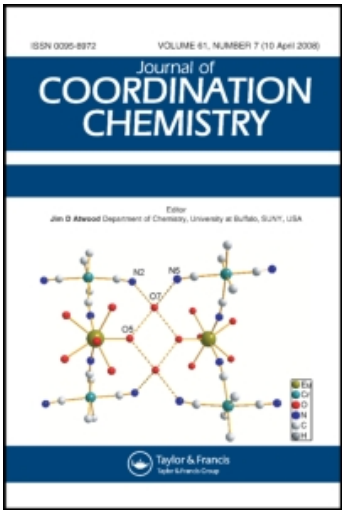

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Spectrometric, catalytic, and antimicrobial studies of mononuclear Ru(III) Schiff-base complexes

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Spectrometric, catalytic, and antimicrobial studies of mononuclear Ru(III) Schiff-base complexes

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A series of air stable low spin Ru(III) complexes, $[RuX_2(EPh_3)(L)]$ (where X = Cl or Br; E = P or As; L = monobasic tridentate Schiff-base ligand), have been synthesized by reacting $[RuCl_3(PPh_3)_3]$, $[RuCl_3(AsPh_3)_3]$, and $[RuBr_3(PPh_3)_3]$ with the Schiff base in 1 : 1 molar ratio in benzene. These complexes have been characterized by elemental analysis, FT-IR, UV-Vis, and EPR spectroscopy together with magnetic susceptibility. The redox behaviors of the complexes have been investigated by cyclic voltammetric technique. Catalytic efficiency of the ruthenium complexes was determined for aryl–aryl coupling and the oxidation of primary and secondary alcohols into their corresponding aldehydes and ketones in the presence of molecular oxygen as co-oxidant. All complexes were screened for antibacterial activity.

Keywords: Schiff base; Aryl–aryl coupling; Oxidation of alcohols; Antibacterial

1. Introduction

There is much current interest in the chemistry of ruthenium [1–10], most of which is due to the fascinating electron-transfer and energy-transfer properties displayed by complexes of this metal. Octahedral ruthenium(III) complexes are the object of great attention in the field of medicinal inorganic chemistry owing to the favorable pharmacological properties of potential antitumor activities manifested by some members of this family of metallodrugs [11]. Schiff bases provide different bonding modes to metals and show that they are found to have a wide range of applications such as industrial, carcinostatic, antitumor, antiviral, and antimalarial activity. Metallic complexes of Schiff bases are biologically important and also serve as catalysts in various chemical and photochemical reactions [12]. Schiff-base complexes of transition metals having O and N donors have shown exponential increase as catalysts for various organic transformations. Transition metal phosphine/arsine complexes, especially ruthenium, show a wide range of applications in catalytic processes such as hydrogenation, isomerization, decarboxylation, reductive elimination, oxidative addition and in C–C coupling reactions [13]. Activation of molecular oxygen for catalytic

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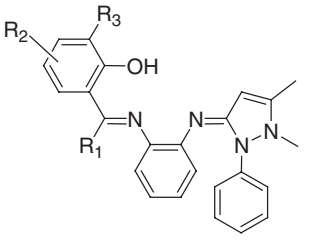


R_1	R_2	R_3	Abbreviation
H	H	H	HL^1
CH_3	H	H	HL^2
H	H	OCH_3	HL^3
H	C_4H_4	H	HL^4

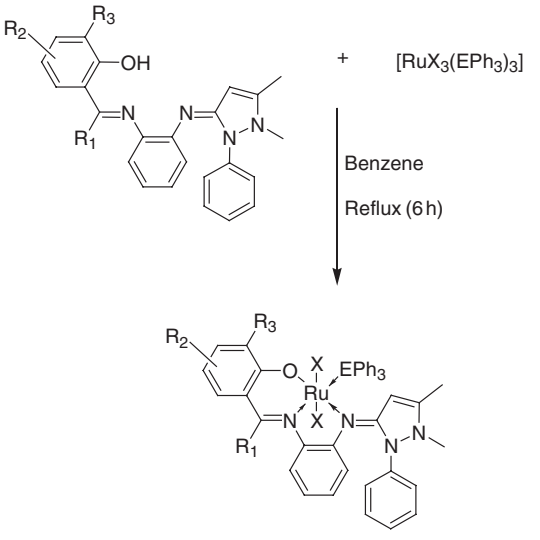
Scheme 1. The general structure of Schiff bases.

