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Synthesis, characterization, electrochemical, catalytic and antimicrobial activity studies of hydrazone Schiff base ruthenium(II) complexes

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Four tridentate O, N, O donor Schiff base ligands were prepared by the reaction of substituted benzhydrazide and appropriate salicylaldehyde. The complexes of these ligands were synthesized by refluxing the ligands with ruthenium(II) starting complexes of the formula $[RuHCl(CO)(EPh_3)_2B]$ in benzene, where E = P or As; B = PPh_3 or $AsPh_3$ or pyridine. The newly synthesized complexes were characterized by elemental, spectral (FT-IR, UV and NMR) and electrochemical data. On the basis of the above studies, an octahedral structure has been proposed for all the complexes. The catalytic efficiency of the complexes in aryl–aryl couplings and oxidation of alcohols was examined and their inhibition activity against the growth of the micro-organisms was also examined. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: hydrazone Schiff base; *N*-methylmorpholine-*N*-oxide; catalytic oxidation; aryl–aryl couplings; cyclic voltammetry

Introduction

Oxidation catalysis constitutes an important research area since it represents the core of a variety of chemical processes for producing bulk and fine chemicals as well as for eliminating pollution. Oxifunctionalization of alcohols to aldehydes and ketones is a widely used chemical transformation in organic synthesis as these products are important precursors or intermediates in the synthesis of many drugs, vitamins and fragrances.[1–3] Many methods for specific catalytic oxidation of various organic substrates such as alcohols, amines, amides and hydrocarbons have been studied extensively using low-valent metal complex catalysts.[4–6] Ranging from the oxidative conversion of water to O_2 to the elegant hydroxylation of olefins and to oxidative dehydrogenation of alcohols, Ru-mediated oxidations are finding increasing application due to the unique properties of this extremely versatile transition metal, whose oxidation state can vary from −II to +VIII.[7] It is well known that the use of nitrogen containing ligands leads to an increased catalytic activity.[8] Although several ruthenium catalytic systems have been reported with a wide range of oxidants, viz. tert-butyl hydroperoxide,[9] chloramine-T,[10] benzoquinone,[11] hydrogen peroxide,[12] molecular oxygen,[13] iodosylbenzene[14] and NaIO4,[15] *N*-methylmorpho- line-*N*-oxide (NMO) as an oxidant is less covered in the literature.

The biaryl structural motif is a predominant feature in many pharmaceutically relevant and biologically active compounds. Although a large variety of routes have been established for the construction of aryl–aryl bonds, the most common method is through the use of transition-metal mediated reactions.[16–18] Recent methods of transition metal-catalyzed aryl–aryl couplings have focused on the development of high-yielding reactions achieved with excellent selectivity and high functional group tolerance under mild reaction conditions. Typically, these reactions involve either the coupling of an aryl halide or pseudohalide with an organometallic reagent.[19] Various studies have shown that the azomethine group having a lone pair of electrons in either 'p' or 'sp^2' hybridized orbital on trigonally hybridized nitrogen has considerable biological importance.[20] The present work deals with the synthesis and characterization by physical methods of the ruthenium complexes of hydrazone Schiff base ligands, catalytic oxidation of alcohols and aryl–aryl couplings in the presence of these complexes and antibacterial activity of these complexes against *Escherichia coli* and *Basillus subtilis*. The ligands used in this work have the general structure shown in Scheme 1.

Experimental

Materials and Methods

$RuCl_3 3H_2O$ was purchased from Loba Chemie and used as received. All the reagents used were of analar or chemically pure grade. Solvents were purified according to the standard procedures.[21] The analyses of carbon, hydrogen and nitrogen were performed using a Vario EL III elemental analyzer at Bharathiar University, Coimbatore, India. IR spectra were recorded

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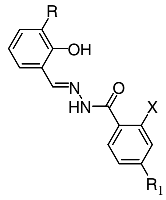


Abbreviation	X	R	R_1
H_2L^1	H	H	OCH_3
H_2L^2	H	OCH_3	OCH_3
H_2L^3	Cl	H	H
H_2L^4	Cl	OCH_3	H

Scheme 1. Structure of ligands.

