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SYNTHESIS AND CHARACTERIZATION OF ORGANOSOLUBLE RUTHENIUM(II) COMPLEXES BEARING SCHIFF BASE LIGANDS: EFFICIENT REUSABLE CATALYST FOR THE HYDROGENATION REACTIONS

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ABSTRACT: Six new organosoluble ruthenium(II) complexes bearing dibasic tetradentate Schiff base ligands of the general formula [Ru(CO)(PPh_3)(L)] (where L = dibasic tetradentate Schiff base ligands derived by condensing actetoacetanilide/acetoacetotoludide with o-aminophenol/o-aminothiophenol/o-aminobenzoic acid in 1:2 molar ratio in ethanolic medium) have been synthesized by reacting [RuHCl(CO)(PPh_3)$_3$] with the respective Schiff base ligands in 1:1 molar ratio. The complexes were characterized by physico-chemical and spectroscopic methods. An octahedral structure has been proposed tentatively for all the complexes. These ruthenium(II) complexes possess N_2O_2/N_2S_2 metal binding sites and act as a potential catalyst for the hydrogenation reactions. Organosoluble ruthenium(II) complexes have been used as catalysts in the hydrogenation of methoxy benzene and benzaldehyde. From the results it was observed that all the new six complexes proved to be better catalyst in the hydrogenation. All the ruthenium(II) complexes decomposes completely to form ruthenium metal, which in turn forms a active ruthenium hydride in the hydrogenation reaction. The reusability of the ruthenium catalysts have also been evaluated up to six consecutive runs, which does not show much variation in the conversion of the substrate.

Keywords: Ruthenium(II) complexs, Schiff base, tetradentate, electrochemical, hydrogenation, N_2O_2, N_2S_2.

INTRODUCTION

Designing, synthesis and structural characterization of Schiff base complexes are a subject of current interest due to their structural, magnetic, spectral, catalytic and redox properties [1–9]. Much research papers have been published concerning the use of Schiff base ligands, which incorporate nitrogen imine, phenolate, thiophenolate and carboxylato [9–13]. Hydrogenation of aromatic compounds to aliphatic cyclic products is an important reaction with potential applications in chemical industry [14–18]. Health risks related to aromatic compounds, such as benzene and some polyaromatic compounds have encouraged legislators to tighten the restrictions on aromatic content in fuels and solvents. Reduction of benzene is of immense application in the industry, as the product, cyclohexene, is used as a raw material for the production of adipic acid and caprolactam, both of which are intermediates used in the production of Nylon 6 and Nylon 66 [19]. Various metal-based catalysts including those of ruthenium and nickel have been extensively used for the partial and complete reduction of benzene [21–28]. The catalytic reduction of benzene nucleus generally requires more severe conditions than that of simple olefins [20,29]. Even though a lot of success has been achieved with regard to transition metal complex catalyzed hydrogenation of olefins [30–33], there are only few reports on studies involving hydrogenations of arenes using homogeneous metal complex catalysts [34–40].

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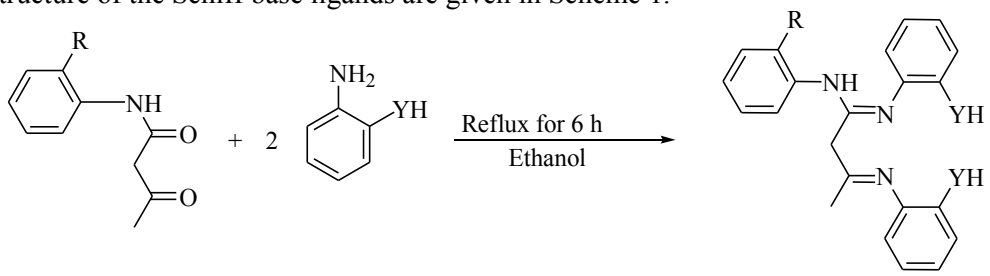
Ruthenium is well known catalyst for the hydrogenation of an aromatic ring cyclohexene and its derivatives [25,41–44]. It is therefore considered as challenge to prepare new and effective homogeneous catalysts for hydrogenation of aromatic compounds. In our reported paper [45-48], efficacy of ruthenium(III) Schiff base complexes have been evaluated as a catalyst for only oxidation of alcohols, C-C coupling reactions and microbial studies. In continuation our work, we have examined the efficacy of ruthenium(II) Schiff bse complexex as a hydrogenating agents, which is a deviated work from the reported papers by our team. In this paper, we report the synthesis and spectral characterization of ruthenium(II) complexes bearing Schiff base ligands and their usability as catalyst in the reduction of benzene. The Schiff bases were prepared by reported literature [45]. The general structure of the Schiff base ligands are given in Scheme 1.



