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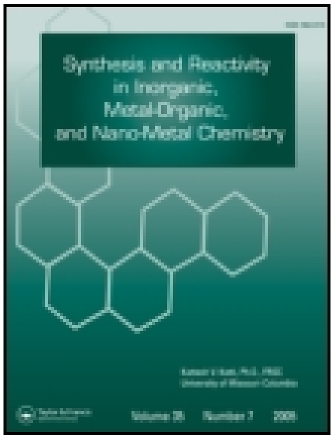

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Ruthenium(II) Carbonyl Complexes Containing Unsymmetrical Schiff Bases: Synthesis, Characterization, and Catalytic Applications

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Ruthenium(II) Carbonyl Complexes Containing Unsymmetrical Schiff Bases: Synthesis, Characterization, and Catalytic Applications

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Unsymmetrical Schiff base complexes of general formula [Ru(CO)(B)(L)] (B = PPh_3, $AsPh_3$, or Py; L = dianion of unsymmetrical Schiff base ligand) have been synthesized from the reaction of [RuHCl(CO)$(EPh_3)_2$(B)] (E = P or As; B = PPh_3, $AsPh_3$, or Py) with unsymmetrical Schiff bases. The new synthesized complexes were characterized by using elemental analysis, IR spectra, electronic spectra, ^{1}H-NMR, ^{13}C-NMR, and ^{31}P-NMR spectra. All the complexes were tentatively assigned an octahedral geometry. The catalytic activities of the synthesized complexes have been studied and found that the complexes showed efficient catalytic activity for oxidation of alcohols and reduction of ketones.

Keywords catalytic oxidation, catalytic transfer hydrogenation, ruthenium(II) carbonyl complexes, spectroscopic studies, unsymmetrical Schiff base

INTRODUCTION

Schiff base complexes have remained an important and popular area of research due to their simple synthesis, versatility, and diverse range of applications. Thus, Schiff bases have played a marvelous role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals.[1,2] Unsymmetrical Schiff bases have advantages than symmetrical Schiff bases because of fine-tuning structures by introducing different electron withdrawing and/or donating groups on the periphery of both imine units. The unsymmetrical Schiff bases have been reported to give improved enantioselective behavior in various organic transformations as compared with their symmetrical derivatives.[3]

Among transition metal complexes ruthenium complexes have been widely used as catalysts in various catalytic reactions such as hydrogenation, oxidation, isomerization, polymerization, nucleophilic addition to multiple bonds, and carbon-carbon bond formation.[4] The searches for catalytic oxidations with inexpensive green oxidants, such as molecular oxygen or air, still play a key role in the development of industrial processes.[5] In this line, triphenylphosphine complexes of ruthenium have been found to be an efficient catalyst for various organic transformations such as oxidation of alcohols and transfer hydrogenation of carbonyl compounds.[6–8] As a part of our continuing efforts to synthesize and characterize ruthenium chelates using simple and inexpensive Schiff base ligands, we herein report the synthesis of a series of hexa-coordinated ruthenium(II) unsymmetrical Schiff base complexes containing carbonyl, PPh_3/$AsPh_3$ and other coligands. 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. The general structure of the unsymmetrical Schiff base ligands used in this study is shown in Figure 1.

EXPERIMENTAL

All the reagents used were analar or chemically pure grade. The solvents used were freshly distilled according to their standard procedure.[9] Elemental analysis was performed by using Vario EL III Elemental analyzer at SAIF Cochin India. FT-IR spectra were recorded in KBr pellets with a Nicolet FT-IR spectrophotometer over the 400–4000 cm^{-1} range. Electronic spectra were recorded in CH_2Cl_2 solution on a Shimadzu UV-1650 PC spectrophotometer over the 200–800 nm range. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded in Jeol GSX-400 instrument using DMSO-D6 and $CDCl_3$ as the solvents. Melting points were recorded with a Technico melting point apparatus and were uncorrected. The catalytic yields were determined using ACME 6000 series GC-FID with a DP-5 column of 30 m length, 0.53 mm diameter, and 5.00 μm film thickness.