as KBr pellets in the 4000–400 cm^{-1} region using a Shimadzu FT-IR 8000 spectrophotometer. Electronic spectra were recorded in dichloromethane solution with a Systronics Double beam UV–vis spectrophotometer 2202. ^1H-, ^{13}C- and ^{31}P-NMR spectra were monitored on a Bruker AMX-400 NMR spectrophotometer using $CDCl_3$ as solvent and tetramethylsilane (^1H and ^{13}C) and orthophosphoric acid (^{31}P) as internal standards at the Indian Institute of Science, Bangalore. Cyclic voltammetric studies were carried out in acetonitrile using a glassy-carbon working electrode and potentials were referenced to saturated calomel electrode (SCE). Melting points were recorded with a Raaga heating table with accuracy ±0.1% and are uncorrected. The starting complexes $[RuHCl(CO)(PPh_3)_3]$,[22] $[RuHCl(CO)(AsPh_3)_3]$,[23] $[RuHCl(CO)(PPh_3)_2(py)]$[24] and the ligands[25] were prepared by reported methods.

Synthesis of Ruthenium(II) Schiff Base Complexes

To a solution of the corresponding starting complex (0.095–0.108 g; 0.1 mmol) in benzene (25 ml), the appropriate hydrazone ligand (0.027–0.030 g; 0.1 mmol) in benzene (25 ml) was added and refluxed for 6 h. The resulting solution was concentrated and the product was precipitated by adding a small quantity of petroleum ether (60–80 °C) and dried in *vacuo*.

NMR data for complex $[Ru(CO)(PPh_3)_2L^1]$: ^1H NMR ($CDCl_3$, 400 MHz) δ ppm 8.9 (CH=N), 7.7–7.9 (aromatic), 3.8 (OCH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) 21.66.

$[Ru(CO)(PPh_3)_2L^2]$: ^1H NMR($CDCl_3$, 400 MHz) δ ppm 8.9 (CH=N), 7.1–7.6 (aromatic), 3.8 (OCH_3); $^{31}P\{^1H\}$NMR ($CDCl_3$, 162 MHz) 21.79.

$[Ru(CO)(PPh_3)_2L^3]$: ^1H NMR ($CDCl_3$, 400 MHz) δ ppm 8.9 (CH=N), 7.0–8.0 (aromatic), 3.9 (OCH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) 21.66.

$[Ru(CO)(PPh_3)_2L^4]$: ^1H NMR ($CDCl_3$, 400 MHz) δ ppm 8.8 (CH=N), 6.8–7.7 (aromatic), 3.9 (OCH_3); $^{31}P\{^1H\}$NMR ($CDCl_3$, 162 MHz) 21.82; $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz) 140 (CH=N), 165 (enolic C), 127–134 (aromatic), 45 (OCH_3).

$[Ru(CO)(AsPh_3)_2L^1]$:^1H NMR ($CDCl_3$, 400 MHz) δ ppm 8.9 (CH=N), 7.2–7.7 (aromatic), 3.8 (OCH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) 142 (CH=N), 167 (enolic C), 127–136 (aromatic), 50 (OCH_3).

$[Ru(CO)(AsPh_3)_2L^2]$: ^1H NMR ($CDCl_3$, 400 MHz) δ ppm 8.9 (CH=N), 7.1–7.7 (aromatic), 3.8 (OCH_3).

$[Ru(CO)(AsPh_3)_2L^3]$: ^1H NMR ($CDCl_3$, 400 MHz) δ ppm 8.9 (CH=N), 6.9–7.3 (aromatic), 3.9 (OCH_3).

$[Ru(CO)(AsPh_3)_2L^4]$: ^1H NMR ($CDCl_3$, 400 MHz) δ ppm 8.8 (CH=N), 6.9–7.5 (aromatic), 3.8 (OCH_3).

$[Ru(CO)(PPh_3)(py)L^1]$: ^1H NMR ($CDCl_3$, 400 MHz) δ ppm 8.8 (CH=N), 6.9–7.7 (aromatic), 3.8 (OCH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): 22, 29, 41; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): 140 (CH=N), 167 (enolic C), 128–136 (aromatic), 45 (OCH_3).

$[Ru(CO)(PPh_3)(py)L^2]$: ^1H NMR ($CDCl_3$, 400 MHz) δ ppm 8.9 (CH=N), 6.9–7.8 (aromatic), 3.9 (OCH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) 21, 29, 39;

$[Ru(CO)(PPh_3)(py)L^3]$: ^1H NMR (CDCl3, 400 MHz) δ ppm 8.9 (CH=N), 7.1–7.7 (aromatic), 3.79 (OCH_3); ^{31}P $\{^1H\}$ NMR ($CDCl_3$, 162 MHz) 22, 29, 39.