Abbreviation	R	Y
H_2L^1	H	O
H_2L^2	H	S
H_2L^3	H	COO
H_2L^4	CH_3	O
H_2L^5	CH_3	S
H_2L^6	CH_3	COO

Scheme 1. Preparation of tetradentate Schiff base ligands

Physical Measurements

Melting Points
Melting points were recorded on a Veego VMP-DS melting point apparatus and are uncorrected.
Elemental analyses
The analysis of carbon, hydrogen, nitrogen and sulphur were performed in Vario EL III CHNS analyzer at Cochin University, Kerala, India.
IR spectra
IR spectra were recorded as KBr pellets in the 400 - 4000 cm^{-1} region using a Perkin Elmer FT–IR 8000 spectro-photometer with a resolution of 4 cm^{-1} in transmittance mode.
UV-Vis spectra
Electronic spectra of all ligands and the complexes were taken in dichloromethane solution in quartz cells. The concentration of the complexes ranges around 0.02 – 0.3N. The spectra were recorded on a Systronics double beam UV-Vis Spectrophotometer 2202 in the range 200-800 nm at room temperature.
NMR spectra
^1H and ^{13}C-NMR spectra for the ligands and complexes were recorded using Bruker 500 MHz instrument in $CDCl_3$ at room temperature in Indian Institute of Science, Bangalore. Minimum quantities of ligands and complexes were dissolved in deuterated $CDCl_3$. ^1H-NMR chemical shifts were referenced to tetramethylsilane (TMS) as an internal solvent standard resonance and ^{13}C-NMR chemical shifts were referenced to the internal solvent resonance. ^{31}P-NMR spectra of the complexes were obtained at room temperature using o-phosphoric acid as a reference. Signals are quoted in parts per million as δ downfield from internal reference.

Cyclic voltammetry

Cyclic voltammetric studies were carried out in acetonitrile using a glassy-carbon working electrode and potentials were referenced to standard calomel electrode at Madurai Kamaraj University, Madurai. Minimum quantity of the complexes was dissolved in acetonitile and decimolar solution of TPAP was added.

GC Analysis

Gas chromatographic (GC) analyses were conducted on an ACME 6000 series instrument equipped with a flame ionization detector (FID) using a DP-5 column of 30 m length, 0.53 mm diameter, and 5.00 mm film thickness at Madurai Kamaraj University.

Material and methods

All the reagents used were of analar grade. $RuCl_3.3H_2O$ was purchased from Loba Chemie and was used without further purification. The starting metal complex $[RuHCl(CO)(PPh_3)_3]$ [49] was prepared by reported literature methods.

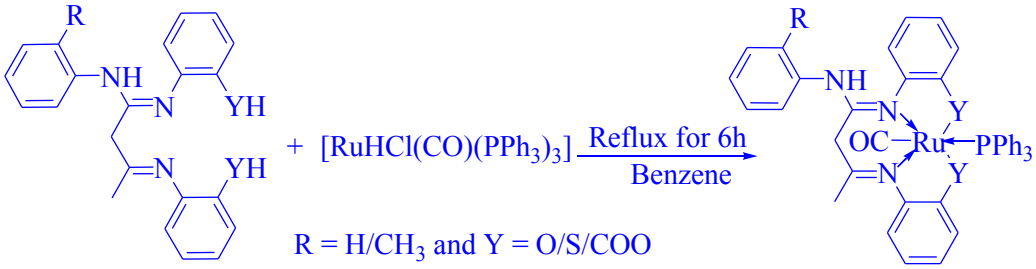
RECOMMENDED PROCEDURES

Preparation of Schiff base ligands

To an ethanolic solution of actetoacetanilide (0.17g; 1 mmol)/acetoacetotoludide (0.19 g; 0.1 mmol) to o-aminophenol(0.20 g; 2 mmol)/ o-aminothiophenol (0.24 g; 2 mmol)/o-aminobenzoic acid (0.27 g; 2 mmol) in ethanol 1:2 molar ratio and the mixture was stirred for about half an hour and then refluxed for about 6 h (Scheme 1). The resultant product was washed with ethanol and the purity of the ligands were checked by TLC.

Synthesis of new ruthenium(II) Schiff base complexes

All the new complexes were prepared by the following general procedure described below (Scheme 2). To a solution of $[RuHCl(CO)(PPh_3)_3]$ (1 mmol) in benzene (20 cm^3) the appropriate Schiff base (1 mmol) was added in 1:1 molar ratio and heated under reflux for 6 h. The solution was then concentrated to 3 mL and cooled. The complex was precipitated by the addition of small quantity of petroleum ether (60-80°C) recrystallized from CH_2Cl_2/petroleum ether and dried in vacuo.



Scheme 2. Formation of new mononuclear Ru(II) Schiff base complexes

Hydrogenation of methoxy benzene and benzaldehyde

Hydrogenation of methoxy benzene and benzaldehyde was carried out by dissolving 0.001 mmol of the catalyst in 10 mL dichloromethane and was treated with 2 g of the substrate under 400^{0}C, 400 psi hydrogen pressure, 400 rpm for 4 h. The Parr reactor was flushed with nitrogen thrice followed by flushing hydrogen twice at room temperature. The reaction was initiated by stirring and after 4 h, the reaction was stopped. The complexes were recovered by adding petroleum ether and the regenerated complexes were used up to six consecutive runs. The converted products have been evaluated using GCMS.

RESULTS AND DISCUSSION

Stable ruthenium(II) Schiff base complexes of the general formula $[Ru(CO)(PPh_3)(L)]$ (L = dianion tetradentate Schiff base) have been prepared by reacting $[RuHCl(CO)(PPh_3)_3]$ with the respective Schiff bases in a 1:1 molar ratio in benzene. All the complexes are soluble in most of the common organic solvents. Their purity was checked by TLC on silica gel. The analytical data (Table 1) obtained for the new complexes agree well with the proposed molecular formula. In all of the above reactions, the Schiff bases behave as binegative tetradentate ligands. The high resolution mass spectra of $[Ru(CO)(PPh_3)(L^1)]$ and $[Ru(CO)(PPh_3)(L^4)]$ displayed the molecular ion isotopic peak at m/z 748.8972 and 762.4591 respectivly and the remaining peaks represents the successive degradation of the complexes into their corresponding fragments. These peaks are consistent with the proposed molecular formula of the corresponding ruthenium(II) Schiff base complexes [50].