oxidation of organic substrates has been of continued interest in organic synthesis and to understand biological processes [14–16]. Schiff-base metal complexes with salen ligands are well known to activate molecular oxygen and catalyze the oxidation of electron rich substrates such as phenols, activated olefins, amines, and hydrazones [17]. Several transition metal Schiff-base complexes possess interesting biological properties such as antibacterial, antifungal, and even antitumor activity [18]. We report here the synthesis, characterization, catalytic, and biological activity of Ru(III) Schiff-base complexes containing triphenyl phosphine/arsine as coligands. Mixed-chelate complexes of ruthenium have been synthesized using tridentate Schiff-base ligands derived by condensation of salicylaldehyde/*o*-hydroxyacetophenone/*o*-vanillin/2-hydroxy-1-naphthaldehyde with *o*-phenylenediamine and antipyrine (scheme 1).

2. Experimental

2.1. *Materials and measurements*

All the reagents used were of analar grade. Solvents were purified and dried according to the literature procedures [19]. $RuCl_3{\cdot}3H_2O$ was purchased from Loba chemie and used without purification. The starting complexes $[RuCl_3(PPh_3)_3]$ [20], $[RuCl_3(AsPh_3)_3]$ [21], and $[RuBr_3(PPh_3)_3]$ [22] were prepared by the literature methods. Microanalyses were performed at Sophisticated Test and Instrumentation Centre (STIC), Cochin University, Kerala. Infrared spectra were recorded using KBr pellets on a Perkin-Elmer FT-IR 8000 spectrometer RX1 model from 4000 to 400 cm^{-1}. Electronic spectra of the complexes were recorded in chloroform with a Systronics-2202 double beam spectrophotometer from 800 to 200 nm. The ^1H and ^{13}C-NMR spectra of the ligands were recorded with a Bruker WM 500 DCX MHz instrument using TMS as an internal standard at the Indian Institute of Science (IISc), Bangalore, Karnataka. Magnetic susceptibility measurements of the complexes were recorded using a vibrating sample magnetometer EG & G model: 155 at SAIF, Indian Institute of Technology (IIT), Chennai.



where R_1 = H/CH_3; R_2 = H/C_4H_4; R_3 = H/OCH_3; X = Cl/Br; E = P/As

Scheme 2. Formation of ruthenium(III) Schiff-base complexes.

Room temperature and liquid nitrogen EPR spectra of powdered samples were recorded on an E-112 Varian model instrument in X-band frequencies at the IIT, Chennai. Cyclic voltammetric studies were carried out on a BAS CV-50 electrochemical analyzer in acetonitrile using a glassy carbon working electrode. A platinum electrode and a saturated calomel electrode were used as counter and reference, respectively. Melting points were recorded with Veego DS model apparatus and are uncorrected.

2.2. *Preparation of tridentate Schiff-base ligands*

To an ethanolic solution of salicylaldehyde/*o*-hydroxyacetophenone/*o*-vanillin/2-hydroxy-1-naphthaldehyde (20 mmol), *o*-phenylenediamine (20 mmol), and the solution of antipyrine (20 mmol) in ethanol were added with stirring. The mixture was then refluxed for 6 h. On cooling, a solid which separated out was filtered, dried, and recrystallized from ethanol. The purity of the ligand was checked by thin layer chromatography (TLC).

2.3. *Preparation of ruthenium(III) Schiff-base complexes*

The Schiff bases (HL^1–HL^4) (0.1 mmol) were added to a solution of [$RuX_3(EPh_3)_3$] (where L = monobasic tridentate Schiff bases; X = Cl/Br; E = P/As) (0.1 mmol) in 1 : 1 molar ratio in benzene (20 cm^3) and the mixture was refluxed for 6 h. The resulting solution was concentrated to about 3 cm^3 and the complexes precipitated by addition of a small quantity of petroleum ether (60–80°C). The complexes were then filtered, washed with petroleum ether and recrystallized from CH_2Cl_2/petroleum ether and dried under vacuum (scheme 2).