$[Ru(CO)(PPh_3)(py)L^4]$: ^1H NMR ($CDCl_3$, 400 MHz) δ ppm 8.8 (CH=N), 6.6–7.7 (aromatic), 3.9 (OCH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): 21, 29, 39; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) 145 (CH=N), 165 (enolic C), 127–135 (aromatic), 47 (OCH_3).

Catalytic Oxidation Experiments with Molecular Oxygen and NMO

To a solution of alcohol (0.07–0.13 ml, 1 mmol) in dichloromethane (20 ml), was added a solution of the ruthenium complex (0.009–0.01 g; 0.01 mmol) in dichloromethane (20 ml) and the mixture was stirred under an oxygen atmosphere at ambient temperature for 6 h. The mixture was evaporated to dryness and extracted with diethyl ether. The combined extracts were filtered and evaporated to give the corresponding carbonyl compound, which was then quantified as its 2, 4-dinitrophenylhydrazone.[21,26]

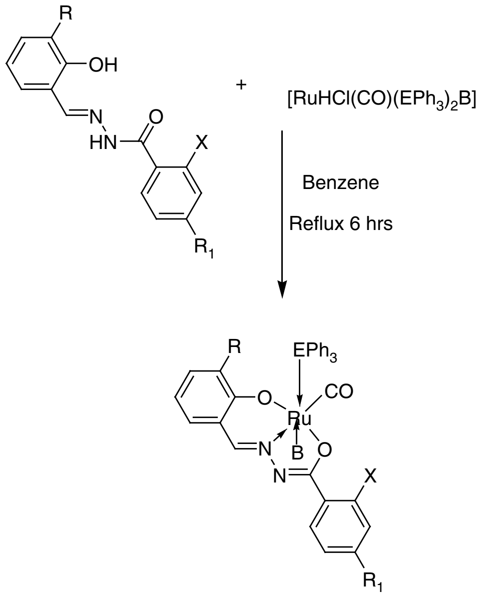
To a solution of the alcohol (0.07–0.13 ml, 1 mmol) in dichloromethane (20 ml), NMO (0.35 g, 3 mmol) and the ruthenium complex (0.009–0.01 g, 0.01 mmol) were added and the solution was heated under reflux for 3 h. The resulting mixture was filtered and the filtrate was dried over anhydrous Na_2SO_4. It was then evaporated to dryness and extracted with diethyl ether. The diethyl ether extract was filtered and evaporated to give the corresponding carbonyl compound, which was then quantified as its 2,4-dinitrophenylhydrazone.[21,27]

Aryl–Aryl Coupling Experiments

Magnesium turnings (0.320 g) were placed in a flask equipped with a $CaCl_2$ guard tube. A crystal of iodine was added. Bromobenzene [0.75 ml of total 1.88 ml] in anhydrous diethyl ether (5 ml) was added with stirring. The remaining bromobenzene in ether (5 ml) was added dropwise and the mixture was refluxed for 40 min. To this mixture, 1.03 ml (0.01 mol) of bromobenzene in anhydrous diethyl ether (5 ml) and the ruthenium complex (0.05 mmol) chosen for investigation were added and heated under reflux for 6 h. The reaction mixture was cooled and hydrolyzed with a saturated solution of aqueous NH_4Cl and the ether extract on evaporation gave a crude product which was purified using chromatography.[28]

Antibacterial Activity

The bacteria, *Escherichia coli* and *Basillus Subtilis*, were cultured in nutrient agar medium in Petri plates and used as inocula for the study. The components to be tested were dissolved in DMSO to a final concentration of 0.5 and 1% and soaked in filter paper disks of 5 mm diameter and 1 mm thickness. These disks were placed on the previously seeded plates and incubated at 35 ± 2 °C for 24 h. The diameter (mm) of the inhibitory zone around each disk was measured after 24 h.[29]



Scheme 2. Preparation of ruthenium(II) Schiff base complexes. R = H or OCH_3, R_1 = H or OCH_3, X = H or Cl, E = P or As, B = PPh_3 or $AsPh_3$ or pyridine.