Table 1. Analytical data of Schiff base and its ruthenium(II) complexes

Complex	Colour	Melting Point °C	Molecular formula	Molecular weight	Found (calculated)(%)			
					C	H	N	S
$[Ru(CO)(PPh_3)(L^1)]$	Green	248	$RuPC_{41}H_{34}N_3O_3$	748.77	65.56(65.77)	4.52(4.58)	5.57(5.61)	-
$[Ru(CO)\ PPh_3)(L^2)]$	Green	212	$RuPS_2C_{41}H_{34}N_3O$	780.90	62.98(63.06)	4.34(4.39)	5.29(5.38)	8.13(8.21)
$[Ru(CO)(PPh_3)(L^3)]$	Brown	223	$RuPC_{43}H_{34}N_3O_5$	804.79	64.01(64.17)	4.19(4.26)	5.17(5.22)	-
$[Ru(CO)(PPh_3)(L^4)]$	Brown	198	$RuPC_{42}H_{36}N_3O_3$	762.79	65.96(66.13)	4.56(4.76)	5.36(5.41)	-
$[Ru(CO)(PPh_3)(L^5)]$	Green	236	$RuPS_2C_{42}H_{36}N_3O$	794.92	63.24(63.46)	4.49(4.56)	5.22(5.29)	7.98(8.07)
$[Ru(CO)(PPh_3)(L^6)]$	Brown	285	$RuPC_{44}H_{36}N_3O_5$	818.81	64.19(64.54)	4.39(4.43)	5.02(5.13)	-

SPECTROSCOPIC STUDIES

FT-IR Spectrascopy

The important IR absorption bands for the synthesized complexes may be classified into those originating from the ligands and those arising from the bonds formed between ruthenium(II) and the coordinating sites are summarised in Table 2. The free Schiff base ligands showed a strong band in the region 1603-1667 cm^{-1}, which is characteristic of the azomethine $\nu_{(C=N)}$ group. Coordination of the Schiff bases to the metal through the nitrogen atom is expected to reduce the electron density in the azomethine link and lower the $\nu_{(C=N)}$ absorption frequency. The band due to $\nu_{(C=N)}$ is shifted to lower frequencies and appears around 1571 -1654 cm^{-1}, indicating coordination of the azomethine nitrogen to the ruthenium metal [11-13,45,50-53]. A strong band observed at 1310-1330 cm^{-1} in the free Schiff bases H_2L^1 and H_2L^4 has been assigned to phenolic C–O stretching. On complexation, this band is shifted to a higher frequency 1439 cm^{-1}, indicating coordination through the phenolic oxygen [11,12,45,50-54]. This has been further supported by the disappearance of the broad $\nu_{(OH)}$ band around 3000 cm^{-1} in the complexes $[Ru(PPh_3)(CO)(L^1)]$ and $[RuCl(PPh_3)(CO)(L^4)]$ indicating deprotonation of the phenolic proton prior to coordination. In the IR spectra of the Schiff base ligand, a very weak absorption band appeared at 2600 cm^{-1} corresponding to $\nu_{(S-H)}$ disappeared in the spectra of the complexes due to the fact that coordination takes place through the sulphur atom after deprotonation. Moreover, the absorption due to $\nu_{(C-S)}$ of the ligand at 1212-1245 cm^{-1} is shifted to a higher frequency 1259-1260 cm^{-1} in the complexes $[Ru(PPh_3)(CO)(L^2)]$ and $[Ru(PPh_3)(L^5)]$ indicating that the other coordination is through phenolic sulphur atom [11,45]. For the anthranilic acid moiety, the free Schiff bases H_2L^3 and H_2L^6 shows the $\nu_{(O-H)}$ absorption observed at 3300cm^{-1} and the $\nu_{(C=O)}$ frequency of the carbonyl was seen as a band at 1680 cm^{-1} and also shows the absorption bands in 1668-1671 cm^{-1} and 1419-1420 cm^{-1} regions for asymmetric $\nu_{(COO^-)}$ and symmetric $\nu_{(COO^-)}$ streching.

In the complexes [Ru(PPh$_3$)(CO)(L^3)] and [Ru(PPh$_3$)(CO)(L^6)] the bands were observed in the 1652 cm^{-1} and 1436 cm^{-1} regions arising from asymmetric $\nu_{(COO^-)}$ and symmetric $\nu_{(COO^-)}$ stretching of the carboxylato group [12,13,45]. This indicates the coordination of the carboxyl group to ruthenium metal ion in the complexes. The differences between the asymmetric and symmetric stretching frequencies of the coordinated carboxyl group lie in the 216 cm^{-1} range, a clear indication of the monodentate coordination of the carboxyl group with of free carbonyl group [12,13,45]. The characteristic bands due to triphenylphosphine were observed in the expected region. In the entire complexes strong band appears in the region 1941-1965 cm^{-1} owing to carbonyl group.

