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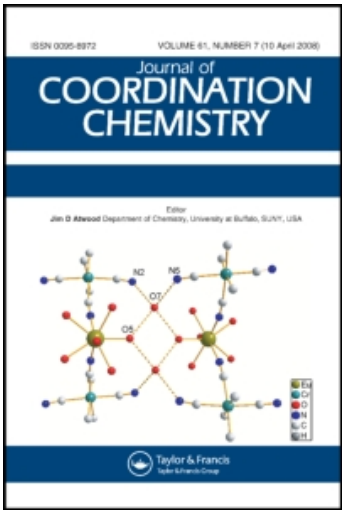

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Tetradentate Schiff-base ruthenium(III) complexes containing triphenylphosphine/arsine as coligands: study of physico-chemical, spectrometric, catalytic, and biocidal activities

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Tetradentate Schiff-base ruthenium(III) complexes containing triphenylphosphine/arsine as coligands: study of physico-chemical, spectrometric, catalytic, and biocidal activities

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A series of air-stable, low-spin Ru(III) octahedral complexes [$RuX(EPh_3)L$] (where X = Cl/Br; E = P/As; and L = dibasic tetradentate Schiff base derived by condensation of ethylenediamine with acetoacetanilide/acetoacetotoluidide/ethylacetoacetate in 1 : 2 molar ratio in ethanol) have been synthesized from $RuX_3(EPh_3)_3$ (where X = Cl/Br and E = P/As) with Schiff bases in 1 : 1 molar ratio in benzene for 6 h. These complexes were characterized by elemental analysis, spectral methods (Fourier transform infrared (FT-IR), UV-Vis, ^{1}H- and ^{13}C-nuclear magnetic resonance (NMR) for the ligands, and electron paramagnetic resonance (EPR)), and are examined electrochemically. The complexes were efficient catalysts for oxidation of primary and secondary alcohols in their corresponding aldehydes and ketones in the presence of molecular oxygen. These complexes were also tested for their antibacterial and antifungal activities.

Keywords: Octahedral; Electrochemical; Molecular oxygen; Antibacterial; Antifungal

1. Introduction

Schiff bases can be easily prepared by condensation between aldehydes and amines [1]. Tetradentate Schiff bases coordinate with many different metal ions forming the stable compounds and some of these complexes are oxygen carriers [2, 3]. Schiff-base complexes of transition metals having O and N donors are catalysts for various organic transformations [4–6]. Ruthenium-mediated oxidations are finding application due to the unique properties of this extremely versatile metal whose oxidation state can vary from −II to +VIII [7–10]. Schiff bases and their biologically active complexes have often been used as chelating agents in radiopharmaceuticals for cancer targeting, agrochemicals, and are used as catalysts and dioxygen carriers [1]. A large number of Schiff bases and their complexes have biological activities including antitumor, antibacterial, fungicidal, and anticarcinogenic properties [11, 12].

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In continuation of our research [13] to understand the role of simple N and O donors toward ruthenium, reaction of dibasic tetradentate Schiff bases (scheme 1) derived from ethylenediamine with acetoacetanilide/acetoacetotoluidide/ethylacetoacetate with Ru(III) precursors have been carried out. This article describes the synthesis, characterization, and redox properties of six-coordinated Ru(III) complexes exhibiting a N and O ligating core, and their catalytic activity toward the oxidation of alcohols in the presence of molecular oxygen. The biocidal activities of Schiff bases and new Ru(III) complexes were examined.

2. Experimental

2.1. *Materials and measurements*

All reagents were of analytical reagent grade. Solvents were purified and dried according to the standard procedures [14]. $RuCl_3 \cdot 3H_2O$ was purchased from Loba Chemie and used without purification. Carbon, hydrogen, and nitrogen were analyzed with the Vario EL III CHNS analyzer at Cochin University, Kerala, India. IR spectra were recorded as KBr pellets from 400 to 4000 cm^{-1} using a Shimadzu FT-IR 8000 spectrophotometer (FT-IR, Fourier transform infrared). Electronic spectra were recorded in dichloromethane with a Systronics double beam UV-Vis Spectrophotometer 2202. ^{1}H- and ^{13}C-nuclear magnetic resonance (NMR) spectra for the ligands were recorded in the Indian Institute of Science, Bangalore. X-band electron paramagnetic resonance (EPR) spectra of the powdered samples were recorded on a JEOL JESFA200 EPR spectrometer at room temperature (RT) and liquid nitrogen temperature (LNT) using diphenylpicryl hydrazyl as a reference at Pondicherry University, Pondicherry. 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. Melting points were

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R	R′	Abbreviation	Name of the Schiff-base ligands
C_6H_5NH	CH_3	H_2L^1	(3E,3′E)-3,3′-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(N-phenylbutanamide)
C_7H_7NH	CH_3	H_2L^2	(3E,3′E)-3,3′-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(N-o-tolylbutanamide)
OC_2H_5	CH_3	H_2L^3	(3E,3′E)-diethyl 3,3′-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))dibutanoate

Scheme 1. Keto-enol form of the Schiff-base ligands.

recorded on a Veego VMP-DS melting point apparatus and are uncorrected. Antibacterial and antifungal studies were carried out in KMCH College of Pharmacy, Coimbatore. The starting complexes $[RuCl_3(PPh_3)_3]$ [15], $[RuCl_3(AsPh_3)_3]$ [16], $[RuBr_3(PPh_3)_3]$, and $[RuBr_3(AsPh_3)_3]$ [17] were prepared by the reported methods. Catalytic oxidation [18] and aryl–aryl coupling reactions [19] have been carried out by using the reported literature methods. The yields in catalytic oxidation and aryl–aryl coupling products were measured by gravimetric methods.