The starting complexes [RuHCl(CO)$(PPh_3)_3$],[10] [RuHCl(CO)(Py)$(PPh_3)_2$],[11] and [RuHCl(CO)$(AsPh_3)_3$][12] were prepared according to the literature methods.

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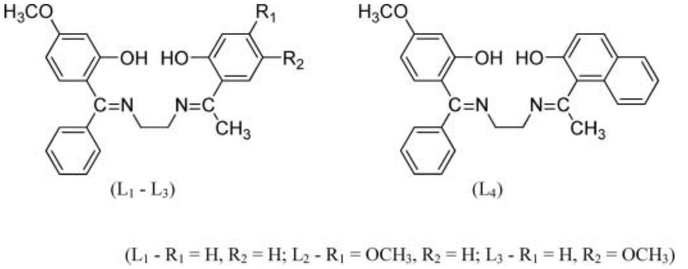


FIG. 1. Structure of unsymmetrical Schiff base ligands.

Preparation of Unsymmetrical Schiff Base Ligands

The unsymmetrical Schiff base ligands were prepared by modification of a literature method.[13] A mixture of ethylenediamine (0.07 mL, 1 mmol), 2-hydroxy-4-methoxybenzophenone (0.2282 g, 1 mmol), and various substituted acetophenone [o-hydroxyacetophenone (0.16 mL, 1 mmol), 2-hydroxy-4-methoxy acetophenone (0.1662 g, 1 mmol), 2-hydroxy-5-methyl acetophenone (0.1502 g, 1 mmol), and 2-hydroxy-1-acetonaphthone (0.1862 g, 1 mmol)] in 20 mL ethanol was refluxed for 5 h. The resulting solution was concentrated under vacuum to remove the solvent. The resulting product was filtered, washed with cold solvent, and purified by column chromatography. It was dried over anhydrous calcium chloride.

Synthesis of New Ruthenium(II) Unsymmetrical Schiff Base Complexes, [Ru(CO)(B)(L)] (B = PPh$_3$, AsPh$_3$, or pyridine (Py); L = Unsymmetrical Schiff Base Ligand Dianion)

All complexes were prepared by the following common 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 unsymmetrical Schiff base ligand (0.0358–0.0570 g, 0.1 mmol) was added in 1:1 molar ratio in a 100 mL round-bottom flask. The resulting mixture was heated under reflux for 5 h in water bath. The reaction mixture gradually changed to a deep color during heating. After the reaction time, the contents were concentrated to 3 cm^3 and cooled. Light petroleum ether (60–80°C) (10 mL) was added, where upon the product separated out. The product was recrystallized from CH$_2$Cl$_2$/light petroleum ether mixture (60–80°C) and dried *in vacuo*. The purity of the complexes was checked by TLC. Yields: 71–80%

Catalytic Oxidation

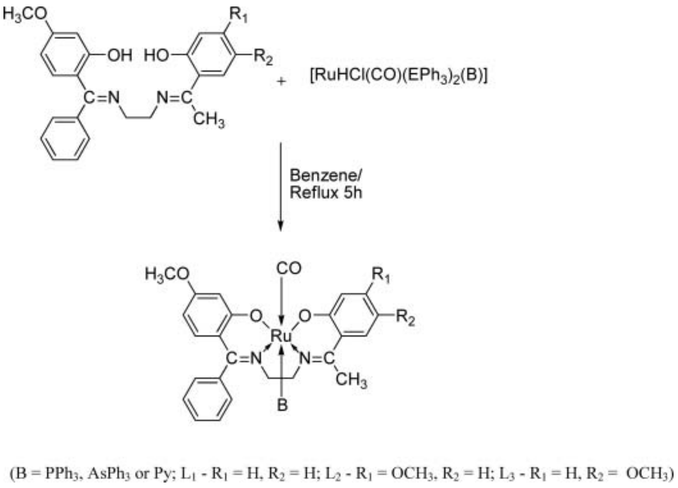
Catalytic oxidation of primary alcohols to corresponding aldehydes and secondary alcohols to ketones by ruthenium(II) unsymmetrical Schiff base complexes were studied in the presence of NMO as co-oxidant. A typical reaction using the complex as a catalyst and primary or secondary alcohol, as substrates at 1:100 molar ratio was described as follows. A solution of ruthenium(II) complex (0.01 mmol) in CH$_2$Cl$_2$ (20 mL) 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 coinjection with authentic samples.