Table 2. IR and Electronic spectral data of ruthenium(II) Schiff base complexes

Complex	FT-IR (cm^{-1})						Electronic spectra (λ_{max}) (nm)
	$\nu_{C=N}$	ν_{asyCOO^-}	ν_{syCOO^-}	ν_{C-O^-}	ν_{C-S^-}	ν_{CO}	
[Ru(CO)(PPh$_3$)(L^1)]	1654	-	-	1439	-	1942	257,315
[Ru(CO)(PPh$_3$)(L^2)]	1653	-	-	-	1260	1965	254,305,372
[Ru(CO)(PPh$_3$)(L^3)]	1595	1652	1436	-	-	1961	256,340
[Ru(CO)(PPh$_3$)(L^4)]	1621	-	-	1439	-	1941	256,299,342
[Ru(CO)(PPh$_3$)(L^5)]	1633	-	-	-	1259	1960	257,302
[Ru(CO)(PPh$_3$)(L^6)]	1571	1652	1436	-	-	1956	257,300,363

Electronic spectra

The electronic spectra of all the ligands and complexes in dichloromethane showed two to four bands in the 254-426 nm regions (Table 2). The electronic spectra of all the free ligands showed two types of transitions, the first one appeared at range 255-294 nm which can be assigned to π-π* transition was due to transitions involving molecular orbitals located on the phenolic, thiophenolic and carboxylic chromophore. These peaks have been shifted in the spectra of the complexes. This shifting may be due to the donation of a lone pair of electrons from the oxygen of the phenolic and carboxylic and thiophenolic sulphur group to the central metal atom respectively. This reveals that one of the coordination site is oxygen of the phenolic and carboxylic and sulphur of the thiophenolic groups respectively. The second type of transitions appeared at range 359-426 nm assigned to n→π* transition due to azomethine groups and benzene ring of the ligands. These bands have also been shifted in the spectra of the new complexes indicating the involvement of imine group nitrogens in coordination with central metal atom. The spectra of the all the complexes showed another types of transitions which is different from the free ligands. All the complexes are diamagnetic, indicating the presence of ruthenium in the +2 oxidation state. The ground state of ruthenium(II) in an octahedral environment is $^1A_{1g}$, arising from the t_{2g}^6 configuration. The excited state terms are $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$. Hence four bands corresponding to the transition $^1A_{1g}\rightarrow{}^3T_{1g}$, $^1A_{1g}\rightarrow{}^3T_{2g}$, $^1A_{1g}\rightarrow{}^1T_{1g}$ and $^1A_{1g}\rightarrow{}^1T_{2g}$ are possible in order of increasing energy. The other high intensity band in the visible region around 254–372 nm has been assigned to charge transfer transitions arising from the metal t_{2g} level to the unfilled π* molecular orbital of the ligand [50-56]. The pattern of the electronic spectra for all the complexes indicate the presence of an octahedral environment around the ruthenium(II) ion similar to that of other ruthenium octahedral complexes [50-56].

^{1}H-NMR Spectra

The ^{1}H-NMR spectra of the ligands have been recorded in $CDCl_3$ solution. All the ligands show multiplets at 6.3-8.1 ppm for the presence of aromatic protons. The –NH proton, -CH_2 proton and methyl protons appears as a singlet in the regions 8.6-10.1 ppm, 2.4-3.5 ppm and 1.8-2.2 ppm for all the ligands. In H_2L^1 and H_2L^4 ligands, the phenolic OH proton appears as a singlet in the region 10.8-10.9 ppm. In H_2L^2 and H_2L^5 ligands, the thiophenolic SH proton appears as a singlet in the region 3.6-3.7 ppm respectively. In the ligands H_2L^4-H_2L^6, the aromatic methyl protons appears as a singlet in the range 2.1-2.7 ppm In the ligand H_2L^3 and H_2L^6, the COOH proton appears as a singlet in the region 9.6-10.8 ppm.

The ^{1}H-NMR spectra of the complexes have been recorded in $CDCl_3$ solution and the values are mentioned in the Table 3. All the complexes show multiplets at 6.3-8.4 ppm for the presence of aromatic protons. In all the complexes, the –NH proton, -CH_2 proton and methyl protons appears as a singlet in the regions 8.9-10.2 ppm, 2.4-3.6 ppm and 1.5-1.9 ppm. In the complexes [Ru(CO)(PPh_3)(L^4)], [Ru(CO)(PPh_3)(L^5)] and [Ru(CO)(PPh_3)(L^6)] a sharp singlet observed in the range 2.2-2.5 ppm indicates the presence of aromatic methyl proton. A sharp singlet observed for -Ph-OH, -Ph-SH and -Ph-COOH protons for all the ligands were disappeared in all the complexes which indicates the coordination of ruthenium through the Ph-O, Ph-S, Ph-COO.

^{13}C-NMR Spectra

The ^{13}C-NMR spectra of the complexes [Ru(CO)(PPh_3)(L^1)], [Ru(CO)(PPh_3)(L^2)] and [Ru(CO)(PPh_3)(L^3)] have been recorded in $CDCl_3$ solution and the values are mentioned in the Table 3. All the complexes show multiplets at 111-136 ppm for the presence of aromatic carbons. In all the complexes, -NH-C=N-Ph-, CH_3-C=N-Ph, CH_3 and –CH_2- appears in the range 148-151 ppm, 136-139 ppm, 16-19 ppm and 4.2-4.4 ppm respectively. For all the complexes, the carbonyl group C≡O appears in the range 160-161 ppm respectively

^{31}P-NMR Spectra

^{31}P-NMR spectra were recorded for the complexes [Ru(CO)(PPh_3)(L^1)], [Ru(CO)(PPh_3)(L^2)] and [Ru(CO)(PPh_3)(L^3)] in order to confirm the presence of triphenylphosphine group. In all the complexes a sharp single signals are observed in the range 23.98-35.51 ppm confirming the presence of one triphenylphopshine [57,58] .