2.4. *Catalytic oxidation experiments*

A solution of alcohol (0.1 mL, 1 mmol) in dichloromethane (20 mL) was added to a solution of the ruthenium complex (0.002 g, 0.01 mmol) and stirred for 6 h under oxygen at ambient temperature. The mixture was evaporated to dryness and extracted with petroleum ether (60–80°C). The combined petroleum ether extracts were filtered and evaporated to give the corresponding carbonyl compound which was then quantified as their 2,4-dinitrophenylhydrazones [23].

2.5. *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. PhBr [0.75 cm^3 of total 1.88 cm^3] in anhydrous Et_2O (5 cm^3) was added with stirring and the mixture was heated under reflux. The remaining PhBr in Et_2O (5 cm^3) was added dropwise and the mixture was refluxed for 40 min. To this mixture, 1.03 cm^3 (0.01 mol) of PhBr in anhydrous Et_2O (5 cm^3) 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 of biphenyl which was chromatographed to get pure biphenyl, compared with an authentic sample (m.p.: 69–72°C) [24].

2.6. *Antibacterial activities*

The precursor complexes, ligands, and their complexes have been tested for *in vitro* growth inhibitory activity against *Escherichia coli*, *Salomonella typhi*, and *Pseudomonas aeuroginosa*. The antibacterial activity of the compounds was determined by disc diffusion method [25]. The test organisms were grown on nutrient agar medium in petri plates. The compounds to be tested were dissolved in DMSO to a concentration of 0.5 and 1.0% and soaked in filter paper discs of 5 mm diameter and 1 mm thickness. These discs were placed on the already seeded plates and incubated at 37°C for 24 h. The diameter (mm) of the inhibition zone around each disc was measured after 24 h; Streptomycin was used as a standard.

3. Results and discussion

New air stable mononuclear octahedral ruthenium(III) Schiff-base complexes of the type $[RuX_2(EPh_3)(L)]$ (X = Cl or Br, E = As or P, L = monobasic tridentate Schiff base) have been prepared from $[RuX_3(EPh_3)_3]$ with the respective Schiff bases in 1 : 1 molar ratio in dry benzene. The analytical data obtained (table 1) for the new complexes agree well with the proposed molecular formula.

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

Complex	Color	m.p. (°C)	Calculated (Found) (%)			FT-IR cm^{-1}			UV-Vis (nm)
			C	H	N	$\nu_{(C=N)}$	ν_{ph-OH}	ν_{ph-C-O}	λ_{max}
HL^1	Yellow	214	75.36 (75.32)	5.79 (5.72)	14.66 (14.62)	1615	3399	1276	306,352,368,388
HL^2	Yellow	240	75.66 (75.61)	6.10 (6.13)	14.13 (14.15)	1610	3333	1296	297,305,369,404,431
HL^3	Orange	260	72.72 (72.75)	5.86 (5.82)	13.58 (13.53)	1626	3328	1280	305,353
HL^4	Yellow	148	77.75 (77.70)	5.59 (5.53)	12.95 (12.92)	1611	3375	1281	299,369,402,434,471,491
$[RuCl_2(PPh_3)(L^1)]$	Green	160	61.83 (61.81)	4.44 (4.48)	6.87 (6.83)	1607	_	1311	251,298,353
$[RuCl_2(PPh_3)(L^2)]$	Brown	210	62.26 (62.29)	4.61 (4.67)	6.75 (6.79)	1595	_	1312	246,291,317,335,468
$[RuCl_2(PPh_3)(L^3)]$	Green	140	60.99 (60.92)	4.64 (4.61)	6.61 (6.59)	1620	_	1312	243,292,316,335,387
$[RuCl_2(PPh_3)(L^4)]$	Black	190	63.81 (63.84)	4.42 (4.39)	6.47 (6.45)	1590	_	1315	251,314,354,392,451
$[RuBr_2(PPh_3)(L^1)]$	Brown	190	54.90 (54.93)	3.95 (3.96)	6.09 (6.13)	1585	_	1300	252,296,371,401,429,470
$[RuBr_2(PPh_3)(L^2)]$	Black	120	56.27 (56.24)	4.17 (4.13)	6.10 (6.02)	1528	_	1314	245,471,474,482,487
$[RuBr_2(PPh_3)(L^3)]$	Brown	120	55.25 (55.27)	4.20 (4.10)	6.00 (5.97)	1620	_	1312	487,249,300,340,370
$[RuBr_2(PPh_3)(L^4)]$	Black	160	57.92 (57.97)	4.01 (3.97)	5.87 (5.85)	1598	_	1311	246,300,338
$[RuCl_2(AsPh_3)(L^1)]$	Gray	160	58.67 (58.64)	4.22 (4.25)	6.51 (6.56)	1585	_	1312	249,298,339,391
$[RuCl_2(AsPh_3)(L^2)]$	Brown	180	59.10 (59.12)	4.38 (4.34)	6.41 (6.45)	1585	_	1310	243,275,321,368,491
$[RuCl_2(Asph_3)(L^3)]$	Green	130	57.98 (57.93)	4.41 (4.45)	6.29 (6.23)	1624	_	1314	251,293,358,391,451
$[RuCl_2(AsPh_3)(L^4)]$	Brown	170	63.81 (63.86)	4.42 (4.47)	6.47 (6.49)	1597	_	1310	251,300,357,401,430,450

