

Ruthenium(II) complexes containing bidentate Schiff bases and triphenylphosphine or triphenylarsine

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Abstract. Reactions of ruthenium(II) complexes [RuHX(CO)(EPh₃)₂(B)] (X = H or Cl; B = EPh₃, pyridine (py) or piperidine (pip); E = P or As) with bidentate Schiff base ligands derived by condensing *o*-hydroxyacetophenone with aniline, *o*- or *p*-methylaniline have been carried out. The products were characterized by analytical, IR, electronic and ¹H-NMR spectral studies and are formulated as [Ru(X)(CO)(L)(EPh₃)(B)] (L = Schiff base anion; X = H or Cl; B = EPh₃, py or pip; E = P or As). An octahedral structure has been tentatively proposed for the new complexes. The new complexes were tested for their catalytic activities in the oxidation of benzyl alcohol to benzaldehyde.

Keywords. Monobasic bidentate; Schiff bases; ruthenium(II) complexes; spectral studies; triphenyl phosphine.

1. Introduction

There has been considerable current interest in the chemistry of ruthenium,¹ primarily because of the fascinating electron-transfer, photochemical and catalytic properties exhibited by the complexes of this metal. As the coordination environment around the central metal ion directs properties of the complexes, complexation of ruthenium by ligands of different types has been of significant importance. Ruthenium–Schiff base complexes, particularly those containing oxygen and nitrogen as donor atoms were found to be very efficient catalysts in the oxidation of alcohols using *N*-methylmorpholine-*N*-oxide as co-oxidant.^{2–5}

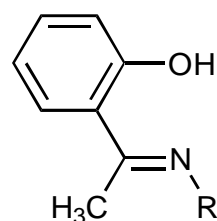
As a part of our continuing efforts to synthesis and characterise ruthenium chelates using simple and inexpensive Schiff base ligands, in this paper, we describe the synthesis, characterisation and catalytic studies of stable ruthenium(II) complexes. The general structure of the Schiff base ligands used in this study is shown in scheme 1.

2. Experimental

RuCl₃·3H₂O was purchased from Loba-Chemie and used as supplied. Solvents were purified according

to standard procedures.⁶ Elemental analyses were performed at Central Drug Research Institute, Lucknow, India. IR spectra were recorded in KBr pellets with a Shimadzu FT-IR spectrophotometer in the 4000–450 cm⁻¹ range. Electronic spectra were recorded in CH₂Cl₂ solution with a Systronics spectrophotometer in the 800–200 nm range. ¹H-NMR spectra were recorded on a Bruker WM 400 instrument using tetramethyl silane (TMS) as internal standard. Melting points were recorded on a Boetius microheating table and are uncorrected.

The precursor complexes [RuHCl(CO)(PPh₃)₃],⁷ [RuH₂(CO)(PPh₃)₃],⁷ [RuHCl(CO)(AsPh₃)₃],⁸ [RuHCl(CO)(PPh₃)₂(py)]⁹ and [RuHCl(CO)(PPh₃)₂(pip)]⁹ and the Schiff base ligands¹⁰ were prepared according to



[R = Ph (Hohyac-an); 2-MeC₆H₄ (Hohyac-oman); 4-MeC₆H₄ (Hohyac-pman)]

Scheme 1. General structure of the Schiff base ligand.

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published procedures. The procedure for catalytic oxidation is similar to that reported in our earlier paper.¹¹

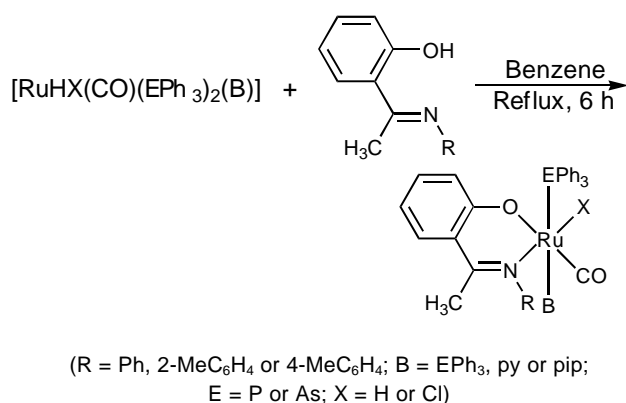
2.1 Preparation of new ruthenium(II) complexes, $[Ru(X)(CO)(L)(EPh_3)(B)]$