Catalytic Transfer Hydrogenation

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

RESULTS AND DISCUSSION

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



SCH. 1. Formation of Ru(II) unsymmetrical Schiff base complexes.

TABLE 1
Analytical data of free ligands and their ruthenium(II) unsymmetrical Schiff base complexes

		Calculated (found) (%)		
Compound	M. Pt (°C)	C	H	N
L_1	165	74.21 (74.13)	6.23 (6.11)	7.21 (7.18)
L_2	188	71.75 (71.66)	6.26 (6.09)	6.26 (6.15)
L_3	168	74.60 (74.48)	6.51 (6.43)	6.96 (6.85)
L_4	172	76.69 (76.57)	5.98 (5.86)	6.38 (6.22)
$[Ru(CO)(PPh_3)(L_1)]$	168	66.40 (66.28)	4.79 (4.65)	3.60 (3.49)
$[Ru(CO)(PPh_3)(L_2)]$	140	65.42 (65.38)	4.86 (4.73)	3.47 (3.36)
$[Ru(CO)(PPh_3)(L_3)]$	135	66.74 (66.65)	4.96 (4.87)	3.54 (3.45)
$[Ru(CO)(PPh_3)(L_4)]$	145	68.19 (68.09)	4.75 (4.67)	3.38 (3.24)
$[Ru(CO)(Py)(L_1)]$	145	60.59 (60.48)	4.58 (4.46)	7.07 (7.01)
$[Ru(CO)(Py)(L_2)]$	152	59.61 (59.52)	4.68 (4.56)	6.73 (6.62)
$[Ru(CO)(Py)(L_3)]$	146	60.39 (60.27)	4.89 (4.79)	7.04 (6.96)
$[Ru(CO)(Py)(L_4)]$	118	63.34 (63.25)	4.53 (4.38)	6.52 (6.42)
$[Ru(CO)(AsPh_3)(L_1)]$	145	62.85 (62.77)	4.54 (4.44)	3.41 (3.29)
$[Ru(CO)(AsPh_3)(L_2)]$	140	62.04 (61.97)	4.61 (4.54)	3.28 (3.11)
$[Ru(CO)(AsPh_3)(L_3)]$	143	63.23 (63.12)	4.70 (4.62)	3.35 (3.22)
$[Ru(CO)(AsPh_3)(L_4)]$	138	64.75 (64.62)	4.51 (4.43)	3.27 (3.15)

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

Infrared Spectroscopic Analysis

The important IR absorption bands for the synthesized ligands and complexes are shown in Table 2. A strong band is observed at 1606–1608 cm^{-1} in the infrared spectra of the free Schiff bases, which is the characteristic of the azomethine group. If the Schiff base coordinates through the nitrogen atom, it is

TABLE 2
FT-IR and electronic spectral data of free ligands and their ruthenium(II) unsymmetrical Schiff base complexes

Compound	$\upsilon_{C=N}$ (cm^{-1})	$\upsilon_{C\text{-}O}$ (cm^{-1})	$\upsilon_{C\equiv O}$ (cm^{-1})	$\upsilon_{O\text{-}H}$ (cm^{-1})	λ_{max} (nm)
L_1	1608	1356	—	3485	219, 215, 209
L_2	1606	1353	—	3456	220, 215, 210
L_3	1608	1352	—	3432	218, 213, 210
L_4	1606	1352	—	3466	216, 213, 208
$[Ru(CO)(PPh_3)(L_1)]$	1593	1375	1951	—	380, 310, 247
$[Ru(CO)(PPh_3)(L_2)]$	1598	1383	1948	—	385, 320, 255
$[Ru(CO)(PPh_3)(L_3)]$	1602	1387	1951	—	423, 345, 235
$[Ru(CO)(PPh_3)(L_4)]$	1604	1366	1951	—	430, 350, 234
$[Ru(CO)(Py)(L_1)]$	1601	1370	1943	—	410, 350, 239
$[Ru(CO)(Py)(L_2)]$	1602	1400	1941	—	397, 354, 237
$[Ru(CO)(Py)(L_3)]$	1597	1361	1942	—	402, 364, 234
$[Ru(CO)(Py)(L_4)]$	1604	1365	1947	—	420, 360, 238
$[Ru(CO)(AsPh_3)(L_1)]$	1580	1372	1958	—	425, 360, 247
$[Ru(CO)(AsPh_3)(L_2)]$	1602	1360	1943	—	402, 380, 260
$[Ru(CO)(AsPh_3)(L_3)]$	1593	1383	1952	—	410, 392, 272
$[Ru(CO)(AsPh_3)(L_4)]$	1581	1362	1957	—	415, 375, 245