3.1. *Spectroscopic studies*

3.1.1. FT-IR spectra. Characteristic IR spectral data of the ligands were compared with those of the ruthenium(III) complexes to confirm the binding mode of the Schiff base to ruthenium ion in the complexes (table 1). The FT-IR spectra of all the ligands exhibited a strong band in the 1626–1610 cm^{-1} region, characteristic of the azomethine $\nu_{(C=N)}$. In all the complexes, $\nu_{(C=N)}$ shifted to lower frequency (1624–1528 cm^{-1}) indicating coordination of the Schiff bases through azomethine nitrogen [14]. All the Schiff bases displayed a band around 3399–3328 cm^{-1}, which could be due to phenolic $\nu_{(OH)}$ stretching. A strong band around 1276–1296 cm^{-1} in the free Schiff base has been assigned to phenolic $\nu_{(C-O)}$. On complexation, this band shifted to higher frequency (1315–1300 cm^{-1}) showing that the other coordination site is phenolic oxygen, further supported by the disappearance of the broad band around 3300 cm^{-1} due to ν_{OH} in the complexes [26]. Thus, it is clear that the Schiff-base ligands are bonded to ruthenium in a ONN fashion through the deprotonated phenolate oxygen and *o*-phenylenediimine nitrogens. All the other characteristic bands due to triphenyl phosphine/arsine were observed in the expected regions.

3.1.2. Electronic spectra. Spectral data of the free ligands and their complexes in CH_2Cl_2 are listed in table 1. Electronic spectra of the free ligands show two types of transitions, the first at range 297–306 nm assigned to π–π^* transition due to molecular orbitals located on the phenolic chromophore. These peaks shift in spectra of the complexes, due to donation of a lone pair of electrons from oxygen of the phenoxy to ruthenium [27]. This reveals that one coordination site is phenolic oxygen. The second type of transition appeared at 352–491 nm assigned to $n \rightarrow \pi^*$ due to azomethine groups and benzene of the ligands. These bands also shift in spectra of the new complexes, indicating involvement of imine nitrogens in coordination with ruthenium [28]. The spectra of all the complexes showed another type of transitions, different from the free ligands, around 243–491 nm. In most ruthenium(III) complexes, the electronic spectra show only charge transfer transitions [29] in this region. Since in a d^5 system, and especially in ruthenium(III) which has relatively high oxidizing properties, the charge transfer bands of the type $L_{\pi y} \rightarrow t_{2g}$ are prominent in the low energy region, they obscure the weaker d–d transitions [29] ($\varepsilon = 2650$–6200 $dm^3\,mol^{-1}\,cm^{-1}$). These bands have been assigned to charge transfer transition of the type $L_{\pi y} \rightarrow t_{2g}$, characteristic of octahedral ruthenium(III) complexes [14].

3.1.3. ^{1}H-NMR and ^{13}C-NMR spectra of Schiff-base ligands (HL^1–HL^4). ^{1}H-NMR spectra of the Schiff bases have been recorded in $DMSO \cdot d_6$ (Supplementary material). All the ligands show multiplets at 6.6–8.0 ppm for aromatic protons. The antipyrine >C=C–CH_3, N–CH_3, and >C–H proton appears as singlets at 2.5 ppm, 3.3 ppm, and 5.1–5.4 ppm for all the Schiff bases. The azomethine and phenolic OH protons appear as singlets around 8.8–9.6 ppm and 13.2–15.1 ppm, respectively. In HL^2 the azomethine methyl protons are a singlet in the region 1.2 ppm. The methoxy protons of HL^3 are a singlet at 4.3 ppm.

