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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 [RuCl(CO)(B)(L)] (were B = PPh_3, $AsPh_3$ or Py; L = hydrazone Schiff base ligands) were synthesized from the reactions of hydrazone Schiff base ligand (obtained from isonicotinoylhydrazide and different hydroxy aldehydes) with $[RuHCl(CO)(EPh_3)_2(B)]$ (where E = P or As; B = PPh_3, $AsPh_3$ or Py) in 1:1 molar ratio. All the new complexes have been characterized by analytical and spectral (FT-IR, electronic, ^1H, ^{13}C and ^{31}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.

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 $R_1C{=}N{-}NR_2$. The hydrazone Schiff bases of acyl, aroyl and heteroacroyl compounds have an additional donor sites like C=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 verity 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 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 carbonyls 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 $RuCl_3$ 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], hypochloride [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], Ru(arene)-(diamine) [19], ruthenium(III) amine-bis(phenolate) tripodal complexes [20] and Ru(BINAP)(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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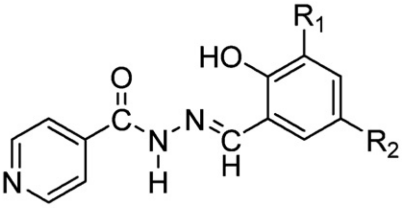
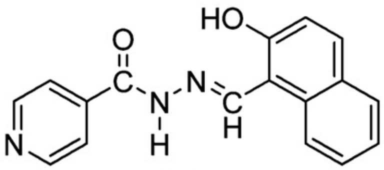


(L_1 - L_3)



(L_4)

Ligand	R_1	R_2
L_1	OCH_3	H
L_2	H	Cl
L_3	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 hexa-coordinated ruthenium(II) hydrazone Schiff base complexes containing PPh_3/$AsPh_3$ and other co-ligands. The characterization of the complexes was accomplished by analytical and spectral (IR, electronic, ^{1}H, ^{13}C and ^{31}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]. $RuCl_3{\cdot}H_2O$ was purchased from Loba Chemie Pvt. Ltd. The starting complexes $[RuHCl(CO)(PPh_3)_3]$ [24], $[RuHCl(CO)(Py)(PPh_3)_2]$ [25] and $[RuHCl(CO)(AsPh_3)_3]$ [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^{-1} 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. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded in Jeol GSX-400 instrument using DMSO as the solvent. ^{1}H NMR and 13C NMR spectra were obtained at room temperature using TMS as the internal standard. ^{31}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^3, 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

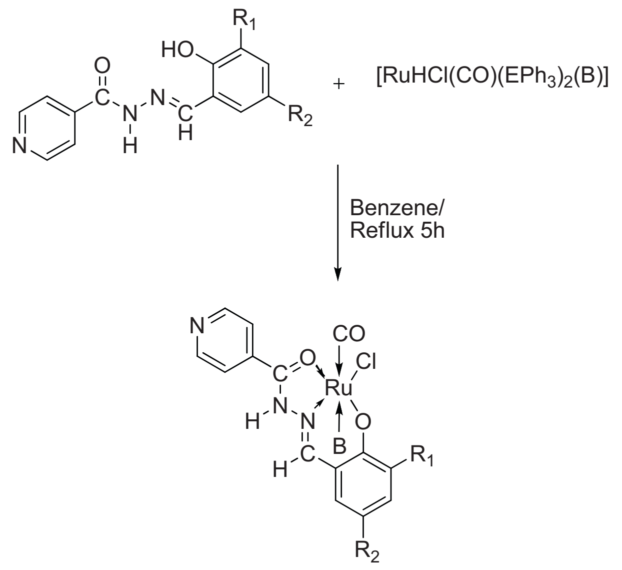
All the new metal complexes were prepared according to the following general procedure. To a solution of $[RuHCl(CO)(EPh_3)_2(B)]$ (E = P or As; B = PPh_3, $AsPh_3$ or Py) (0.1 g; 0.1 mmol) in benzene (20 ml), the appropriate hydrazone Schiff base ligand (0.022–0.0378 g, 0.1 mmol) was added in 1:1 molar 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_2Cl_2. 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_2Cl_2 (20 cm^3) 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.



(B = PPh$_3$, AsPh$_3$ or Py; R$_1$ = OCH$_3$ or H; R$_2$ = Cl or H)

Scheme 1. Formation of Ru(II) hydrazone Schiff base complexes.

