\text{B})]$  (where  $\text{E} = \text{P}$  or  $\text{As}$ ;  $\text{B} = \text{PPh}_3, \text{AsPh}_3$  or  $\text{Py}$ ) in 1:1 molar ratio. All the new complexes have been characterized by analytical and spectral (FT-IR, electronic,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR) data. They have been tentatively assigned an octahedral structure. The synthesized complexes have exhibited catalytic activity for oxidation of benzyl alcohol to benzaldehyde and cyclohexanol to cyclohexanone in the presence of N-methyl morpholine N-oxide (NMO) as co-oxidant. They were also found to catalyze the transfer hydrogenation of aliphatic and aromatic ketones to alcohols in KOH/isopropanol.

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## 1. Introduction

The effect of ligand on the structure and reactivity of transition metal complexes is an important topic of research in coordination and organometallic chemistry as well as in catalysis. The large impact of the use of Schiff base ligands in metal complexes is evident from their utility in various catalytic reactions such as, hydrogenation of olefins and carbonyl groups, transfer of an amino group, photochromic properties, complexing ability towards some toxic metals, etc. [1–4]. Hydrazones a special group of compounds in Schiff base family, characterized by the presence of  $\text{R}_1\text{C}=\text{N}-\text{NR}_2$ . The hydrazone Schiff bases of acyl, aroyl and heteroacroyl compounds have an additional donor sites like  $\text{C}=\text{O}$ . The additional donor sites make them more flexible and versatile. This versatility has made hydrazones as good polydentate chelating agents that can form a variety of complexes with number of transition metals. Various studies have also shown that the azomethine group having a lone pair of electrons in either p or  $\text{sp}^2$  hybridized orbital on nitrogen has considerable biological and catalytic importance [5,6].

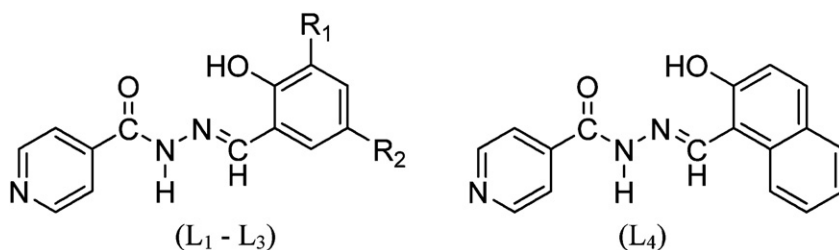
Among the transition metals, ruthenium complexes have been focused the attention of many research groups [7] since, ruthenium complexes have been used as catalyst precursors for variety of purposes including hydrogenation, oxidation, polymerization and carbon–carbon bond formation [8]. The oxidation of primary and

secondary alcohols into their corresponding aldehydes and ketones plays a central role in organic synthesis [9]. From both an economic and environmental point of view, the quest for effective catalytic systems that use clean, inexpensive primary oxidants such as molecular oxygen or hydrogen peroxide, i.e., a green method for converting alcohols to carbonyl compounds on an industrial scale remains an important challenge [10]. Most studies of alcohol oxidation using both homogeneous and heterogeneous catalysts involve the use of group VIII metal complexes. Ruthenium compounds such as  $\text{RuCl}_3$  and some other high valent oxoruthenium complexes have been extensively investigated as catalyst for alcohol oxidation using variety of primary oxidants like iodobenzene, NMO [11], tert-hydroperoxide [12], hypochlorite [13], bromated or a combination of oxygen and an aldehyde.

Ruthenium complexes have a long pedigree as catalysts for transfer hydrogenation reactions in the presence of isopropanol as hydrogen source [14,15]. Several recent examples of ruthenium N-heterocyclic carbene complexes [16–18],  $\text{Ru}(\text{arene})-(\text{diamine})$  [19], ruthenium(III) amine-bis(phenolate) tripodal complexes [20] and  $\text{Ru}(\text{BINAP})(\text{diamine})$  [21] have become the most prominent members for the reduction of ketones in high yields. Pincer-type arylruthenium(II) complexes containing the monoanionic tridentate NCN and PCP ligands have been reported by Koten as active catalysts for the transfer hydrogenation of ketones in the presence of isopropanol and KOH [22]. Even though there are number of reports available on the transfer hydrogenation of ketones by ruthenium complexes, only limited reports are available for catalytic transfer hydrogenation of ketones by ruthenium hydrazone Schiff base complexes. Hence, synthesis of new

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Ligand	R <sub>1</sub>	R <sub>2</sub>
L <sub>1</sub>	OCH <sub>3</sub>	H
L <sub>2</sub>	H	Cl
L <sub>3</sub>	H	H

Fig. 1. Structure of hydrazone Schiff base ligands.

ruthenium complexes containing triphenylphosphine/triphenylarsine with hydrazone Schiff base ligands is of greater importance among various transition metal complexes.