Results and Discussion

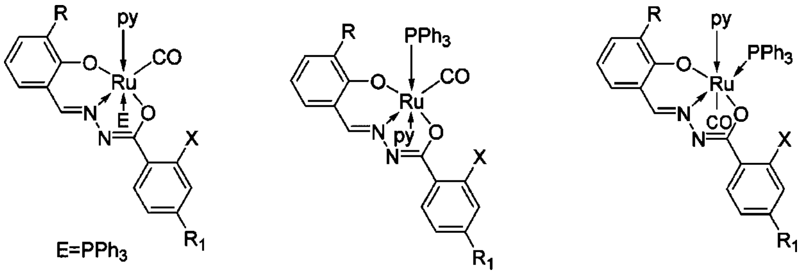
All the complexes were stable to air and light and soluble in organic solvents such as DMSO, $CHCl_3$ and dichloromethane. Their molar conductivities in DMSO were very low (10.4–14.6 ohm^{-1} cm^2 mol^{-1}), indicating the non-electrolytic nature of the complexes. Analytical data of the complexes were in accordance with the formula proposed (Scheme 2, Table 1).

IR Spectra

Important spectral bands of the ligands and their metal complexes are presented in Table 1. The $\nu_{(NH)}$ vibration at 3265–3396 cm^{-1} and $\nu_{(C=O)}$ vibration at 1623 cm^{-1} in the free ligand disappear in the complexes, but new strong bands appear at 1521–1541 cm^{-1} which are attributed to the newly formed N=C bond vibration. These new bands in the spectra reflect the amide ↔ imidol tautomerism and subsequent coordination of the imidol oxygen. This is further supported by the appearance of new peak characteristic of $\nu_{(NCO)}{}^-$ at 1510–1515 cm^{-1} in the spectra of the complexes. Absence of OH vibrations confirms the coordination of the deprotonated enolic oxygen to Ru. The bands, which appear around 3400 cm^{-1} due to the $\nu_{(O-H)}$ vibration of the phenolic group in the ligand spectra, disappear in the spectrum of the complexes and an increase in frequency of phenolic C–O vibration from ligand (1261–1278 cm^{-1}) to metal complex (1313–1319 cm^{-1}) is observed. These results suggest that the other coordinating atom is phenolic oxygen. The third coordination via the azomethine nitrogen is inferred from the following observations. The $\nu_{(C=N)}$ vibration, which is observed at 1573–1577 cm^{-1} in the ligands, undergoes a negative shift to 1558–1560 cm^{-1} in the spectrum of the complexes. The $\nu_{(N-N)}$ vibration, which occurs at 964–983 cm^{-1}, shifts to higher energy, 991–999 cm^{-1}, in the complexes. Bands corresponding to ruthenium-bound PPh_3–$AsPh_3$ vibrations are seen around 1400, 740, 520 and 476 cm^{-1}. Vibration of the terminally coordinated C≡O group is observed as a strong band at 1946–1965 cm^{-1}. In the complexes containing a coordinated