The procedure was described as follows. A mixture containing ketone (3.75 mmol), the ruthenium complex (0.0125 mmol) and KOH (0.03 mmol) was heated to reflux in 10 ml of *i*-PrOH for 3 h. After completion of reaction the catalyst was removed from the reaction mixture by the addition of petroleum ether followed by filtration and subsequent neutralization with 1 M HCl. The ether layer was filtered through a short path of silica gel by column chromatography. The filtrate was subjected to GC analysis and the hydrogenated product was identified and determined with authentic samples.

3. Result and discussion

Diamagnetic, hexa-coordinated low spin ruthenium(II) hydrazone Schiff base complexes of general formula [RuCl(CO)(B)(L)] (B = PPh$_3$, AsPh$_3$ or Py; L = hydrazone Schiff base ligand) were synthesized in quantitative yield from the reaction of [RuHCl(CO)(EPh$_3$)$_2$(B)] (E = P or As; B = PPh$_3$, AsPh$_3$ or Py) with hydrazone Schiff base ligands in dry benzene in 1:1 molar ratio (Scheme 1). In all these reactions, it was observed that the hydrazone Schiff base behave as mononegative tridentate ligands by replacing two molecules of triphenylphosphine or triphenylarsine and one molecule of hydride from the starting complexes.

All the complexes are stable in air at room temperature, brown in color, non-hygroscopic in nature and highly soluble in common organic solvents such as dichloromethane, benzene, acetonitrile, chloroform and DMSO. The analytical data are listed in Table 1 and are in good agreement with the general molecular formula proposed for all the complexes.

3.1. Infrared spectroscopic analysis

A comparison between the IR spectral data of the free ligand and the metal complexes was made to study the binding mode of the ligand to the ruthenium ion in the new metal complexes. Some of the important IR absorption bands of synthesized ligands and complexes are shown in Table 2.

The broad band centered at 3436–3444 cm^{-1} in the free ligands [28] can be assigned to $\upsilon_{\text{N–H}}$, which is a remains unaltered in the complexes. This suggests that the non-participation of NH group in bonding. A strong band at 1327–1331 cm^{-1} in the free ligands is assigned to phenolic C–O stretching. This band shifted to 1350–1387 cm^{-1} in complexes, showing that the coordination through the phenolic oxygen [29]. This is further supported by the disappearance of $\upsilon_{\text{O–H}}$ band [28] around 3200–3222 cm^{-1} and $\delta_{\text{O–H}}$ peak [30] around 1340–1362 cm^{-1}. The $\upsilon_{\text{C=O}}$ observed at 1680–1686 cm^{-1} in the spectra of the ligands showed a downward shift to 1642–1679 cm^{-1} in all the complexes indicating the coordination through the carbonyl oxygen [31]. The band at 1620–1626 cm^{-1} is assigned to $\upsilon_{\text{C=N}}$ in the spectra of ligands which is shifted to 1595–1615 cm^{-1} in the spectra of the complexes indicated that the other coordination is through azomethine nitrogen [32]. Hence, from the infrared spectroscopic data, it is inferred that both azomethine, carbonyl and phenolic oxygen atoms are involved in the coordination of the tridentate Schiff bases to ruthenium ion in all the complexes. Further the strong absorption around the 1950–1957 cm^{-1} has been assigned to the terminally coordinated carbonyl group in the new ruthenium complexes [33]. In the case of complexes containing coordinated heterocyclic nitrogen bases [34], a medium intensity band was observed in the region 1027–1031 cm^{-1}. In addition, the other characteristic bands due to triphenylphosphine and triphenylarsine (around 700, 1090 and 1440 cm^{-1}) were also present in the spectra of all the complexes [35]. The observed bands in the region 460–475 cm^{-1} in the mono nuclear complexes were tentatively assigned to the $\upsilon_{\text{Ru–Cl}}$ vibrations [36].

Table 1
Analytical data of free ligands and their ruthenium(II) hydrazone Schiff base complexes.