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 1580–1604 cm^{-1}, indicating the coordination of Schiff bases through the azomethine nitrogen atom.[14] A strong band observed around 1352–1356 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 1360–1400 cm^{-1} showing that the other coordination is through the phenolic oxygen atom.[15] This has been further supported by the disappearance of the broad $\upsilon_{O\text{-}H}$ band around 3432–3485 cm^{-1} in the complexes indicating deprotonation of the phenolic proton prior to coordination to ruthenium ion. Hence, from the infrared spectroscopic data it is inferred that both the azomethine nitrogen and phenolic oxygen atoms are involved in the coordination of the unsymmetrical Schiff bases to ruthenium ion in all the complexes. The strong absorption around 1941–1958 cm^{-1} has been assigned to the terminally coordinated carbonyl group in the new ruthenium complexes.[16] In the case of complexes containing coordinated pyridine,[17] 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.[18]

Electronic Spectroscopic Analysis

All the Schiff base ruthenium(II) 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 ${}^1A_{1g} \rightarrow {}^3T_{1g}$, ${}^1A_{1g} \rightarrow {}^3T_{2g}$, ${}^1A_{1g} \rightarrow {}^1T_{1g}$, and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ are possible in the order of increasing energy.

The electronic spectra of all the complexes in CH_2Cl_2 showed three bands in the region 234–430 nm (Table 2). The bands around 310–430 nm have been assigned to charge transfer transitions arising from the metal t_{2g} level to the unfilled π molecular orbital of the ligand.[19–22] The other high-intensity bands in the region below 300 nm are characterized by the ligand-centered transitions, and they have been designated as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition of electron, localized on the azomethine group of the Schiff bases.[23] This assignment made for similar other octahedral complexes.[24,25]

¹H NMR Spectroscopic Analysis

Further evidence for the coordination of the ligand to the metal atom is provided by the ${}^1H$ NMR spectra of ruthenium(II) unsymmetrical Schiff base complexes (Table 3). ${}^1H$ NMR

TABLE 3

${}^1H$ NMR data of free ligands and their ruthenium(II) unsymmetrical Schiff base complexes