Table 1. Analytical, FT-IR and electronic spectroscopic data for the complexes

Complex	Colour	Yield (%)	m.p. (°C)	Analytical data % (found) calculated			IR spectral data (cm^{-1})				UV spectral data, λ_{max} (nm)
				C	H	N	$\nu_{C=N}$	$\nu_{C\equiv O}$	ν_{Ph-CO}	ν_{NCO^-}	
$[Ru(CO)(PPh_3)_2L^1]$ $(C_{52}H_{42}O_4N_2P_2Ru)$	Brown	72.4	187	(67.02) 67.74	(4.45) 4.59	(3.07) 3.04	1560	1959	1319	1513	252, 287, 345, 389, 516
$[Ru(CO)(PPh_3)_2L^2]$ $(C_{53}H_{44}O_5N_2P_2Ru)$	Brown	75.5	208	(67.00) 66.86	(4.79) 4.66	(3.08) 2.94	1558	1965	1315	1514	252, 297, 341, 417, 690
$[Ru(CO)(PPh_3)_2L^3]$ $(C_{51}H_{39}O_3N_2P_2ClRu)$	Brown	67.9	213	(66.32) 66.12	(4.39) 4.24	(3.14) 3.02	1560	1959	1317	1514	254, 294, 363, 430, 638
$[Ru(CO)(PPh_3)_2L^4]$ $(C_{52}H_{41}O_4N_2P_2ClRu)$	Brown	68.9	230	(65.10) 65.30	(4.42) 4.32	(3.04) 2.93	1558	1965	1317	1514	246,345, 516, 638
$[Ru(CO)(AsPh_3)_2L^1]$ $(C_{52}H_{42}O_4N_2As_2Ru)$	Cream	82.7	153	(62.03) 61.84	(4.10) 4.19	(2.65) 2.77	1558	1965	1315	1514	254, 309, 395, 635
$[Ru(CO)(AsPh_3)_2L^2]$ $(C_{53}H_{44}O_5N_2As_2Ru)$	Pale brown	77.7	155	(61.18) 61.21	(4.30) 4.26	(2.75) 2.69	1558	1959	1317	1514	252,298,359, 441, 688
$[Ru(CO)(AsPh_3)_2L^3]$ $(C_{51}H_{39}O_3N_2As_2ClRu)$	Pale brown	81.1	167	(60.58) 60.39	(3.92) 3.88	(2.80) 2.76	1558	1961	1315	1511	254, 298, 364, 424, 639
$[Ru(CO)(AsPh_3)_2L^4]$ $(C_{52}H_{41}O_4N_2As_2ClRu)$	orange	69.4	183	(59.74) 59.80	(4.04) 3.96	(2.76) 2.68	1558	1963	1315	1514	254, 297,363, 437, 665
$[Ru(CO)(PPh_3)(py)L^1]$ $(C_{39}H_{32}O_4N_3PRu)$	Green	79.8	216	(63.85) 63.40	(4.56) 4.37	(5.74) 5.69	1558	1946	1317	1510	255, 295, 368, 397, 460, 587
$[Ru(CO)(PPh_3)(py)L^2]$ $(C_{40}H_{34}O_5N_3PRu)$	Green	74.3	212	(62.04) 62.49	(4.50) 4.46	(5.50) 5.47	1558	1946	1317	1515	254, 299, 368, 402, 490, 592
$[Ru(CO)(PPh_3)(py)L^3]$ $(C_{38}H_{29}O_3N_3PClRu)$	Green	83.4	210	(61.89) 61.41	(3.98) 3.93	(5.61) 5.65	1558	1946	1313	1514	256, 295, 402, 428, 560
$[Ru(CO)(PPh_3)(py)L^4]$ $(C_{39}H_{31}O_4N_3PClRu)$	Green	81.5	220	(60.23) 60.58	(4.13) 4.04	(5.51) 5.43	1558	1946	1315	1515	254, 298, 390, 432, 663



Scheme 3. Possible isomeric structures for complexes [Ru(CO)(PPh$_3$)(py)(L^n)] ($n = 1-4$).

Table 2. Cyclic voltammetric data[a] of the complexes

Complex	Ru (II)–Ru(III)			
	E_{pa} (V)	E_{pc} (V)	E_f (V)	ΔE_p (mV)
[Ru(CO)(PPh$_3$)$_2$L^1]	0.80	0.38	0.59	420
[Ru(CO)(PPh$_3$)$_2$L^2]	1.26	0.90	1.08	360
[Ru(CO)(PPh$_3$)$_2$L^3]	1.18	1.10	1.14	80
[Ru(CO)(PPh$_3$)$_2$L^4]	1.24	1.10	1.17	140
[Ru(CO)(AsPh$_3$)$_2$L^1]	0.82	0.40	0.61	420
[Ru(CO)(AsPh$_3$)$_2$L^2]	1.10	0.88	0.99	220
[Ru(CO)(AsPh$_3$)$_2$L^3]	1.18	1.09	1.14	90
[Ru(CO)(AsPh$_3$)$_2$L^4]	1.22	1.10	1.16	120
[Ru(CO)(PPh$_3$)(py)L^1]	0.60	0.28	0.44	320
[Ru(CO)(PPh$_3$)(py)L^2]	1.26	0.90	1.08	360
[Ru(CO)(PPh$_3$)(py)L^3]	1.20	1.10	1.15	100
[Ru(CO)(PPh$_3$)(py)L^4]	1.28	1.14	1.21	140

[a] Supporting electrolyte [NBu$_4$]ClO$_4$ (0.1 M); all potentials are referenced to SCE; $E_f = 0.5(E_{pa} + E_{pc})$; $\Delta E(p) = (E_{pa} - E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic potentials respectively; scan rate = 100 mV s^{-1}.

nitrogen base, a medium intensity band is observed in the 1006–1027 cm^{-1} region, characteristic of coordinated pyridine. Replacement of hydride ion by the ligand is confirmed by the absence of bands around 2020 cm^{-1}.[30–33] Thus, the aroyl hydrazones coordinate to ruthenium as dianionic tridentate ligands.