2.2. *Preparation of tetradentate Schiff bases*

To an ethanolic solution of ethylenediammine (0.67 mL; 10 mmol), acetoacetanilide/acetoacetotoluidide/ethylacetoacetate (3.54/3.82/2.52 g, 20 mmol) was added with stirring and the solution was refluxed for 6 h [20]. The product was washed with ethanol and dried *in vacuo*. The purity of the ligand was checked by thin layer chromatography (TLC).

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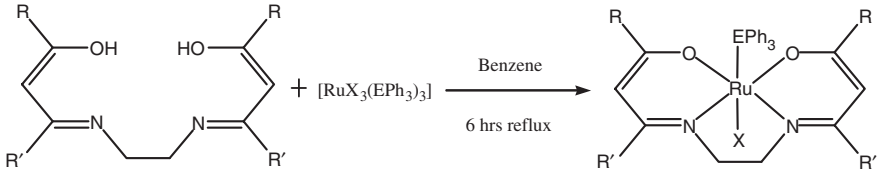
2.3. *Preparation of Ru(III) Schiff-base complexes*

All reactions were carried out strictly under anhydrous conditions. The Schiff base (0.028–0.041 g, 0.1 mmol) was added to a solution of $[RuX_3(EPh_3)_3]$ (0.1–0.113 g, 0.2 mmol) in benzene (20 mL). The resulting solution was heated under reflux for 6 h and then concentrated to 3 mL. The complex was separated by adding a small amount of petroleum ether (60–80°C), filtered, recrystallized from CH_2Cl_2/petroleum ether, and dried *in vacuo* (scheme 2).

2.4. *Catalytic oxidation experiments*

Alcohol (0.1 mL, 1 mmol) in dichloromethane (20 mL) and a solution of the ruthenium complex (0.002 g, 0.01 mmol) were stirred under oxygen atmosphere at ambient temperature for 6 h. The mixture was evaporated to dryness and extracted with petroleum ether (60–80°C). The combined petroleum ether extracts were filtered and



$R = C_6H_5NH/C_7H_7NH/CH_3$;

$R' = CH_3/OC_2H_5$; X = Cl/Br; E = P/As

Scheme 2. Synthesis of Ru(III) Schiff-base complexes.

evaporated to give the corresponding carbonyl compounds, which were then quantified as their 2,4-dinitrophenylhydrazones [18].

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 to activate the magnesium. PhBr [0.75 cm^3 of total 1.88 mL] in anhydrous Et_2O (5 mL) was added with stirring and the mixture was heated under reflux. The remaining PhBr in Et_2O (5 mL) was added dropwise and the mixture was refluxed for 40 min. To this mixture, 1.03 mL (0.01 mol) of PhBr in anhydrous Et_2O (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. The ether extract on evaporation gave crude biphenyl that was chromatographed to get pure biphenyl, which compared well with an authentic sample (m.p. 69–72°C) [19].

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2.6. *Antibacterial and antifungal activities*

The *in vitro* antimicrobial screenings of the solvent, free ligands, metal starting complexes, and the new Ru(III) complexes were tested for their effect on certain human pathogenic bacteria and fungus by the disc diffusion method. The ligands, metal starting complexes, and their Ru(III) complexes were stored dry at RT and dissolved in dichloromethane. Both the Gram-positive (*Staphylococcus albus*) and Gram-negative (*Escherichia coli*) bacteria were grown in Mueller–Hinton agar medium and incubated at 37°C for 48 h followed by frequent subculture to fresh medium and were used as test bacteria. *Candida albicans* and *Aspergillus niger* grown in Sabouraud dextrose agar medium were incubated at 27°C for 72 h followed by periodic subculturing to fresh medium and were used as test fungi. Then, the Petri plates were inoculated with a loop full of bacterial and fungal culture and spread throughout the Petri plates uniformly with a sterile glass spreader. To each disc, the test samples and reference antibiotic (ciprofloxacin/co-trimazine) were added with a sterile micropipette. The plates were then incubated at 35 ± 2°C for 24 h for bacteria and at 27 ± 1°C for 48 h for fungi, respectively. Plates with discs containing respective solvents served as control. Inhibition was recorded by measuring the diameter of the inhibitory zone after incubation [21].

3. Results and discussion

New air-stable mononuclear octahedral Ru(III) Schiff-base complexes, $Ru(X)(EPh_3)(L)$ (where X = Cl/Br; E = As/P; and L = bifunctional tetradentate Schiff base), have been prepared from $[RuX_3(EPh_3)_3]$ with respective Schiff bases in 1 : 1 molar ratio in dry benzene. The analytical data obtained for the new complexes agree well with the proposed molecular formulae (table 1).