Compound	${}^1H$ NMR (ppm)
L_1	15.87, 15.60 (s, -OH), 6.40-7.47 (m, Ar), 3.96 (s, $-OCH_3$), 3.72, 3.48 (t, $-CH_2-CH_2-$), 2.28 (s, $CH_3-C{=}N-$)
L_2	15.56, 15.34 (s, -OH), 6.20-7.48 (m, Ar), 3.98, 3.94 (s, $-OCH_3$), 3.81, 3.52 (t, $-CH_2-CH_2-$), 2.35 (s, $CH_3-C{=}N-$)
L_3	15.83, 15.59 (s, -OH), 6.13-7.47 (m, Ar), 3.96 (s, $-OCH_3$), 3.78, 3.53 (t, $-CH_2-CH_2-$), 2.30 (s, $CH_3-C{=}N-$), 1.56 (s, $Ar-CH_3$)
L_4	15.69, 15.41 (s, -OH), 6.12-7.83 (m, Ar), 3.99 (s, $-OCH_3$), 3.64, 3.57 (t, $-CH_2-CH_2-$), 2.31 (s, $CH_3-C{=}N-$)
$[Ru(CO)(PPh_3)(L_1)]$	6.40-7.47 (m, Ar), 3.95 (s, $-OCH_3$), 3.72, 3.48 (t, $-CH_2-CH_2-$), 2.28 (s, $CH_3-C{=}N-$)
$[Ru(CO)(PPh_3)(L_2)]$	6.20-7.49 (m, Ar), 3.98, 3.94 (s, $-OCH_3$), 3.83, 3.55 (t, $-CH_2-CH_2-$), 2.35 (s, $CH_3-C{=}N-$)
$[Ru(CO)(PPh_3)(L_3)]$	6.35-7.63 (m, Ar), 3.96 (s, $-OCH_3$), 3.78, 3.53 (t, $-CH_2-CH_2-$), 2.30 (s, $CH_3-C = N-$), 1.56 (s, $Ar-CH_3$)
$[Ru(CO)(PPh_3)(L_4)]$	6.12-7.87 (m, Ar), 3.99 (s, $-OCH_3$), 3.64, 3.57 (t, $-CH_2-CH_2-$), 2.31 (s, $CH_3-C{=}N-$)
$[Ru(CO)(Py)(L_1)]$	6.40-8.14 (m, Ar), 3.96 (s, $-OCH_3$), 3.73, 3.50 (t, $-CH_2-CH_2-$), 2.28 (s, $CH_3-C{=}N-$)
$[Ru(CO)(Py)(L_2)]$	6.23-7.96 (m, Ar), 3.96, 3.89 (s, $-OCH_3$), 3.78, 3.52 (t, $-CH_2-CH_2-$), 2.36 (s, $CH_3-C{=}N-$)
$[Ru(CO)(Py)(L_3)]$	6.14-7.78 (m, Ar), 3.99 (s, $-OCH_3$), 3.75, 3.52 (t, $-CH_2-CH_2-$), 2.36 (s, $CH_3-C{=}N-$), 1.54 (s, $Ar-CH_3$)
$[Ru(CO)(Py)(L_4)]$	6.32-7.99 (m, Ar), 3.98 (s, $-OCH_3$), 3.65, 3.57 (t, $-CH_2-CH_2-$), 2.31 (s, $CH_3-C{=}N-$)
$[Ru(CO)(AsPh_3)(L_1)]$	6.14-7.87 (m, Ar), 3.95 (s, $-OCH_3$), 3.72, 3.48 (t, $-CH_2-CH_2-$), 2.27 (s, $CH_3-C{=}N-$)
$[Ru(CO)(AsPh_3)(L_2)]$	6.20-7.63 (m, Ar), 4.03, 3.99 (s, $-OCH_3$), 3.82, 3.52 (t, $-CH_2-CH_2-$), 2.36 (s, $CH_3-C{=}N-$)
$[Ru(CO)(AsPh_3)(L_3)]$	6.21-7.49 (m, Ar), 3.97 (s, $-OCH_3$), 3.78, 3.54 (t, $-CH_2-CH_2-$), 2.35 (s, $CH_3-C{=}N-$), 1.56 (s, $Ar-CH_3$)
$[Ru(CO)(AsPh_3)(L_4)]$	6.12-7.83 (m, Ar), 3.93 (s, $-OCH_3$), 3.64, 3.57 (t, $-CH_2-CH_2-$), 2.33 (s, $CH_3-C{=}N-$)

TABLE 4
^{13}C NMR and ^{31}P NMR data of ruthenium(II) unsymmetrical Schiff base complexes