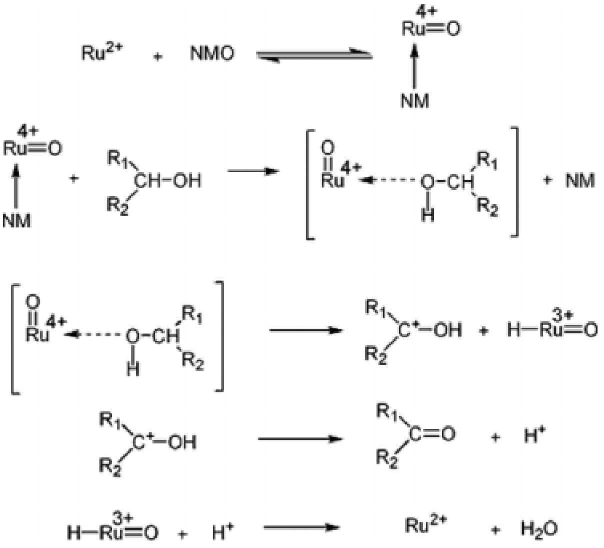
Electronic Spectra

The room temperature magnetic moments of the complexes indicate that the ruthenium is in the +2 oxidation state which corresponds to the electronic configuration $t_{2g}{}^6\ e_g{}^0$. The ground state of ruthenium(II) in an octahedral environment is $^1A_{1g}$. The excited state terms 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 order of increasing energy. The electronic spectra of the complexes show several absorptions in the ultraviolet and visible region at 246–690 nm. The bands observed at 246–309 nm are assignable to $\pi \rightarrow \pi^*$ transitions and those appearing at 341–402 nm are due to $n \rightarrow \pi^*$ transitions of the ligand orbitals. These bands are seen in the spectra of the ligands also but at a slightly lower wavelength, indicating the coordination of the ligands to ruthenium. The high intensity charge-transfer transitions occurring in the visible region (417–490 nm) obscure the weak d–d transitions of the type $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. Transitions observed at 516–690 nm are much weaker in intensity and are assigned to $^1A_{1g} \rightarrow {}^3T_{1g}$ and $^1A_{1g} \rightarrow {}^3T_{2g}$ transitions.[34,35] From the electronic spectra, it is inferred that ruthenium is present in an octahedral environment.

NMR Spectra

Signals of phenolic and NH protons appear at 11.3 and 10.4 ppm, respectively, in the ^{1}H NMR spectrum of the ligands. These signals are not present in the spectra of the complexes indicating the deprotonation of these groups. The azomethine proton signal, due to CH=N, is observed in the 8.7 ppm region in ligands and in complexes it has shifted downfield, appearing in the 8.8–8.9 ppm range, indicating the involvement of azomethine nitrogen in coordination. The multiplets as strong bands in the region 6.6–8.0 ppm were assigned to aromatic ring protons, PPh$_3$/AsPh$_3$ protons and the protons of the pyridine ring in the complexes. The resonance for the methoxy protons appeared as a singlet at 3.8–3.9 ppm in ligands and in complexes no significant change was observed.[25,32]

^{13}C NMR spectral data also support the authenticity of the proposed structures. The signal for the –OCH$_3$ group was seen at 45–50 ppm. A signal for the azomethine carbon occurred at 140–145 ppm. A band at 165–167 ppm was assigned to the enolic carbon. The multiplet observed at 127–136 ppm was assigned to the aromatic carbon atoms.[36,37]



Scheme 4. Proposed mechanism for the oxidation of alcohols using Ru/NMO. R$_1$, aryl or alkyl; R$_2$, alkyl or H.

Table 3. Oxidation of alcohols catalyzed by ruthenium (II) complexes

Complex	Substrate	Product	NMO co-oxidant		Molecular oxygen co-oxidant	
			Yield (%)[a]	TON[b]	Yield (%)[a]	TON[b]
[Ru(CO)(PPh$_3$)$_2$L^1]	Benzyl alcohol	Benzaldehyde	88	89	30	31
	Cyclohexanol	Cyclohexanone	89	91	32	33
	Cinnamyl alcohol	Cinnamaldehyde	83	84	31	32
	n-Butanol	Butyraldehyde	70	71	25	26
	Isobutyl alcohol	Ethyl methyl ketone	66	68	26	26
	n-Propanol	Propionaldehyde	69	71	28	29
[Ru(CO)(PPh$_3$)$_2$L^2]	Benzyl alcohol	Benzaldehyde	88	90	32	33
	Cyclohexanol	Cyclohexanone	90	92	33	34
	Cinnamyl alcohol	Cinnamaldehyde	81	83	33	33
	n-Butanol	Butyraldehyde	69	71	26	26
	Isobutyl alcohol	Ethyl methyl ketone	68	69	27	28
	n-Propanol	Propionaldehyde	71	73	30	31
[Ru(CO)(PPh$_3$)$_2$L^3]	Benzyl alcohol	Benzaldehyde	89	91	33	34
	Cyclohexanol	Cyclohexanone	93	95	34	35
	Cinnamyl alcohol	Cinnamaldehyde	85	86	34	35
	n-Butanol	Butyraldehyde	72	74	27	28
	Isobutyl alcohol	Ethyl methyl ketone	70	71	28	29
	n-Propanol	Propionaldehyde	71	74	32	34
[Ru(CO)(PPh$_3$)$_2$L^4]	Benzyl alcohol	Benzaldehyde	92	94	40	38
	Cyclohexanol	Cyclohexanone	93	95	41	42
	Cinnamyl alcohol	Cinnamaldehyde	88	89	39	39
	n-Butanol	Butyraldehyde	73	75	34	35
	Isobutyl alcohol	Ethyl methyl ketone	72	73	31	32
	n-Propanol	Propionaldehyde	81	84	33	34