Table 3. ^{1}H, ^{13}C NMR spectral data of ruthenium (II) Schiff base complexes

Complex	^{1}H-NMR	^{13}C-NMR
[Ru(CO)(PPh_3)(L^1)]	6.3-7.8 (m, ar), 9.3 (s, NH), 2.4 (s,-CH_2-), 1.5 (s,-CH_3)	111-136 (m, ar), 42 (s, -CH_2-), 16 (s, CH_3), 149 (s, NH-C=N-Ph), 136 (s, CH_3-C=N-Ph), 160 (s, Ru-CO)
[Ru(CO)(PPh_3)(L^2)]	6.3-8.1 (m, ar), 8.9 (s, NH), 2.6 (s,-CH_2-), 1.5 (s,-CH_3)	121-132 (m, ar), 44 (s, -CH_2-), 19 (s, CH_3), 151 (s, NH-C=N-Ph), 139 (s, CH_3-C=N-Ph), 160 (s, Ru-CO)
[Ru(CO)(PPh_3)(L^3)]	6.3-7.6 (m, ar), 10.2 (s, NH), 3.1 (s,-CH_2-), 1.9 (s,-CH_3)	118-131 (m, ar), 43 (s, -CH_2-), 18 (s, CH_3), 148 (s, NH-C=N-Ph), 137 (s, CH_3-C=N-Ph), 161 (s, Ru-CO)
[Ru(CO)(PPh_3)(L^4)]	6.3-7.3 (m, ar), 10.0 (s, NH), 3.5 (s,-CH_2-), 1.7 (s,-CH_3), 2.2 (s, ar-CH_3)	-
[Ru(CO)(PPh_3)(L^5)]	6.3 -8.1(m, ar), 9.8 (s, NH), 3.6 (s,-CH_2-), 1.6 (s,-CH_3), 2.3 (s, ar-CH_3)	-
[Ru(CO)(PPh_3)(L^6)]	6.3-8.4 (m, ar), 9.1 (s, NH), 2.9 (s,-CH_2-), 1.7 (s,-CH_3), 2.5 (s, ar-CH_3)	-

Electrochemistry

Ruthenium(II) Schiff base complexes were electrochemically examined at a glass carbon working electrode in dichloromethane solution using cyclic voltammetry (Table 4). All the complexes shows reduction potential [E_p^a = -0.435 to -0.670V; E_p^c = -0.325 to -0.459V] only and the peak to peak separation value ΔE_p ranges from 110 to 276mV is best quasi-reversible. This is attributed to slow electron transfer and adsorption of the complex on to the electrode surface [51,58,59]. Reduction potentials of ruthenium(II)- ruthenium(I) in the complexes were found to be sensitive to the nature of the substituents Y in the Schiff base ligands.

The cyclic voltammogram of the complex [Ru(CO)(PPh_3)(L^4)] show that the electron transfer (i_p^a/ i_p^c = 1.8) occurring for the reduction reaction is two electron reduction [$Ru^{2+} \rightarrow Ru^0$]. The electrochemical behavior of the complex [Ru(CO)(PPh_3)(L^4)] was different from that observed for other five complexes. This high value of ΔE_p (276mV) of the complex [Ru(CO)(PPh_3)(L^4)] reflects the stability of complex in different oxidation states [58].

Table 4. Electrochemical data of new ruthenium(II) Schiff base complexes

Complexes	$Ru^{II} - Ru^{I}$ (reduction)			
	E_{pa}(V)	E_{pc}(V)	E_f(V)	ΔE_p(mV)
[Ru(CO)(PPh_3)(L^1)]	-0.623	-0.435	-0.529	188
[Ru(CO)(PPh_3)(L^2)]	-0.623	-0.443	0.533	180
[Ru(CO)(PPh_3)(L^3)]	-0.670	-0.459	-0.564	211
[Ru(CO)(PPh_3)(L^4)]	-0.616	-0.340	-0.478	276
[Ru(CO)(PPh_3)(L^5)]	-0.650	-0.450	-0.486	244
[Ru(CO)(PPh_3)(L^6)]	-0.435	-0.325	-0.380	110

Supporting electrolyte: [NBu_4]ClO_4 (0.1M); Scan rate, 0.1 mV^{-1}; reference electrode, Ag-AgCl.
$\Delta E_p = E_{pa} - E_{pc}$; $E_{1/2} = 0.5 (E_{pa} + E_{pc})$, Where E_{pa} and E_{pc} are the anodic and cathodic peak potentials in volts, respectively.