The ^{13}C-NMR data have been recorded (Supplementary material). The chemical shift for the carbons of the aromatic rings was between 117 and 133 ppm. The ^{13}C-NMR spectra of HL^1–HL^4 have a single resonance at 151–167 ppm, showing that the

azomethine carbons are equivalent, confirming the structure of ligands. The phenolic antipyrine C–OH, –C–N, C–CH_3, N–CH_3, and C–C carbons appear around 148–156 ppm, 140–142 ppm, 18–20 ppm, 38–40 ppm, and 118–120 ppm, respectively. In HL^3 the methoxy carbon appears at 55 ppm. The azomethine methyl carbon in HL^2 appears at 14.5 ppm.

3.1.4. Magnetic susceptibility and EPR spectra. Magnetic susceptibility measurements provide information regarding the structure of the complexes. The room temperature magnetic moments show that the complexes are one electron paramagnetic, in the range 1.69–1.82 BM, corresponding to +3 ruthenium, suggesting a low spin $4d^5$, $S = 1/2$ configuration around octahedral ruthenium(III) with t_{2g}^5 configuration [30].

The room temperature and liquid nitrogen temperature EPR spectra of powder samples were recorded at X-band frequencies and the spectral data are given in table 2. The spectrum is represented in Supplementary data. $[RuCl_2(PPh_3)(L^2)]$, $[RuBr_2(PPh_3)(L^1)]$, $[RuBr_2(PPh_3)(L^4)]$, and $[RuCl_2(AsPh_3)(L^3)]$ exhibited three lines with different '*g*' values g_x, g_y, and g_z in the range 1.72–1.80, 1.81–1.86, and 1.86–1.90, indicating the presence of magnetic anisotropy. The presence of three '*g*' values is indicative of a rhombic distortion in these complexes. Moreover, eight of the complexes $[RuCl_2(PPh_3)(L^1)]$, $[RuCl_2(PPh_3)(L^3)]$, $[RuCl_2(PPh_3)(L^4)]$, $[RuBr_2(PPh_3)(L^2)]$, $[RuBr_2(PPh_3)(L^3)]$, $[RuCl_2(AsPh_3)(L^1]$, $[RuCl_2(AsPh_3)(L^2)]$, and $[RuCl_2(AsPh_3)(L^4)]$ exhibit a single isotropic resonance with '*g*' values in the range 1.62–1.87, indicating very high symmetry around ruthenium; such isotropic lines are usually observed either due to intermolecular spin exchange which can broaden the lines or occupancy of the unpaired electrons in a degenerate orbital. EPR spectra for $[RuCl_2(PPh_3)(L^1)]$ at liquid nitrogen temperature did not show much variation from that observed at room temperature, indicating isotropic resonance in this complex [31, 32]. Moreover, the nature and position of the lines in the spectra of these complexes are similar to those of the other octahedral ruthenium(III) complexes [33].

Table 2. EPR and cyclic voltammetry[a] data of Ru(III) Schiff-base complexes.