[a] Yield based on substrate; [b] moles of product per mole of catalyst. TON, turnover number.

In the ^{31}P NMR spectra of the complexes [Ru(CO)(PPh$_3$)$_2$L^1], [Ru(CO)(PPh$_3$)$_2$L^2], [Ru(CO)(PPh$_3$)$_2$L^3] and [Ru(CO)(PPh$_3$)$_2$L^4], the singlet found around 21 ppm was attributed to the two phosphine ligands which are *trans* to each other. The ^{31}P-NMR spectrum of [Ru(CO)(PPh$_3$)(py)L^1], [Ru(CO)(PPh$_3$)(py)L^2], [Ru(CO)(PPh$_3$)(py)L^3] and [Ru(CO)(PPh$_3$)(py)L^4], which contain only one triphenylphosophine group, showed three singlets at 22 ppm, 29 ppm and 39–41 ppm. This may be due to three possible structures (Scheme 3) arising from a mixture of three isomers.[32,38]

Electrochemistry

The electrochemical properties of the complexes were studied in acetonitrile solution by cyclic voltammetry. Each complex shows one metal-centered oxidative response on the positive side of the SCE (Table 2). The oxidative response, observed in the range of 0.44–1.21 V, is assigned to the ruthenium(II)–ruthenium–(III) oxidation. This oxidation is quasi-reversible, with a peak-to-peak separation of 80–420 mV.[39,40] Potentials of the ruthenium(II)–ruthenium(III) oxidation in the complexes were found to be sensitive to the nature of the substituent R in the ligands. The potentials increase with increasing electron-withdrawing character of the substituents.[41]

Catalytic Oxidation of Alcohols

We used the prepared complexes for catalytic oxidation of primary and secondary alcohols in the presence of NMO/molecular oxygen as oxidant. The oxidations were carried out at room temperature in CH$_2$Cl$_2$. Results of this study indicate that NMO is an efficient oxidant when compared with molecular oxygen which is in accordance with a previous observation.[42] The higher catalytic efficiency of NMO vs molecular oxygen is inferred from the high yield and turnover number. Unsaturated alcohol, i.e. cinnamyl alcohol, is effectively oxidized without competing double bond attack. It seems that a high-valent ruthenium oxo species is formed in the presence of NMO and it abstracts a hydride ion from the alcohol.

N-methylmorpholine and water are the by-products (Scheme 4).[43,44] It is clear from Table 3 that the catalyst [Ru(CO)(PPh$_3$)$_2$L^4] is more effective than the other three complexes with respect to both yield and turnover of the corresponding aldehyde or ketone. The oxidation of cyclohexanol by [Ru(CO)(PPh$_3$)$_2$L^4] gave the highest turnover number, probably arising from high peak-to-peak separation (stable higher ruthenium oxidation state), as shown by its voltammogram. It is obvious from the cyclic voltammetric data that oxidations by ruthenium catalysts are likely to occur via ruthenium(III) or its higher oxidation states which should be accessible through chemical oxidation with common co-oxidants (NMO).[45] An IR spectral change has been observed by the addition of NMO to a dichloromethane solution of the ruthenium complex. The appearance of a band at 859 cm^{-1} after addition of NMO is attributed to the formation of highly valent Ru^{4+} = O species. Hence, it has been concluded that catalytic oxidation proceeds through metal-oxo intermediate.[46,47]