Complex	^{13}C NMR (ppm)	^{31}P NMR (ppm)
[Ru(CO)(PPh$_3$)(L$_1$)]	207.53 (C≡O), 167.43, 165.28 (C-O), 149.83, 147.05 (C=N), 128.20–140.09 (Ar, C), 59.56 (OCH$_3$), 41.78, 39.17 (-CH$_2$-CH$_2$), 21.28 (CH$_3$)	30.20
[Ru(CO)(PPh$_3$)(L$_2$)]	205.98 (C≡O), 168.21, 165.36 (C-O), 151.56, 147.83 (C=N), 127.69–137.73 (Ar, C), 57.68, 55.43 (OCH$_3$), 43.07, 42.24 (-CH$_2$-CH$_2$), 20.86 (CH$_3$)	30.62
[Ru(CO)(PPh$_3$)(L$_3$)]	208.39 (C≡O), 167.29, 164.83 (C-O), 152.17, 149.26 (C=N), 131.83–139.76 (Ar, C), 55.74 (OCH$_3$), 43.25, 41.90 (-CH$_2$-CH$_2$), 21.23, 20.06 (CH$_3$)	30.38
[Ru(CO)(PPh$_3$)(L$_4$)]	203.09 (C≡O), 169.27, 165.79 (C-O), 149.89, 149.21 (C=N), 123.26–138.27 (Ar, C), 56.84 (OCH$_3$), 44.28, 42.37 (-CH$_2$-CH$_2$), 23.80 (CH$_3$)	30.26
[Ru(CO)(Py)(L$_1$)]	205.37 (C≡O), 167.08, 166.24 (C-O), 151.73, 147.65 (C=N), 130.82–139.42 (Ar, C), 57.26 (OCH$_3$), 43.43, 42.38 (-CH$_2$-CH$_2$), 22.06 (CH$_3$)	—
[Ru(CO)(AsPh$_3$)(L$_1$)]	208.63 (C≡O), 168.77, 166.72 (C-O), 150.75, 148.28 (C=N), 132.20–139.27 (Ar, C), 57.56 (OCH$_3$), 44.13, 42.06 (-CH$_2$-CH$_2$), 21.48 (CH$_3$)	—

spectra of all the ligands showed a peak in the region 15.34–15.87 ppm, which has been assigned to the phenolic proton. The disappearance of the previous peak in all the complexes proved the formation of metal-oxygen bond through the deprotonation of phenolic O-H group. Multiplets around 6.12–8.14 ppm in the spectra of ligands and complexes are assigned to aromatic protons. The peak appeared at 2.27–2.36 ppm have been assigned to azomethine methyl group and peak at 1.54–1.56 ppm have been assigned to methyl group attached to benzene ring.[26] In addition, methoxy protons and methylene protons appeared as in the region at 3.93–4.03 and 3.48–3.83 ppm, respectively, for all the complexes.[27]

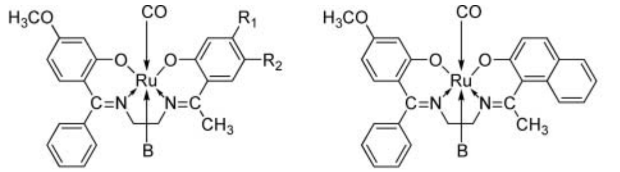
^{13}C NMR Spectroscopic Analysis

The ^{13}C NMR spectra of some of the new complexes were recorded to confirm the coordination of ligands to ruthenium metal (Table 4). The appearance of peak at 203.09–208.63 ppm region is due to C≡O carbon. The presence of a peak at 164.83– 169.27 ppm region is assigned to phenolic C-O carbon. The azomethine (>C=N) carbon exhibit its peak in the region of 147.05–152.17 ppm. The multiplets appeared around 123.34–140.09 ppm region are assigned to aromatic carbons. A sharp singlet at 55.74–59.56 ppm, 39.12–44.28 ppm, and 20.06–23.80 ppm is assigned to methoxy, metyhylene, and methyl carbons respectively. This confirms the formation of new ruthenium(II) unsymmetrical Schiff base complexes.

^{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 complexes (Table 4). A sharp singlet was observed around 30.20–30.62 ppm due to the 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 (Figure 2) has been tentatively proposed for all the new ruthenium(II) unsymmetrical Schiff base complexes.



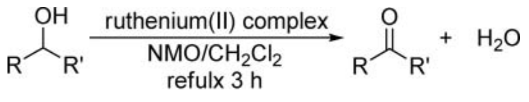
(B = PPh$_3$, AsPh$_3$ or Py; L$_1$ - R$_1$ = H, R$_2$ = H; L$_2$ - R$_1$ = OCH$_3$, R$_2$ = H; L$_3$ - R$_1$ = H, R$_2$ = OCH$_3$)

FIG. 2. Proposed structure of new ruthenium(II) unsymmetrical Schiff base complexes.

Catalytic Oxidation

Catalytic oxidation of primary alcohols and secondary alcohols by the synthesized ruthenium(II) unsymmetrical 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) with high yields and the results are listed in Table 5 and Figure 3. 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 90–99% yield and cyclohexanol to cyclohexanone resulted in



R, R' = alkyl or aryl or H

SCH. 2. Catalytic oxidation of alcohols.