	EPR spectroscopic data				Cyclic voltammetry data Ru^{IV}–Ru^{III}				Ru^{III}–Ru^{II}			
Complexes	g_x	g_y	g_z	$<g>^*$	E_{p_c} (V)	E_{p_a} (V)	E_f (V)	ΔE_P (mV)	E_{p_c} (V)	E_{p_a} (V)	E_f (V)	ΔE_P (mV)
$[RuCl_2(PPh_3)(L^1)]$	1.87	–	–	–	0.76	0.60	0.68	160	–	–	–	–
$[RuCl_2(PPh_3)(L^1)]$-LNT	1.73	–	–	–	–	–	–	–	–	–	–	–
$[RuCl_2(PPh_3)(L^2)]$	1.80	1.86	1.90	1.86	0.92	0.62	0.50	300	−0.60	−0.32	−0.46	280
$[RuCl_2(PPh_3)(L^3)]$	1.76	–	–	–	0.80	0.46	0.63	340	–	–	–	–
$[RuCl_2(PPh_3)(L^4)]$	1.80	–	–	–	0.70	0.52	0.61	180	−0.64	−0.43	−1.07	210
$[RuBr_2(PPh_3)(L^1)]$	1.72	1.82	1.86	1.80	0.78	0.58	0.68	200	–	−0.49	–	–
$[RuBr_2(PPh_3)(L^2)]$	1.86	–	–	–	0.77	0.62	0.69	150	–	−0.29	–	–
$[RuBr_2(PPh_3)(L^3)]$	1.77	–	–	–	0.85	0.62	0.73	230	−0.68	−0.42	−0.55	260
$[RuBr_2(PPh_3)(L^4)]$	1.77	1.81	1.87	1.81	0.68	0.42	0.55	260	–	−0.47	–	–
$[RuCl_2(AsPh_3)(L^1)]$	1.62	–	–	–	0.85	0.55	0.70	300	–	–	–	–
$[RuCl_2(AsPh_3)(L^2)]$	1.82	–	–	–	0.55	0.14	0.35	410	−0.85	−0.70	−0.77	150
$[RuCl_2(AsPh_3)(L^3)]$	1.78	1.82	1.88	1.83	0.66	0.25	0.46	410	−0.74	−0.60	−0.69	140
$[RuCl_2(AsPh_3)(L^4)]$	1.83	–	–	–	0.70	0.23	0.47	470	−0.65	−0.44	−0.55	210

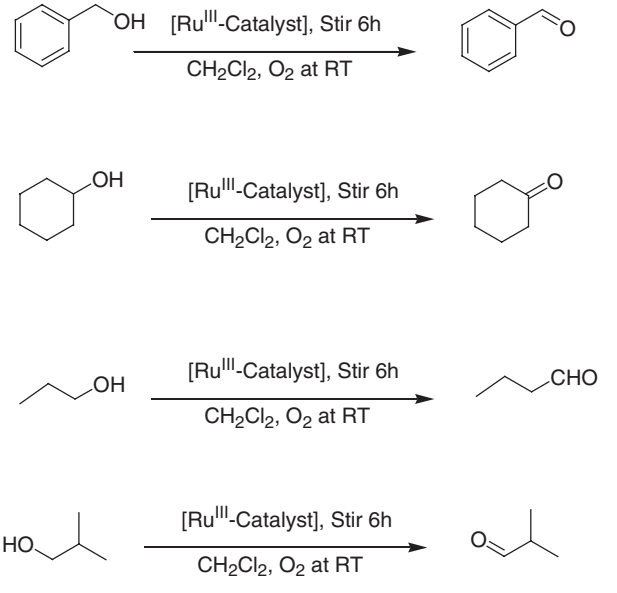
[a]Supporting electrolyte $[NBu_4]ClO_4$ (0.1 M); scan rate, all potentials are referenced to Ag/AgCl; $E_f = 0.5(E_{p_a} + E_{p_c})$, where E_{p_a} and E_{p_c} are anodic and cathodic peak potentials, respectively; scan rate, 100 mVs^{-1}. $<g>^* = [1/3g_x^2 + 1/3g_y^2 + 1/3g_z^2]^{1/2}$.

3.2. *Electrochemistry*

The ruthenium complexes were studied by cyclic voltammetry with scan rates of $0.1\,Vs^{-1}$ in CH_3CN containing $[NBu_4]BF_4$ (0.1 M) as a supporting electrolyte. Representative voltammograms are provided in Supplementary material and potential data are listed in table 2. The complexes display Ru(III)–Ru(II) and Ru(III)–Ru(IV) couples in the potential ranges −0.29 to −0.85 and 0.14 to 0.92 V, respectively, *versus* SCE. The Ru(III)–Ru(IV) redox couple is quasi-reversible, with a peak to peak separation (ΔE_p) of 150–470 mV. For the Ru(III)–Ru(II) couple, $[RuBr_2(PPh_3)(L^1)]$, $[RuBr_2(PPh_3)(L^2)]$, and $[RuBr_2(PPh_3)(L^4)]$ are irreversible, while the remaining complexes are quasi-reversible with peak to peak separation (ΔE_p) of 140–280 mV. The reason for the irreversibility of the above three complexes may be oxidative degradation or the short-lived oxidized state of the metal ion [34].