Compound	Formula	M.Pt (°C)	Calculated (found) (%)		
			C	H	N
L$_1$	$C_{14}H_{13}N_3O_3$	218	61.98(61.13)	4.83(4.11)	15.49(15.18)
L$_2$	$C_{13}H_{10}N_3O_2Cl$	232	56.64(56.66)	3.66(3.49)	15.24(15.15)
L$_3$	$C_{13}H_{11}N_3O_2$	229	64.72(64.54)	4.59(4.43)	17.42(17.55)
L$_4$	$C_{17}H_{13}N_3O_2$	238	70.09(70.23)	4.49(4.86)	14.42(14.22)
[RuCl(CO)(PPh$_3$)(L$_1$)]	$C_{33}H_{27}N_3O_4ClPRu$	230	56.85(56.58)	3.90(3.46)	06.03(6.16)
[RuCl(CO)(PPh$_3$)(L$_2$)]	$C_{32}H_{24}N_3O_3Cl_2PRu$	160	54.79(54.38)	3.44(2.96)	05.99(5.26)
[RuCl(CO)(PPh$_3$)(L$_3$)]	$C_{32}H_{25}N_3O_3ClPRu$	185	57.62(57.65)	3.75(3.79)	06.28(6.25)
[RuCl(CO)(PPh$_3$)(L$_4$)]	$C_{36}H_{27}N_3O_3ClPRu$	138	60.29(68.09)	3.79(3.38)	05.86(5.74)
[RuCl(CO)(Py)(L$_1$)]	$C_{20}H_{17}N_4O_4ClRu$	175	46.74(46.48)	3.31(3.12)	10.90(10.60)
[RuCl(CO)(Py)(L$_2$)]	$C_{19}H_{14}N_4O_3Cl_2Ru$	180	44.03(44.52)	2.72(2.54)	10.81(10.62)
[RuCl(CO)(Py)(L$_3$)]	$C_{19}H_{15}N_4O_3ClRu$	183	47.16(46.97)	3.12(3.62)	11.58(11.96)
[RuCl(CO)(Py)(L$_4$)]	$C_{23}H_{17}N_4O_3ClRu$	203	51.74(51.65)	3.21(3.43)	10.49(10.42)
[RuCl(CO)(AsPh$_3$)(L$_1$)]	$C_{33}H_{27}N_3O_4ClAsRu$	210	53.48(53.77)	3.67(2.99)	05.67(5.29)
[RuCl(CO)(AsPh$_3$)(L$_2$)]	$C_{32}H_{24}N_3O_3Cl_2AsRu$	150	51.56(51.57)	3.25(3.55)	05.64(5.11)
[RuCl(CO)(AsPh$_3$)(L$_3$)]	$C_{32}H_{25}N_3O_3ClAsRu$	120	54.06(53.82)	3.54(3.12)	05.91(5.81)
[RuCl(CO)(AsPh$_3$)(L$_4$)]	$C_{36}H_{27}N_3O_3ClAsRu$	200	56.81(56.62)	3.5(3.72)	05.52(4.95)

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

Compound	νN–H	νO–H	νC≡O	νC═O	νC═N	δO–H	νC–O	λmax
L_1	3444	3202	–	1686	1626	1348	1327	297, 234
L_2	3436	3200	–	1681	1620	1340	1330	241, 273, 341
L_3	3436	3220	–	1682	1624	1355	1331	238, 279, 329
L_4	3440	3222	–	1680	1624	1362	1330	229, 258, 323, 347, 364
$[RuCl(CO)(PPh_3)(L_1)]$	3446	–	1955	1678	1609	–	1375	240, 302, 347, 394, 470
$[RuCl(CO)(PPh_3)(L_2)]$	3445	–	1953	1668	1610	–	1375	247, 347, 371, 464
$[RuCl(CO)(PPh_3)(L_3)]$	3436	–	1954	1679	1611	–	1370	252, 347, 358, 470
$[RuCl(CO)(PPh_3)(L_4)]$	3444	–	1953	1678	1615	–	1383	247, 344, 382, 476
$[RuCl(CO)(Py)(L_1)]$	3446	–	1955	1663	1609	–	1375	252, 312, 352, 364
$[RuCl(CO)(Py)(L_2)]$	3445	–	1956	1672	1610	–	1374	241, 347, 371, 464
$[RuCl(CO)(Py)(L_3)]$	3436	–	1957	1654	1610	–	1371	247, 341, 361, 462
$[RuCl(CO)(Py)(L_4)]$	3447	–	1954	1674	1615	–	1375	247, 326, 350, 370, 476
$[RuCl(CO)(AsPh_3)(L_1)]$	3446	–	1952	1642	1595	–	1377	237, 304, 352, 437
$[RuCl(CO)(AsPh_3)(L_2)]$	3445	–	1952	1666	1598	–	1350	258, 329, 370, 461
$[RuCl(CO)(AsPh_3)(L_3)]$	3434	–	1952	1678	1598	–	1376	238, 270, 347, 355, 452
$[RuCl(CO)(AsPh_3)(L_4)]$	3434	–	1950	1650	1615	–	1387	261, 320, 347, 379, 485

Table 3
^1H NMR data (ppm) of free ligands and their ruthenium(II) hydrazone Schiff base complexes.