Table 4. Aryl–aryl coupling catalyzed by ruthenium(II) complexes

Complex	Biphenyl yield (%)
$[Ru(CO)(PPh_3)_2L^1]$	20
$[Ru(CO)(PPh_3)_2L^2]$	20
$[Ru(CO)(PPh_3)_2L^3]$	21
$[Ru(CO)(PPh_3)_2L^4]$	21
$[Ru(CO)(AsPh_3)_2L^1]$	24
$[Ru(CO)(AsPh_3)_2L^2]$	23
$[Ru(CO)(AsPh_3)_2L^3]$	21
$[Ru(CO)(AsPh_3)_2L^4]$	23
$[Ru(CO)(PPh_3)(py)L^1]$	22
$[Ru(CO)(PPh_3)(py)L^2]$	24
$[Ru(CO)(PPh_3)(py)L^3]$	22
$[Ru(CO)(PPh_3)(py)L^4]$	24

Aryl–Aryl Couplings

The percentage yield of biphenyl was calculated for the newly synthesized aroyl hydrazone ruthenium(II) complexes. All the complexes showed only moderate activity (Table 4). This may be due to the fact that the active species produced from ruthenium(II) had a d^8 configuration, which is less stable. Very similar moderate catalytic activities have been reported for other similar ruthenium complexes.[48]

Antibacterial Activity

In view of the biological relevance of ruthenium(II) complexes, in the present studies, the antibacterial activities of ruthenium(II) and standard drug, ampicillin, were screened by the disk diffusion method in DMSO solvent at a concentration of 0.5 and 1.0%, and were checked against Gram-positive bacteria *B. subtilis* and Gram-negative bacteria *E. coli* (Table 5). Diameters of the zones of inhibition (in millimetres) of standard drug ampicillin against *B. subtilis* and *E. coli* were found to be 27 and 24, respectively. The results of this study are: (i) ruthenium complexes are more active in killing the bacteria than their ligands, since chelation makes the ligand a powerful bactericidal agent; (ii) as the concentration of the complexes increases degree of inhibition also increases; (iii) complexes containing heterocyclic nitrogen base possess more activity than other complexes.[49] The mode of action of the compounds may involve the formation of hydrogen bonds through the azomethine nitrogen with the microbes or ribosomes of the cell constituents, thereby disturbing the respiration process of the cell and thus blocking the synthesis of proteins which restrict the further growth of the organism.[50] The variation in the effectiveness of different compounds against different organisms depends either on the impermeability of the cells of the microbes or the difference in ribosomes of microbial cells.[51]

Table 5. Antibacterial activity of ruthenium(II) complexes[a]

	Zone of inhibition (mm)			
	B. subtilis		*E. coli*	
Complex/ligand	0.5%	1.0%	0.5%	1.0%
H_2L^1	9	14	10	13
$[Ru(CO)(PPh_3)_2L^1]$	15	19	15	18
$[Ru(CO)(AsPh_3)_2L^1]$	13	18	14	16
$[Ru(CO)(PPh_3)(py)L^1]$	16	20	16	20
H_2L^2	8	13	12	15
$[Ru(CO)(PPh_3)_2L^2]$	11	16	15	20
$[Ru(CO)(AsPh_3)_2L^2]$	12	15	14	18
$[Ru(CO)(PPh_3)(py)L^2]$	14	18	17	21
H_2L^3	10	13	12	15
$[Ru(CO)(PPh_3)_2L^3]$	12	16	16	17
$[Ru(CO)(AsPh_3)_2L^3]$	14	18	19	22
$[Ru(CO)(PPh_3)(py)L^3]$	16	19	17	22
H_2L^4	9	13	11	17
$[Ru(CO)(PPh_3)_2L^4]$	14	18	14	20
$[Ru(CO)(AsPh_3)_2L^4]$	16	19	15	21
$[Ru(CO)(PPh_3)(py)L^4]$	17	22	17	22
Ampicillin	27	27	24	24

[a] 0.5 and 1.0% indicate 0.5 and 1.0 g of the compound in 100 ml of the solvent.

Conclusion

The present study reveals that the aroyl hydrazone Schiff bases, H_2L^1, H_2L^2, H_2L^3 and H_2L^4, act as dibasic tridentate ligands coordinating Ru^{2+} ion through O, N, O donor sites. The overall experimental evidence reveals that the studied Ru(II) complexes display a coordination number of 6 and have octahedral structure and the complexes are nonionic in nature. These complexes were found to be efficient catalysts for the oxidation of alcohols and aryl–aryl couplings reactions. The complexes showed significant biological activities.

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