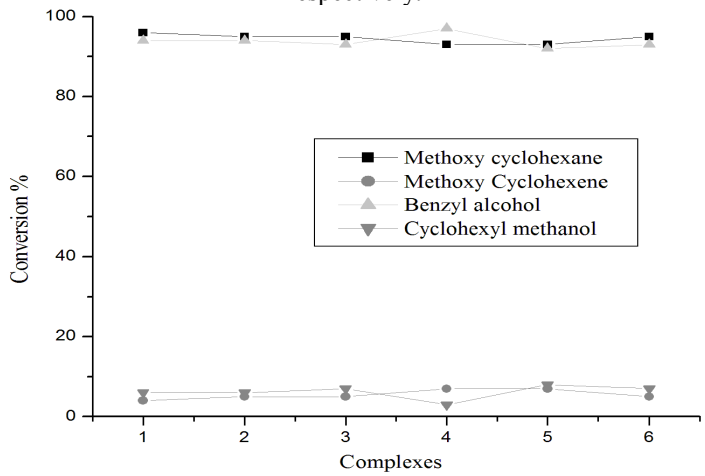


Fig 1. Turnover of methoxy benzene and benzaldehyde

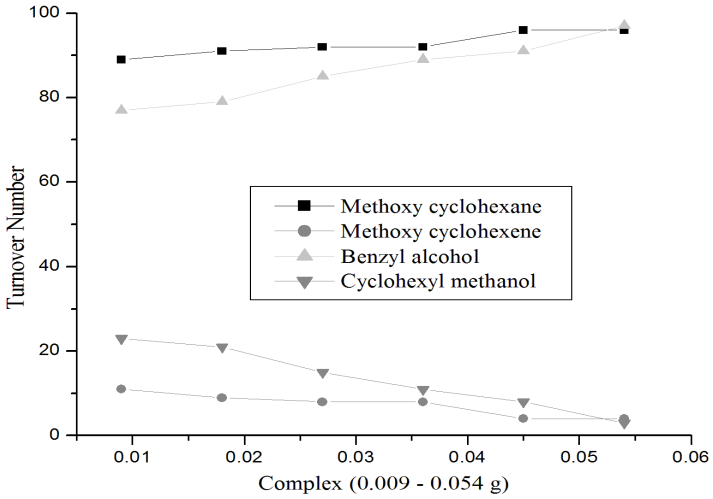


Fig 2. Effect of complex concentration in hydrogenation reaction

Hydrogenation of methoxy benzene and benzaldehyde

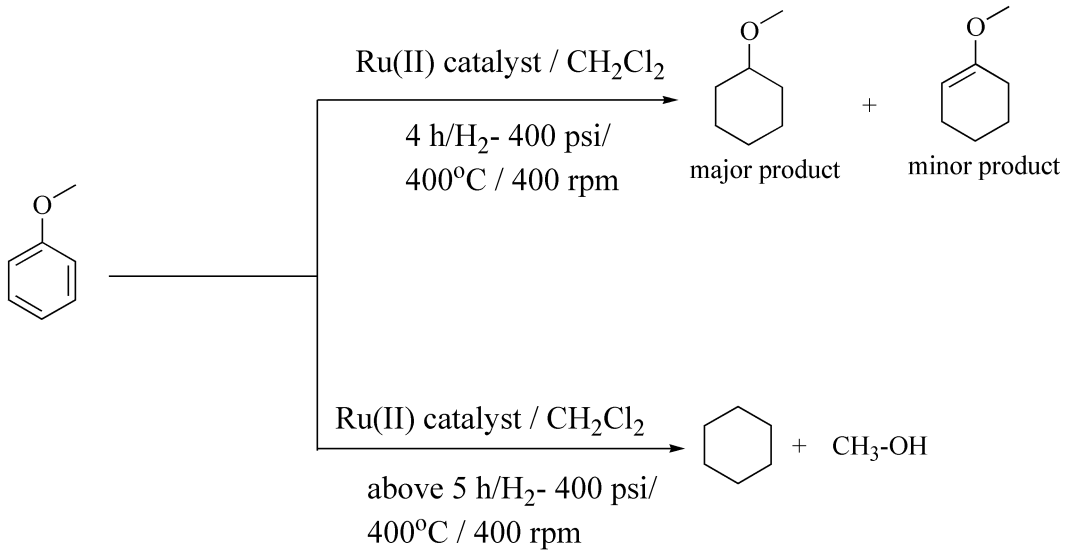
The hydrogenation of methoxy benzene yielded the products namely methoxy cyclohexane and methoxy cyclohexene respectively. The reactivity of methoxy benzene was very high in the hydrogenation reactions and the results obtained have been summarized in the Table 5 (Scheme 3 and Figure 1). On hydrogenation, the ruthenium(II) complexes decomposes completely leading to the formation of ruthenium metal[59] at high temperature and it was confirmed by mass spectral analysis. An active ruthenium hydride is formed after passing hydrogen gas. A possible mechanism[60] has been proposed for the hydrogenation of methoxy benzene (Scheme 4). Benzene ring is hydrogenated completely due to the formation of a planar π complex[61] with ruthenium metal which undergoes a stepwise hydrogenation via linear σ bonded benzene ring in the presence of hydrides bonded in the ruthenium metal sites[61]. Formation of methoxycyclohexene may be an intermediate in the hydrogenation reaction. By increasing the reaction time more than 5 h, formation of methanol and cyclohexane takes place (Scheme 3). The conversion of methoxybenzene to methoxycyclohexane is high when compared with the previous literature[62]. A detailed catalytic study towards the reduction of methoxybenzene using complex $[Ru(CO)(PPh_3)_2(L^1)]$ was carried out at different catalyst concentrations and the data thus obtained are summarized (Table 6 and Figure 2) and also the reusability of the ruthenium catalyst has been evaluated and characterized by mass spectral study. In the hydrogenation reactions, the reusability of the ruthenium catalysts does not show much variation in the conversion (Table 7 and Figure 3).