To a solution of $[RuHX(CO)(EPh_3)_2(B)]$ [$X = H$ or Cl ; $B = EPh_3$, pyridine (py) or piperidine (pip); $E = P$ or As] (0.1 g, 0.1–0.13 mmol) in benzene (25 ml), was added the appropriate Schiff base (0.021–0.051 g, 0.1–0.13 mmol) (molar ratio of ruthenium complex: Schiff base was 1 : 1). The solution was heated under reflux for 6 h. Then, it was concentrated to a small volume (3 ml) and the new complex $[Ru(X)(CO)(L)(EPh_3)(B)]$ ($L =$ Schiff base anion) was separated from it by the addition of a small quantity (6 ml) of light petroleum (60–80°C). The product was filtered, washed with light petroleum and recrystallised from CH_2Cl_2 /light petroleum (60–80°C) mixture and dried *in vacuo* (Yields: 71–80%).

3. Results and discussion

New hexa-coordinated ruthenium(II) complexes of the type $[Ru(X)(CO)(L)(EPh_3)(B)]$ ($L =$ Schiff base anion; $X = H$ or Cl ; $B = EPh_3$, py or pip; $E = P$ or As) have been prepared from the reaction between $[RuHX(CO)(EPh_3)_2(B)]$ and the respective Schiff bases (molar ratio 1 : 1) in dry benzene as shown in scheme 2.

The analytical data of the new complexes (table 1) agree very well with the proposed molecular formula. The catalytic activity of the complexes in the oxidation of benzyl alcohol was tested in the presence of N-methylmorpholine-N-oxide as co-oxidant



Scheme 2. Formation of new ruthenium(II) complexes.

and CH_2Cl_2 as solvent. There is no detectable oxidation of alcohol in the presence of N-methylmorpholine-N-oxide alone. All the synthesised ruthenium–Schiff base complexes were found to catalyse the oxidation of alcohol to aldehydes but the yield and the turnover were found to vary with the different catalysts used. The percentage yield of product and turnover number range from 0.16–5.5 to 1.6–55.6% respectively. The catalytic efficiency of the new ruthenium(II) complexes is lower compared to that of already reported ruthenium(II)-Schiff base complexes.^{5,11}

3.1 IR spectra

In order to study the binding mode of the Schiff bases to ruthenium in the new complexes, the IR spectra of the free ligands were compared with the spectra of the ruthenium complexes. A strong band is observed at 1620–1610 cm^{-1} in the infrared spectra of the free Schiff bases which is characteristic of the azomethine group. If the Schiff bases coordinate through the nitrogen atom, it is expected that there must be a reduction in the azomethine frequency due to the lowering of electron density upon coordination. In the spectra of all the new complexes, this band is shifted to the region 1620–1590 cm^{-1} indicating the coordination of the Schiff bases through nitrogen atom.¹¹ A strong band observed around 1270–1260 cm^{-1} in the free Schiff bases has been assigned to phenolic C–O stretching. On complexation, this band has been shifted to higher frequency (1320–1300 cm^{-1}) showing that the other coordination is through the phenolic oxygen atom.¹² The strong absorption around 1950–1940 cm^{-1} has been assigned to the terminally coordinated carbonyl group in the new ruthenium complexes. In the complexes containing coordinated pyridine,⁹ a weak band is observed at about 1020 cm^{-1} . The $\nu(Ru-H)$ and $\nu(Ru-Cl)$ absorption bands appear around 2020 cm^{-1} and 320 cm^{-1} respectively. All other characteristic bands due to triphenylphosphine and arsine are also present in the expected region.

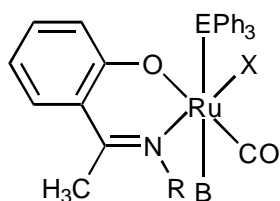
3.2 Electronic spectra

The new ruthenium(II) Schiff base complexes are diamagnetic, indicating the presence of ruthenium in the +2 oxidation state. The electronic spectra of all the complexes in CH_2Cl_2 show a band in the 260–280 nm region. This band has been assigned to the

Table 1. Physical characterization and analytical data of the ruthenium(II) complexes.