3.3. *Catalytic activity studies*

3.3.1. Oxidation of alcohols. Catalytic oxidations of primary and secondary alcohols by ruthenium(III) Schiff-base complexes were carried out in CH_2Cl_2 under oxygen at ambient temperature (scheme 3) and the results are summarized in table 3. Benzaldehyde, cyclohexanone, propionaldehyde, and 2-methylpropionaldehyde were formed from benzylalcohol, cyclohexanol, propane-1-ol, and 2-methylpropanol, respectively, after stirring for 6 h and the carbonyl compounds were quantified as 2,4-dinitrophenylhydrazone derivatives. Only a very little amount of carbonyl compound is formed when reaction is carried out without the catalyst in oxygen at ambient temperature, which is insignificant compared with the yields of carbonyl



Scheme 3. Catalytic oxidation reactions catalyzed by Ru(III) Schiff-base complexes.

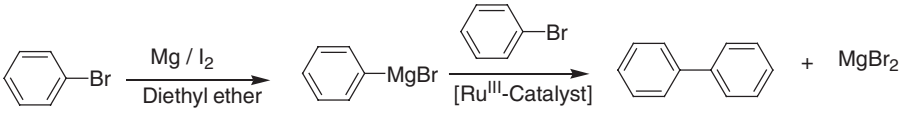
Table 3. Catalytic activities of ruthenium(III) Schiff-base complexes.

	Aryl–aryl coupling reaction		Oxidation of alcohols							
	Biphenyl		Benzylalcohol → Benzaldehyde		Cyclohexanol → Cyclohexanone		Propane-1-ol → Propionaldehyde		Isobutyl alcohol → 2-Methyl-propionaldehyde	
Complexes	In mg	Yield (%)	Yield (%)	Turnover number[a]	Yield (%)	Turnover number[a]	Yield (%)	Turnover number[a]	Yield (%)	Turnover number[a]
$[RuCl_2(PPh_3)(L^1)]$	300	31.17	77.47	86.53	70.29	73.4	39.14	65.15	45.94	68.00
$[RuCl_2(PPh_3)(L^2)]$	323	33.56	83.53	85.21	68.57	71.59	28.41	46.60	40.00	59.00
$[RuCl_2(PPh_3)(L^3)]$	320	33.25	82.19	83.00	67.54	70.54	30.83	51.20	37.00	55.00
$[RuCl_2(PPh_3)(L^4)]$	298	30.96	80.84	69.15	69.95	73.01	31.36	52.10	39.00	57.00
$[RuBr_2(PPh_3)(L^1)]$	310	32.21	66.69	69.85	65.15	68.04	29.49	49.00	36.86	54.00
$[RuBr_2(PPh_3)(L^2)]$	321	33.35	67.36	64.00	63.77	66.60	29.75	49.00	35.79	53.00
$[RuBr_2(PPh_3)(L^3)]$	330	33.00	61.64	73.34	64.8	67.67	32.17	53.40	34.72	51.00
$[RuBr_2(PPh_3)(L^4)]$	290	30.13	70.73	68.06	65.83	68.74	28.68	47.60	33.66	49.00
$[RuCl_2(AsPh_3)(L^1)]$	288	29.92	65.68	79.27	66.52	69.40	35.39	58.80	34.19	50.70
$[RuCl_2(AsPh_3)(L^2)]$	291	30.23	76.46	74.37	65.15	68.04	31.63	51.00	32.32	47.00
$[RuCl_2(AsPh_3)(L^3)]$	294	30.34	71.74	70.20	65.83	68.74	32.70	54.4	37.13	55.00
$[RuCl_2(AsPh_3)(L^4)]$	288	29.92	67.7	80.3	63.77	66.66	29.20	48.60	34.18	50.70

[a] Moles of product per mole or catalyst.

compounds that have been obtained from the reaction catalyzed by ruthenium complexes. The relatively higher product yield obtained for oxidation of benzylalcohol compared with cyclohexanol, propane-1-ol, and 2-methylpropanol is due to the α-CH of benzyl alcohol that is more acidic than cyclohexanol and 2-methylpropanol [35, 36].