Table 5. Hydrogenation of methoxy benzene and benzaldehyde

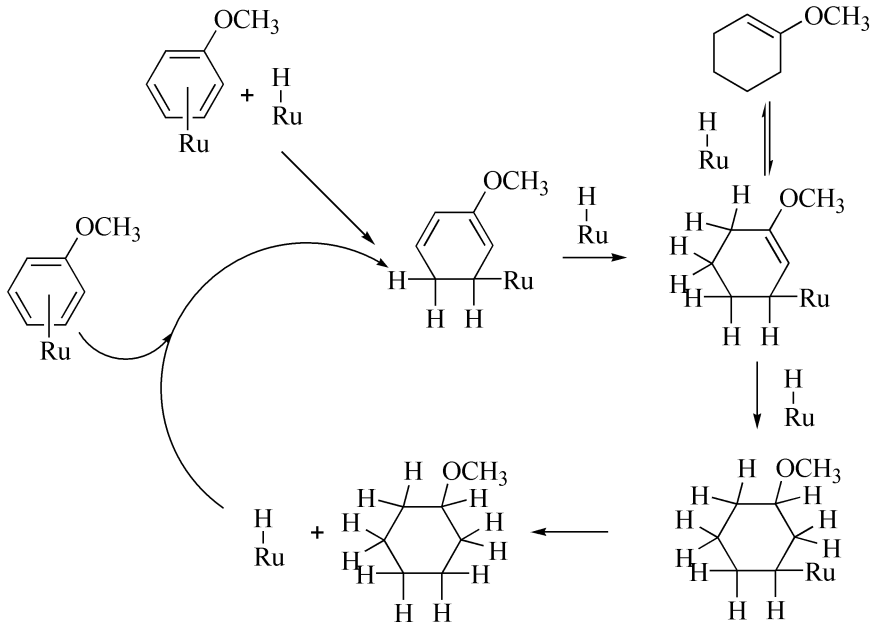
Complexes	Methoxy benzene		Benzaldehyde	
	Methoxy cyclohexane(%)	Methoxycyclohexene (%)	Benzyl alcohol (%)	Cyclohexylmethanol (%)
$[Ru(CO)(PPh_3)_2(L^1)]$	96	4	94	6
$[Ru(CO)(PPh_3)_2(L^2)]$	95	5	94	6
$[Ru(CO)(PPh_3)_2(L^3)]$	95	5	93	7
$[Ru(CO)(PPh_3)_2(L^1)]$	93	7	97	3
$[Ru(CO)(PPh_3)_2(L^2)]$	93	7	92	8
$[Ru(CO)(PPh_3)_2(L^3)]$	95	5	93	7

Table 6. Influence of catalyst $[Ru(CO)(PPh_3)_2(L^1)]$ concentration in the hydrogenation of methoxybenzene

$[Ru(CO)(AsPh_3)_2(L^1)]$ (g)	Methoxybenzene	
	Methoxycyclohexane(%)	Methoxycyclohexene(%)
0.009	89	11
0.018	91	9
0.027	92	8
0.036	92	8
0.045	96	4
0.054	96	4



Scheme 3. Hydrogenation of methoxy benzene



Scheme 4. Possible mechanism for the hydrogenation of methoxy benzene

In the hydrogenation of benzaldehyde (Scheme 5), it was observed that benzyl alcohol is formed as major product (Table 5 and Figure 1 and 2). During the hydrogenation of benzaldehyde, ruthenium(II) complexes decomposes to form ruthenium metal and it further forms ruthenium hydride after the passage of hydrogen gas. A possible mechanism has been proposed for the hydrogenation of benzaldehyde (Scheme 6). In this reaction, first hydrogenation of aldehyde takes place, because aldehyde group present in the benzene ring can be converted easily to its corresponding alcohol and after this, hydrogenation of benzene ring takes place. There is no intermediate formation in this reaction as reported in the previous literature[41].

A detailed catalytic study towards the reduction of benzaldehyde using complex $[Ru(CO)(PPh_3)_2(L^1)]$ was carried out at different catalyst concentrations and the results obtained are summed up in the Table 7. The complex $[Ru(CO)(PPh_3)_2(L^1)]$ showed maximum conversion in the formation of benzyl alcohol and the reusability has been evaluated up to six consecutive runs which does not show much variation in the conversion of benzaldehyde and the results are given in the Table 8 (Figure 3). By increasing the reaction temperature, time and hydrogen pressure to above 500 °C, 10 h and 600 psi respectively, the formation of cyclohexyl methanol reached 100% conversion (Scheme 3).