TABLE 5
Catalytic oxidation data of ruthenium(II) unsymmetrical Schiff base complexes

Complex	Substrate	Product	Yield (%)[a]
[Ru(CO)(PPh$_3$)(L$_1$)]	Benzyl alcohol	Benzaldehyde	93
	Cyclohexanol	Cyclohexanone	77
[Ru(CO)(PPh$_3$)(L$_2$)]	Benzyl alcohol	Benzaldehyde	99
	Cyclohexanol	Cyclohexanone	84
[Ru(CO)(PPh$_3$)(L$_3$)]	Benzyl alcohol	Benzaldehyde	97
	Cyclohexanol	Cyclohexanone	81
[Ru(CO)(PPh$_3$)(L$_4$)]	Benzyl alcohol	Benzaldehyde	94
	Cyclohexanol	Cyclohexanone	76
[Ru(CO)(Py)(L$_1$)]	Benzyl alcohol	Benzaldehyde	90
	Cyclohexanol	Cyclohexanone	78
[Ru(CO)(Py)(L$_2$)]	Benzyl alcohol	Benzaldehyde	97
	Cyclohexanol	Cyclohexanone	79
[Ru(CO)(Py)(L$_3$)]	Benzyl alcohol	Benzaldehyde	94
	Cyclohexanol	Cyclohexanone	78
[Ru(CO)(AsPh$_3$)(L$_1$)]	Benzyl alcohol	Benzaldehyde	92
	Cyclohexanol	Cyclohexanone	78
[Ru(CO)(AsPh$_3$)(L$_3$)]	Benzyl alcohol	Benzaldehyde	97
	Cyclohexanol	Cyclohexanone	80
[Ru(CO)(AsPh$_3$)(L$_4$)]	Benzyl alcohol	Benzaldehyde	96
	Cyclohexanol	Cyclohexanone	78

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

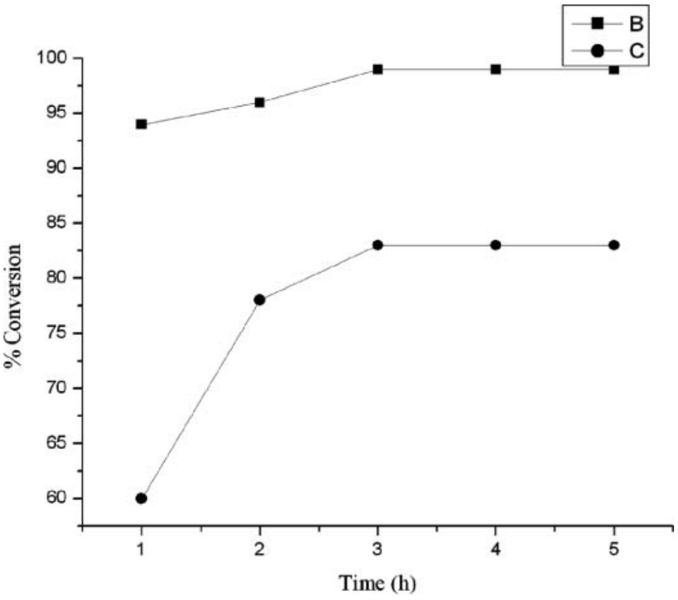


FIG. 3. Catalytic oxidation of benzylalcohol (B) and cyclohexanol (C) in different time intervals.