3.3.2. Phenyl–phenyl coupling reaction. The new ruthenium(III) complexes have been used as catalysts for phenyl–phenyl coupling (scheme 4). The system chosen for the study is the coupling of phenyl magnesium bromide with bromobenzene to give biphenyl as the product. Bromobenzene was first converted into the corresponding Grignard reagent, then bromobenzene followed by the complex was added and the mixture was heated under reflux for 6 h. After workup, the mixture yielded biphenyl which was compared with an authentic sample. Only very little biphenyl was isolated when the reaction was carried out without the catalyst, which is insignificant compared with the yield of biphenyl obtained from the reaction catalyzed by ruthenium(III) complexes [37].



Scheme 4. C–C coupling reaction catalyzed by Ru(III) Schiff-base complexes.

Table 4. Antibacterial studies of ruthenium(III) Schiff-base complexes.

	Diameter of inhibition zone (mm)			
	E. coli		*Pseudomonas* sps.	
Complexes	0.5%	1%	0.5%	1%
HL^1	3.0	4.0	3.0	4.0
$[RuCl_2(PPh_3)(L^1)]$	4.0	5.0	4.0	5.0
$[RuBr_2(PPh_3)(L^1)]$	4.2	6.0	4.2	6.0
$[RuCl_2(AsPh_3)(L^1]$	4.0	6.4	4.0	6.4
HL^2	4.0	6.0	4.0	6.0
$[RuCl_2(PPh_3)(L^2)]$	5.0	7.5	5.0	7.5
$[RuBr_2(PPh_3)(L^2)]$	6.0	7.2	6.0	7.2
$[RuCl_2(AsPh_3)(L^2]$	5.0	7.9	5.0	7.9
HL^3	3.0	4.1	3.0	4.1
$[RuCl_2(PPh_3)(L^3)]$	5.0	6.0	5.0	6.0
$[RuBr_2(PPh_3)(L^3)]$	6.0	7.8	6.0	7.8
$[RuCl_2(AsPh_3)(L^3]$	3.0	7.8	3.0	7.8
HL^4	4.0	6.0	4.0	6.0
$[RuCl_2(PPh_3)(L^4)]$	4.0	7.6	4.0	7.6
$[RuBr_2(PPh_3)(L^4)]$	4.4	6.0	4.6	6.0
$[RuCl_2(AsPh_3)(L^4)]$	5.0	6.3	5.0	6.2
$[RuCl_3(PPh_3)_3]$	3.5	4.4	3.3	4.5
$[RuBr_3(PPh_3)_3]$	3.7	4.3	3.6	4.9
$[RuCl_3(AsPh_3)_3]$	3.3	5.1	3.2	4.8
Streptomycin	20	24	12	17
DMSO-solvent		No activity		

3.4. *Antibacterial activities*

The *in vitro* antibacterial screening of the ligands and their ruthenium complexes have been carried out against *E. coli*, *S. typhi*, and *P. aeuroginosa* using a nutrient agar medium by the disc diffusion method. The results in table 4 show that the complexes exhibit moderate activity against all species of bacteria, except *S. typhi*. The inhibition activity of the complexes increases with increase in the concentration of the complex solution. The variation in effectiveness of different compounds against different organisms depends either on the impermeability of the cells of the microbes or differences in ribosomes of the microbial cells [38]. The antibacterial activity of the precursor complexes, namely, $[RuCl_3(PPh_3)_3]$, $[RuCl_3(AsPh_3)_3]$, and $[RuBr_3(PPh_3)_3]$ have higher activity than that of the Schiff base but lower than that of the complexes. These observations indicate an enhanced activity for the chelated complex [39]. Although there is a sufficient increase in the antibacterial activity of ruthenium complexes as compared with free ligands, they did not attain the effectiveness of the conventional bacteriocide, streptomycin.

4. Conclusion

A series of mononuclear octahedral ruthenium(III) Schiff-base complexes incorporating triphenylphosphine/triphenylarsine and chloride/bromide ligands have been synthesized and the structures are proposed on the basis of analytical and spectral data. The electronic spectral studies and EPR spectra at RT and LNT reveal that the Ru(III) center in the monomeric complex is octahedral. All the ruthenium(III) Schiff-base complexes have been tested for their catalytic efficiency in oxidation of alcohols to their corresponding carbonyl compounds by using molecular oxygen at ambient temperature and also for C–C coupling reactions. The complexes show good antibacterial activity.

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