Compound	OH (s)	NH (s)	2, 6-Pyridine H (m)	N═CH (s)	3, 5-Pyridine H (m)	Aromatic H (m)	OCH_3 (s)
L_1	11.91	10.37	8.60–8.79	8.25	7.56–7.85	6.84–7.45	3.90
L_2	12.14	10.16	8.72–8.79	8.30	7.93–8.08	6.72–7.38	–
L_3	11.06	9.98	8.77–8.79	8.35	7.82–7.84	6.89–7.60	–
L_4	12.96	9.90	8.60–8.64	8.23	8.10–8.18	6.83–7.66	–
$[RuCl(CO)(PPh_3)(L_1)]$	–	9.98	8.10–8.18	8.65	7.43–7.49	6.64–7.28	3.92
$[RuCl(CO)(PPh_3)(L_2)]$	–	9.87	7.81–7.88	8.52	7.38–7.46	6.75–7.36	–
$[RuCl(CO)(PPh_3)(L_3)]$	–	9.78	7.82–7.90	8.72	7.55–7.57	6.93–7.44	–
$[RuCl(CO)(PPh_3)(L_4)]$	–	9.49	8.20–8.34	8.83	7.84–7.89	6.88–7.60	–
$[RuCl(CO)(Py)(L_1)]$	–	9.88	8.20–8.23	8.70	7.45–7.48	6.62–7.14	3.90
$[RuCl(CO)(Py)(L_2)]$	–	9.74	7.82–7.90	8.62	7.62–7.68	6.75–7.36	–
$[RuCl(CO)(Py)(L_3)]$	–	9.76	7.82–7.84	8.75	7.54–7.57	6.83–7.41	–
$[RuCl(CO)(Py)(L_4)]$	–	9.44	8.20–8.30	8.80	7.83–7.92	6.93–7.58	–
$[RuCl(CO)(AsPh_3)(L_1)]$	–	9.80	8.20–8.29	8.70	7.51–7.58	6.44–7.03	3.93
$[RuCl(CO)(AsPh_3)(L_2)]$	–	9.73	7.90–8.28	8.65	7.43–7.48	6.76–7.38	–
$[RuCl(CO)(AsPh_3)(L_3)]$	–	9.75	8.23–8.29	8.84	7.83–7.85	6.78–7.25	–
$[RuCl(CO)(AsPh_3)(L_4)]$	–	9.48	8.00–8.13	8.85	7.72–7.78	6.54–7.48	–

s, singlet; m, multiplet.

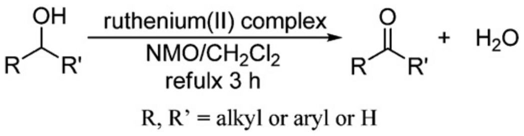
Table 4
^{13}C NMR data (ppm) of ruthenium(II) hydrazone Schiff base complexes.

Compound	C≡O	C═O	C═N	Aromatic C	OCH_3
$[RuCl(CO)(PPh_3)(L_1)]$	205.35	180.62	163.73	124.85–135.48	53.60
$[RuCl(CO)(PPh_3)(L_2)]$	206.15	182.33	161.06	122.34–135.07	–
$[RuCl(CO)(PPh_3)(L_3)]$	203.10	178.95	164.21	127.86–136.98	–
$[RuCl(CO)(PPh_3)(L_4)]$	204.30	180.56	162.57	122.85–138.43	–
$[RuCl(CO)(Py)(L_1)]$	205.25	181.12	164.33	124.45–132.37	55.34
$[RuCl(CO)(Py)(L_3)]$	203.37	178.36	163.58	127.66–133.48	–
$[RuCl(CO)(AsPh_3)(L_1)]$	205.25	180.53	163.27	124.55–133.62	53.20
$[RuCl(CO)(AsPh_3)(L_4)]$	205.32	182.54	160.80	126.23–136.04	–

Table 5
Catalytic oxidation data of ruthenium(II) hydrazone Schiff base complexes.