We, herein report the synthesis of a series of hexacoordinated ruthenium(II) hydrazone Schiff base complexes containing PPh<sub>3</sub>/AsPh<sub>3</sub> and other co-ligands. The characterization of the complexes was accomplished by analytical and spectral (IR, electronic, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR) methods. Further, some of the synthesized complexes have been effectively used as catalyst in oxidation of alcohols in the presence of NMO and transfer hydrogenation of ketones in isopropanol and KOH as base.

## 2. Experimental

### 2.1. Materials and reagents

All the reagents used were chemically pure and AR grade. The solvents were purified and dried according to standard procedures [23]. RuCl<sub>3</sub>·H<sub>2</sub>O was purchased from Loba Chemie Pvt. Ltd. The starting complexes [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] [24], [RuHCl(CO)(Py)(PPh<sub>3</sub>)<sub>2</sub>] [25] and [RuHCl(CO)(AsPh<sub>3</sub>)<sub>3</sub>] [26] were prepared according to the literature reports.

### 2.2. Physical measurements

Microanalysis of carbon, hydrogen and nitrogen was carried out using Vario EL III Elemental analyzer at SAIF – Cochin, India. The IR spectra of the ligand and their complexes were recorded as KBr pellets on a Nicolet Avatar model in 4000–400 cm<sup>-1</sup> range. Electronic spectra of the ligand and their complexes have been recorded in dichloromethane using a Shimadzu UV-1650 PC spectrophotometer in 200–800 nm range. <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded in Jeol GSX-400 instrument using DMSO as the solvent. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained at room temperature using TMS as the internal standard. <sup>31</sup>P NMR spectra of the complexes were obtained at room temperature using o-phosphoric acid as a reference. Melting points were recorded on a Technico micro heating table and are uncorrected. The catalytic yields were determined using ACME 6000 series GC-FID with DP-5 column of 30 m length, 0.53 mm diameter and 5.00 μm film thickness.

### 2.3. Synthesis of hydrazone Schiff base ligands

The hydrazone Schiff base ligands were prepared by the condensing 2-hydroxy aldehyde {3-methoxysalicylaldehyde (0.1522 g,

1 mmol), 5-chlorosalicylaldehyde (0.1566 g, 1 mmol), salicylaldehyde (0.11 cm<sup>3</sup>, 1 mmol) or 2-hydroxy-1-naphthaldehyde (0.1722 g, 1 mmol)} with isonicotinoylhydrazide (0.1371 g, 1 mmol) in methanol (20 ml) under reflux for 2 h. The resulting yellow solid was separated, filtered, washed with methanol and dried in vacuo [27]. The general structures of the hydrazone Schiff base ligands used in this study are given below (Fig. 1) (73–80% yield).

### 2.4. Synthesis of new ruthenium(II) hydrazone Schiff base complexes

All the new metal complexes were prepared according to the following general procedure. To a solution of [RuHCl(CO)(EPh<sub>3</sub>)<sub>2</sub>(B)] (E=P or As; B=PPh<sub>3</sub>, AsPh<sub>3</sub> or Py) (0.1 g; 0.1 mmol) in benzene (20 ml), the appropriate hydrazone Schiff base ligand (0.022–0.0378 g, 0.1 mmol) was added in 1:1 molar ratio. The mixture was heated under reflux for 5 h in water bath. Then the resulting solution was concentrated to 3 ml and the product precipitated by the addition of petroleum ether (60–80 °C) was recrystallised using CH<sub>2</sub>Cl<sub>2</sub>. The compounds were dried under vacuum and the purity of the complexes was checked by TLC.

### 2.5. Catalytic oxidation

Catalytic oxidation of primary alcohols to corresponding aldehydes and secondary alcohols to ketones by ruthenium(II) hydrazone Schiff base complexes were studied in the presence of NMO as co-oxidant. In a typical reaction, ruthenium(II) complexes as a catalyst and primary or secondary alcohol, as substrates at 1:100 molar ratio was described as follows. A solution of ruthenium complexes (0.01 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) was added to the mixture containing substrate (1 mmol), NMO (3 mmol) and molecular sieves. 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 extracted with petroleum ether (60–80 °C) (20 ml) concentrated to ~1 ml and was analyzed by GC. The oxidation products were identified by GC co-injection with authentic samples.

### 2.6. Catalytic transfer hydrogenation of ketones

The catalytic transfer hydrogenation reactions were also studied using ruthenium(II) hydrazone Schiff base complexes as a catalyst, ketone as substrate and KOH as base at 1:300:2.5 molar ratios.

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