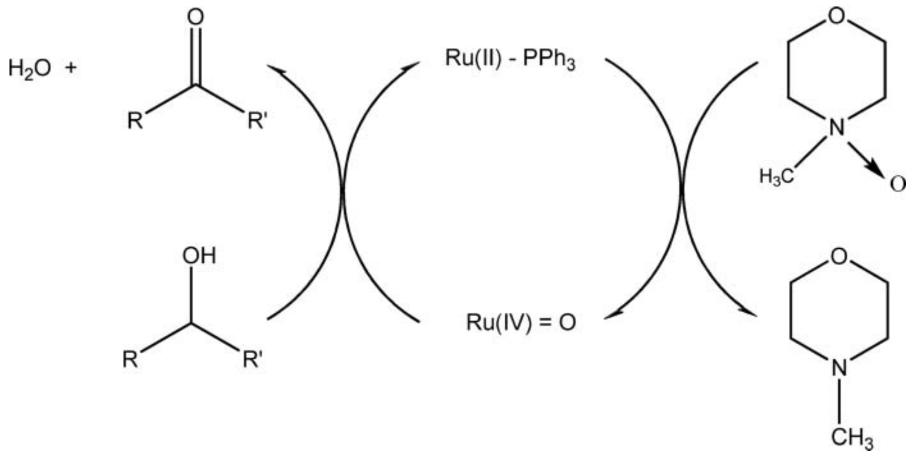
76–84% yield. The relatively higher yield obtained for the oxidation of benzylalcohol as compared to cyclohexanol is due to the fact that the α-CH unit of benzylalcohol is more acidic than cyclohexanol.[28]

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 band at 390 nm in the electronic spectra is attributed to the formation of $\mathrm{Ru^{IV}} = \mathrm{O}$ species, which is in confirmed with other oxo ruthenium(IV) complexes.[29,30] Further support in favor 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 $\mathrm{cm^{-1}}$, characteristic of $\mathrm{Ru^{IV}} = \mathrm{O}$ species (Scheme 3).[31]

Catalytic Transfer Hydrogenation

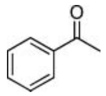
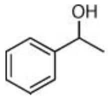
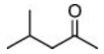
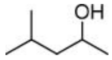
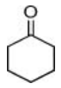
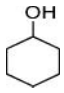
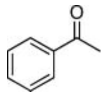
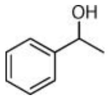
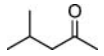
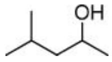
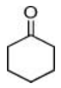
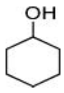
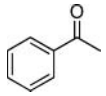
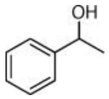
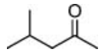
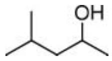
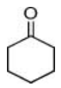
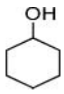
The catalytic transfer hydrogenation of ketones in the presence of ruthenium(II) unsymmetrical Schiff base complexes has been studied in isopropanol-KOH medium using a molar ratio 1:2.5:300 for the catalyst, KOH and the ketone in 10 $\mathrm{cm^{-3}}$ of isopropanol (Scheme 4).

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 up to 74–79% yield. Isobutyl methyl ketone underwent transfer hydrogenation to afford the corresponding alcohol up to 66–70% yield. Similarly, cyclohexanone was converted to cyclohexanol up to 80–86% yield.



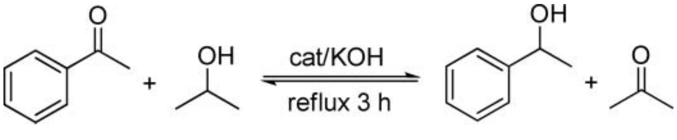
SCH. 3. Proposed mechanism for catalytic oxidation of alcohols by the Ru(II) unsymmetrical Schiff base complexes.

TABLE 6
Catalytic transfer hydrogenation of ketones by ruthenium(II) unsymmetrical Schiff base complexes

Complex	Substrate	Product	Conversion (%)
[Ru(CO)(PPh$_3$)(L$_2$)]			76
			69
			83
[Ru(CO)(Py)(L$_2$)]			74
			66
			80
[Ru(CO)(AsPh$_3$)(L$_2$)]			79
			70
			86

CONCLUSION

Several ruthenium(II) unsymmetrical Schiff base complexes were synthesized using unsymmetrical Schiff base ligand and [RuHCl(CO)(EPh$_3$)$_2$(B)] (E = P or As, B = PPh$_3$, AsPh$_3$, or Py). The new complexes have been characterized by analytical and spectral data. An octahedral structure has been tentatively proposed for all the complexes. The complexes showed efficient catalytic property for oxidation of primary and secondary alcohols to the corresponding carbonyl compounds in the presence of NMO and also for transfer



SCH. 4. Catalytic transfer hydrogenation of ketone.

hydrogenation of aliphatic and aromatic ketones with high conversions.

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