Complex	Substrate	Product	Yield(%)[a]
$[RuCl(CO)(PPh_3)(L_1)]$	Benzyl alcohol	Benzaldehyde	99
	Cyclohexanol	Cyclohexanone	83
$[RuCl(CO)(PPh_3)(L_2)]$	Benzyl alcohol	Benzaldehyde	93
	Cyclohexanol	Cyclohexanone	87
$[RuCl(CO)(PPh_3)(L_3)]$	Benzyl alcohol	Benzaldehyde	97
	Cyclohexanol	Cyclohexanone	79
$[RuCl(CO)(PPh_3)(L_4)]$	Benzyl alcohol	Benzaldehyde	99
	Cyclohexanol	Cyclohexanone	76
$[RuCl(CO)(Py)(L_2)]$	Benzyl alcohol	Benzaldehyde	96
	Cyclohexanol	Cyclohexanone	74
$[RuCl(CO)(AsPh_3)(L_2)]$	Benzyl alcohol	Benzaldehyde	97
	Cyclohexanol	Cyclohexanone	70

[a] Yield determined by GC and comparing with the analysis authentic samples.



Scheme 2. Catalytic oxidation of alcohols.

3.2. *Electronic spectroscopic analysis*

All the new ruthenium(II) hydrazone Schiff base complexes are diamagnetic indicating the presence of ruthenium in the +2 oxidation state. The ground state of ruthenium(II) is $^1A_{1g}$ arising from the $t^6{}_{2g}$ configuration in an octahedral environment. The excited state corresponding to the $t^5{}_{2g}\, e^1{}_g$ configuration are $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$. Hence, four bands corresponding to the transitions $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$, $^1A_{1g} \rightarrow {}^1T_{2g}$ and possible in the order of increasing energy.

The electronic spectra of all the complexes in CH_2Cl_2 showed four to five bands in the region 234–485 nm (Table 2). The band around 437–485 nm range has been assigned to the spin allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. The other high intensity bands around 312–394 nm have been assigned to charge transfer transitions arising from the metal t_{2g} level to the unfilled molecular orbitals derived from the π^* level of the ligands [37–40] based on their extinction coefficient values. The bands below 300 nm were characterized by intra-ligand charge transfer. The electronic spectra are similar to those observed for other octahedral ruthenium(II) complexes [41].

3.3. *^1H NMR spectroscopic analysis*

The ^1H NMR spectra of the ligand and the corresponding ruthenium(II) hydrazone Schiff base complexes were recorded in DMSO to confirm the presence of coordinated ligand in the complexes. The spectral data and their assignments are listed in Table 3. The spectra of the free ligands showed a signal at δ 11.06–12.96 ppm characteristics of phenolic OH proton which is absent in the complexes, suggesting that the coordination is through deprotonated phenolic oxygen [42–44]. Signal due to NH proton at δ 9.90–10.37 ppm in free ligands is shifted to δ 9.44–9.98 in the complexes [45]. The presence of NH proton in the complexes indicating that the ligand coordinated through the keto form. A singlet observed at δ 8.23–8.35 ppm in the spectra of the free ligands assigned to azomethine proton which undergo downfield shift to δ 8.52–8.85 ppm in the complexes indicating the coordination of azomethine nitrogen to ruthenium metal [42–44]. The signals at δ 7.38–8.34 ppm as multiplets for all complexes are assigned to the protons of pyridinyl group of ligand [46], which is shifting slightly to the upfield compared with the free ligands. The multiplets at δ 6.44–7.60 ppm in the spectra of ligands and complexes are assigned to aromatic protons. The methoxy protons appeared at δ 3.90–3.93 ppm. The new complexes did not show any signal in the upfield region at δ −5 to −12 ppm for the hydride ligand, thus proving its substitution by the mono negative hydrazone Schiff base ligands.