Complex	Colour	m.p./decomp.* (°C)	Found (calculated) (%)		
			C	H	N
[RuCl(CO)(PPh ₃) ₂ (ohyac-an)]	Green	153	68.18 (68.02)	4.60 (4.82)	1.55 (1.45)
[RuCl(CO)(PPh ₃) ₂ (ohyac-oman)]	Brown	182	67.95 (68.37)	4.42 (4.85)	1.25 (1.53)
[RuCl(CO)(PPh ₃) ₂ (ohyac-pman)]	Green	162	68.18 (68.37)	4.51 (4.85)	1.45 (1.53)
[RuH(CO)(PPh ₃) ₂ (ohyac-an)]	Green	147	67.56 (67.98)	3.96 (4.33)	1.23 (1.58)
[RuH(CO)(PPh ₃) ₂ (ohyac-oman)]	Brown	176	69.78 (71.05)	4.76 (5.16)	1.27 (1.59)
[RuH(CO)(PPh ₃) ₂ (ohyac-pman)]	Green	162	69.85 (71.05)	4.98 (5.16)	5.27 (5.16)
[RuCl(CO)(AsPh ₃) ₂ (ohyac-an)]	Green	153	61.89 (62.10)	4.07 (4.19)	1.16 (1.42)
[RuCl(CO)(AsPh ₃) ₂ (ohyac-oman)]	Brown	168	62.18 (62.37)	4.17 (4.42)	1.06 (1.39)
[RuCl(CO)(AsPh ₃) ₂ (ohyac-pman)]	Green	176	62.08 (62.37)	4.09 (4.42)	1.02 (1.39)
[RuCl(CO)(PPh ₃)(py)(ohyac-an)]	Green	210	63.70 (63.90)	4.08 (4.37)	3.78 (3.92)
[RuCl(CO)(PPh ₃)(py)(ohyac-oman)]	Brown	143	64.08 (64.14)	4.51 (4.69)	3.67 (3.80)
[RuCl(CO)(PPh ₃)(py)(ohyac-pman)]	Green	180	63.69 (64.14)	4.32 (4.69)	3.35 (3.80)
[RuCl(CO)(PPh ₃)(pip)(ohyac-an)]	Green	205	63.01 (63.28)	5.01 (5.17)	3.50 (3.88)
[RuCl(CO)(PPh ₃)(pip)(ohyac-oman)]	Brown	142	63.46 (63.61)	5.17 (5.47)	3.55 (3.80)
[RuCl(CO)(PPh ₃)(pip)(ohyac-pman)]	Green	172	63.45 (63.61)	5.19 (5.47)	3.56 (3.80)

*Decomposition



(R = Ph, 2-MeC₆H₄ or 4-MeC₆H₄; B = EPh₃, py or pip;
E = P or As; X = H or Cl)

Scheme 3. Proposed structure of ruthenium(II) complexes.

charge-transfer transition arising from the excitation of an electron from the metal t_{2g} level to the unfilled molecular orbitals derived from the p^* level of the ligands, in accordance with the assignments made for other similar octahedral ruthenium(II) complexes.¹³⁻¹⁵

3.3 ¹H-NMR spectra

Coordination of the Schiff bases in the new ruthenium(II) complexes is further confirmed by ¹H-NMR spectra. The peak observed at 1.65 ppm has been assigned to the methyl group of the Schiff base ligands. The signal for aromatic protons appears as multiplets in the 8.49–6.02 ppm region in all the complexes. In the hydrido complex, [RuH(CO)(PPh₃)₂(ohyac-an)], the metal hydride signal corresponding to one proton has been observed as a singlet in the very high upfield region (–12.04 ppm).

On the basis of elemental analyses, IR, electronic, and ¹H-NMR spectral data, the following octahedral structure (scheme 3) has been tentatively proposed for all the new ruthenium(II) complexes.

4. Conclusion

Ruthenium(II) complexes containing monobasic bidentate Schiff bases and triphenylphosphine/triphenylarsine were synthesized and characterized by analytical and spectral techniques. These complexes exhibited catalytic activity in the oxidation of alcohols using N-methylmorpholin-N-oxide as co-oxidant.

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