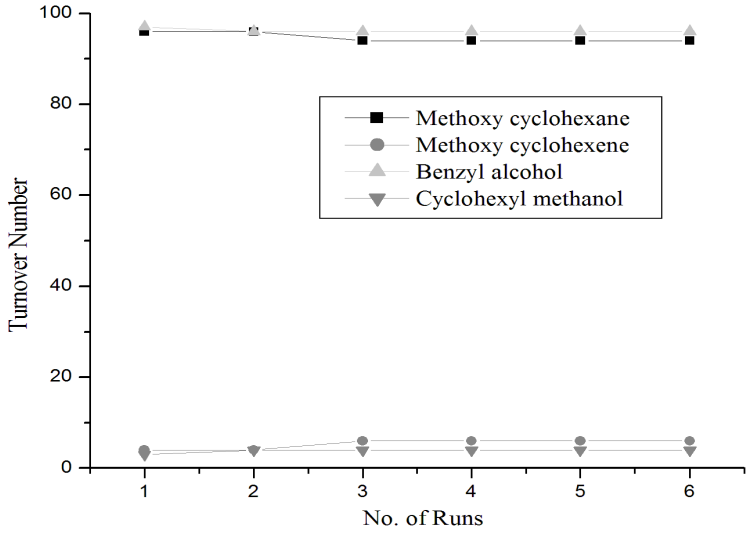


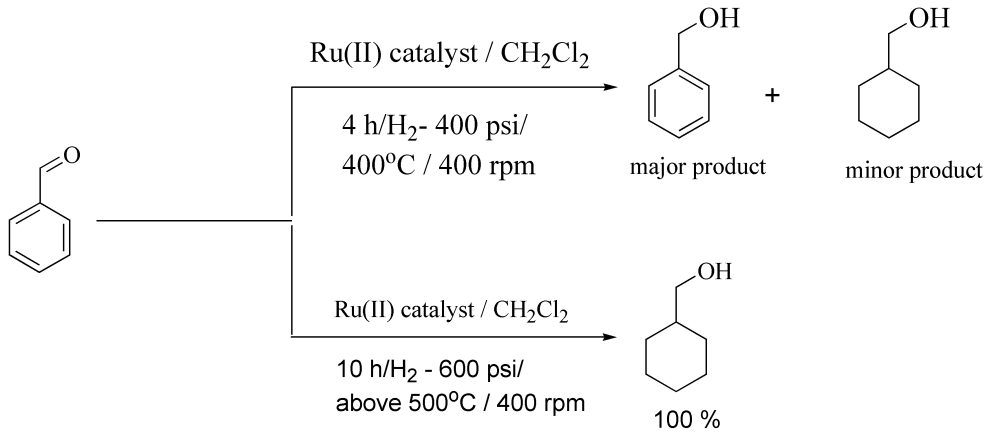
Fig 3. Reusability of ruthenium catalyst in hydrogenation reaction

Table 7. Influence of catalyst $[Ru(CO)(PPh_3)_2(L^4)]$ concentration in the hydrogenation of benzaldehyde

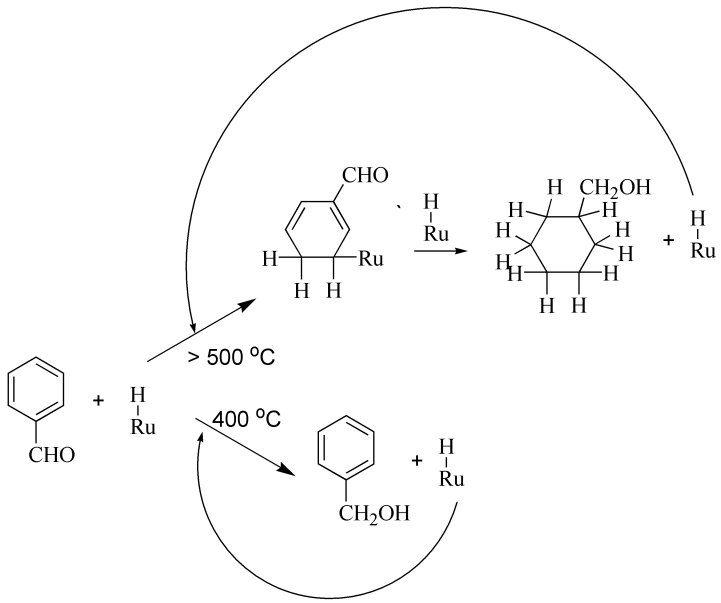
$[Ru(CO)(PPh_3)_2(L^4)]$ (g)	Benzaldehyde	
	Benzyl alcohol (%)	Cyclohexylmethanol (%)
0.009	77	23
0.018	79	21
0.027	85	15
0.036	89	11
0.045	91	8
0.054	97	3

Table 8. Reusability of $[Ru(CO)(PPh_3)_2(L^1)]$ and $[Ru(CO)(PPh_3)_2(L^4)]$ in the hydrogenation of methoxy benzene and benzaldehyde

Run	Methoxybenzene		Benzaldehyde	
	Methoxycyclohexane (%)	Methoxycyclohexene (%)	Benzylalcohol (%)	Cyclohexylmethanol (%)
1	96	4	97	3
2	96	4	96	4
3	94	6	96	4
4	94	6	96	4
5	94	6	96	4
6	94	6	96	4



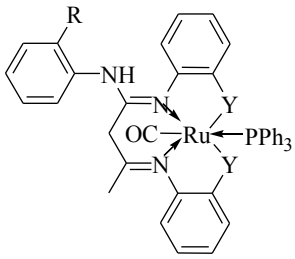
Scheme 5. Hydrogenation of benzaldehyde



Scheme 6. Possible mechanism for the hydrogenation of benzaldehyde

CONCLUSION

An octahedral structure has tentatively proposed to the new ruthenium(II) complexes having the general formula of the type [Ru(CO)(PPh_3)(L)] (scheme 7). The activity of the ruthenium(II) Schiff base complexes in the hydrogenation of methoxy benzene and benzaldehyde were evaluated using GCMS. During the hydrogenation all the complexes decomposed completely to ruthenium metal, leading to the formation of a active ruthenium hydride after the passage of hydrogen gas. In the conversion of methoxy benzene a positive effect was observed in the hydrogenation of aromatic ring. By increasing the reaction time above 5 h, methoxy cyclohexane decomposes to form methanol and cyclohexane. By increasing the reaction temperature, time and hydrogen pressure to above 500 °C, 10 h and 600 psi respectively, the formation of cyclohexyl methanol reached 100% conversion. The six ruthenium(II) complexes shows high conversion in the formation of methoxycyclohexane and benzyl alcohol. The reusability of the ruthenium catalysts were evaluated upto six consecutive runs. All the six ruthenium(II) Schiff base complexes acted as an efficient catalysts in the hydrogenation reactions.



R= H/CH_3; Y = O/S/COO

Scheme 5. Proposed Structure of the new ruthenium(II) Complexes

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