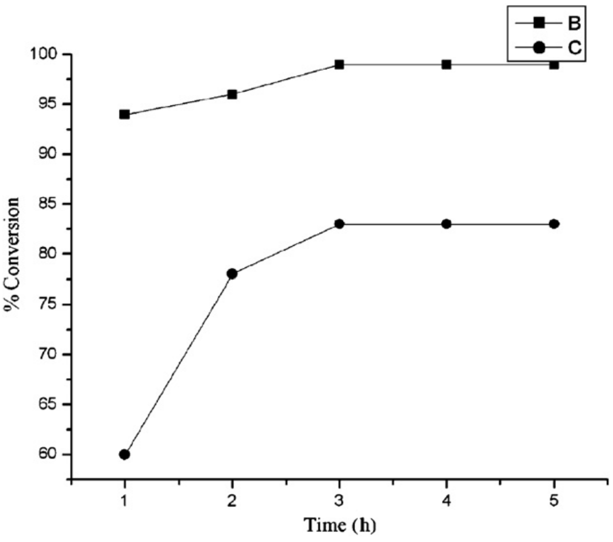
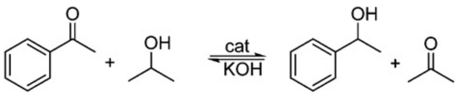


Fig. 2. Catalytic oxidation of benzylalcohol (B) and cyclohexanol (C) in different time intervals.



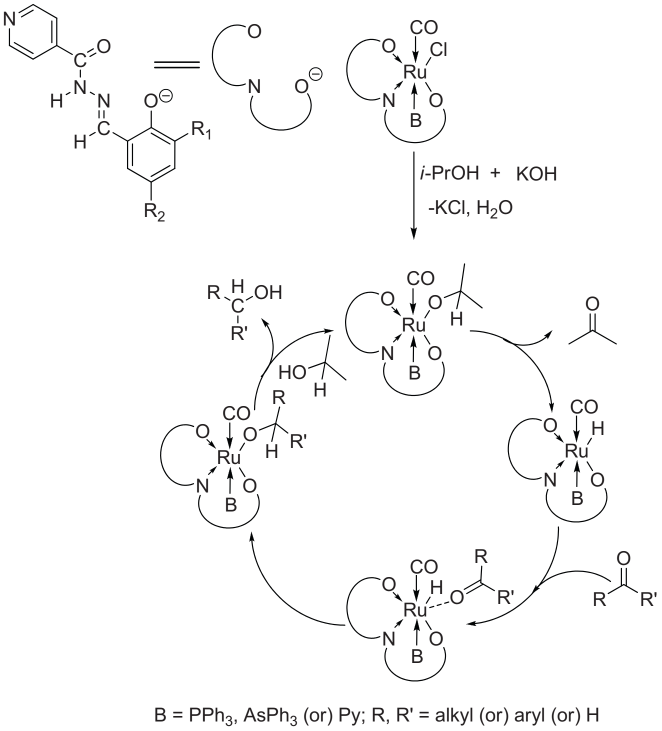
Scheme 3. Catalytic transfer hydrogenation of ketone.

3.4. *^{13}C NMR spectroscopic analysis*

The ^{13}C NMR spectra of some of the complexes have showed (Table 4) a peak at 203.10–206.15 ppm region is due to C≡O carbon. The presence of a peak at 178.36–182.54 ppm region is assigned to carbonyl carbon. In addition, the azomethine (C=N) carbon exhibit its peak in the region of 160.80–164.33 ppm. The multiplets appear around 122.34–138.43 ppm region are assigned to aromatic and pyridine carbons. A sharp singlet at 53.20–55.34 ppm are assigned to methoxy carbon. This confirms the formation of new ruthenium(II) hydrazone Schiff base complexes.

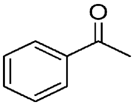
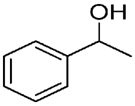
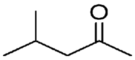
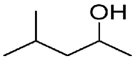
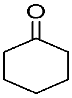
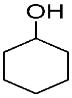
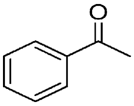
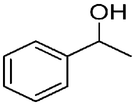
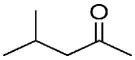
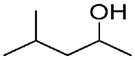
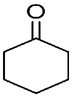
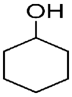
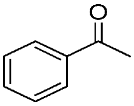
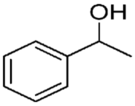
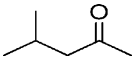
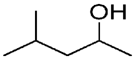
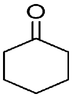
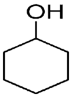
3.5. *^{31}P NMR spectroscopic analysis*

^{31}P NMR spectra of some of the complexes were recorded to confirm the presence of triphenylphosphine groups in the



Scheme 4. Mechanism of catalytic transfer hydrogenation reactions.

Table 6
Catalytic transfer hydrogenation of ketones by ruthenium(II) hydrazone Schiff base complexes.

Complex	Substrate	Product	Conversion (%)
$[RuCl(CO)(PPh_3)(L_2)]$			83
			76
			93
$[RuCl(CO)(Py)(L_2)]$			84
			81
			90
$[RuCl(CO)(AsPh_3)(L_2)]$			80
			80
			86

complexes. A sharp singlet was observed around 22.47–22.62 ppm due to presence of triphenylphosphine ligand in the complexes.

On the basis of analytical and spectral (IR, electronic, ^{1}H, ^{13}C and ^{31}P NMR) data, an octahedral structure has been tentatively proposed for all the new ruthenium(II) hydrazone Schiff base complexes.

3.6. Catalytic oxidation

Catalytic oxidation of primary alcohols and secondary alcohols by the synthesized ruthenium(II) hydrazone Schiff base complexes were carried out in CH_2Cl_2 in the presence of NMO, and the by product water was removed by using molecular sieves. All the complexes oxidized primary alcohols to corresponding aldehydes and secondary alcohols to ketones (Scheme 2 and Fig. 2) with high yields and the results are listed in Table 5. The aldehydes or ketones formed after 3 h of reflux were determined by GC and there was no detectable oxidation in the absence of ruthenium complexes.

The oxidation of benzylalcohol to benzaldehyde resulted in 93–99% yield and cyclohexanol to cyclohexanone resulted in 70–87% yield. The relatively higher yield obtained for the oxidation of benzylalcohol as compared to cyclohexanol is due to the fact that the α-CH unit of benzylalcohol is more acidic than cyclohexanol [47].

Results of the present investigations suggest that the complexes are able to react efficiently with NMO to yield a high valent ruthenium-oxo species capable of oxygen atom transfer to alcohols. This was further supported by spectral changes that occur by addition of NMO to dichloromethane solution of the ruthenium(II) complexes. The appearance of a peak at 390 nm is attributed to the formation of RuIV=O species, which is in confirmed with other oxo ruthenium(IV) complexes [48,49]. Further support in favour of the formation of such species was identified from the IR spectrum of the solid mass (obtained by evaporation of the resultant solution to dryness), which showed a band at 860 cm^{-1}, characteristic of RuIV=O species [50].

3.7. Catalytic transfer hydrogenation

The catalytic transfer hydrogenation of ketones in the presence of ruthenium(II) hydrazone Schiff base complexes has been studied in isopropanol-KOH medium using a molar ratio 1:2.5:300 for the catalyst, KOH and the ketone in 10 cm^3 of isopropanol (Scheme 3).

Typical results are shown in Table 6. The catalyst performed efficiently for both aliphatic and aromatic ketones with high conversion, acetophenone was converted into corresponding alcohol upto 80–84% yield. Isobutyl methyl ketone underwent transfer hydrogenation to afford the corresponding alcohol upto 76–81% yield. Similarly, cyclohexanone was converted to cyclohexanol upto 86–93% yield. The role of KOH is to generate the catalyst from the chloro precursor and the reaction mediates through the hydride species [51]. The base facilitated the formation of the ruthenium alkoxide by abstracting the proton of the alcohol and subsequently, the alkoxide underwent β-elimination to give a ruthenium hydride which is the active species in this reaction [52] (Scheme 4).

4. Conclusions

Several ruthenium(II) hydrazone Schiff base complexes of the composition [RuCl(CO)(B)(L)] (where B = PPh_3, $AsPh_3$ or Py; L = hydrazone Schiff base ligand) have been prepared by reacting ruthenium(II) starting complexes [RuHCl(CO)(EPh_3)$_2$(B)] (where E = P or As; B = PPh_3, $AsPh_3$ or Py) with hydrazone Schiff base ligand under reflux conditions. The new complexes obtained were characterized on the basis of elemental analysis and spectral (FT-IR, electronic, ^{1}H, ^{13}C NMR and ^{31}P NMR) data. An octahedral structure has been tentatively proposed for all the complexes. The complexes showed efficient catalytic property for oxidation of both primary and secondary alcohols to the corresponding carbonyl compounds in the presence of NMO, and also for transfer hydrogenation of aliphatic and aromatic ketones with high conversions.

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