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Table 1. Analytical, IR, and electronic spectroscopic data for the Ru(III) complexes.

Complexes	Color	m.p. (°C)	Calculated (Found) (%)			FT-IR (cm^{-1})		UV-Vis λ_{max}(nm) (ε_{max}) $dm^3 mol^{-1}$
			C	H	N	$\nu_{(C=CH)}+\nu_{(C=N)}$	$\nu_{(C=N)}$	
H_2L^1	Yellow	146	69.83 (69.77)	6.92 (6.85)	14.81 (14.80)	1592	1631	307(343), 343(401)
H_2L^2	Orange	212	70.92 (70.88)	7.43 (7.41)	13.78 (13.73)	1587	1645	307(387), 347(412)
H_2L^3	Brown	184	59.15 (59.11)	8.50 (8.46)	9.85 (9.84)	1603	1648	306(621), 341(626)
$[RuCl(PPh_3)L^1]$	Brown	112	61.98 (61.93)	5.07 (4.95)	7.23 (7.18)	1585	1613	259(1669), 299(1673), 368(1968), 390(1935)
$[RuCl(AsPh_3)L^1]$	Brown	142	58.65 (58.62)	4.79 (4.77)	6.84 (6.80)	1578	1599	258(835), 298(832), 365(947), 392(866)
$[RuBr(PPh_3)L^1]$	Brown	136	58.61 (58.58)	4.79 (4.74)	6.84 (6.83)	1576	1628	258(1668), 298(1668), 350(1676)
$[RuBr(AsPh_3)L^1]$	Black	124	55.63 (55.62)	4.55 (4.50)	6.49 (6.43)	1577	1626	259(666), 298(666), 347(665)
$[RuCl(PPh_3)L^2]$	Brown	104	62.80 (62.76)	5.39 (5.37)	6.98 (6.92)	1560	1637	256(1122), 296(1096), 363(858)
$[RuCl(AsPh_3)L^2]$	Brown	110	59.54 (59.51)	5.11 (5.10)	6.61 (6.57)	1577	1637	258(561), 296(552), 355(430)
$[RuBr(PPh_3)L^2]$	Black	126	59.51 (59.50)	5.11 (5.05)	6.61 (6.56)	1560	1637	258(1669), 299(1669), 349(1674)
$[RuBr(AsPh_3)L^2]$	Brown	122	56.58 (56.56)	4.86 (4.83)	6.28 (6.24)	1578	1627	258(478), 299(476), 344(433)
$[RuCl(PPh_3)L^3]$	Brown	108	56.43 (56.40)	5.47 (5.46)	4.11 (4.09)	1572	1637	258(561), 296(555), 365(630), 388(631)
$[RuCl(AsPh_3)L^3]$	Brown	116	53.01 (53.00)	5.14 (5.10)	3.86 (3.84)	1584	1636	259(843), 294(839), 370(987), 389(1025)
$[RuBr(PPh_3)L^3]$	Black	128	52.98 (52.95)	5.14 (5.12)	3.86 (3.85)	1585	1637	258(3370), 296(3358), 349(3258), 387(2673), 443(2808), 520(2538)
$[RuBr(AsPh_3)L^3]$	Brown	107	49.94 (49.91)	4.84 (4.82)	3.64 (3.60)	1578	1627	259(1121), 299(1113), 352(1079), 392(989), 442(1099), 512(901)

3.1. *Spectroscopic studies*

3.1.1. FT-IR spectra. IR spectra of free Schiff bases were compared with those of the ruthenium complexes in order to ascertain the binding mode of the Schiff base to the ruthenium metal ion in the complexes (table 1). A strong band in spectra of the ligands around 1700 cm^{-1} due to $\nu_{C=O}$ completely disappeared on complexation due to enolization and subsequent coordination through the deprotonated enolic oxygen [22, 23]. Bands at 1560–1585 cm^{-1} for the complexes have been assigned to the mixed vibrational mode arising from $\nu_{C=N}$ and $\nu_{C=C}$ [24]. The free Schiff base shows a very strong absorption at 1631–1648 cm^{-1}, which is a characteristic of the azomethine $\nu_{C=N}$ group. In the complexes, this absorption shifts from 1599 to 1637 cm^{-1} indicating the coordination of the Schiff bases through nitrogen [20, 25].

3.1.2. UV-Vis spectra. Electronic spectroscopic data for the free ligands and their complexes in DMSO are listed in table 1. The electronic spectra of ligands showed 306–307 nm and 341–347 nm due to π–π^* and n–π^* transitions, respectively, involving the molecular orbital of the >C=N chromophore. These bands shift in spectra of the new complexes indicating the involvement of imine nitrogens in coordination. Spectra of the complexes showed another transition different from that of the free ligands at 258–443 nm, which can be assigned to ligand to metal charge transfer [26]. In most Ru(III) Schiff-base complexes, the electronic spectra show only charge-transfer transitions in this region. In a d^5 system, and especially in Ru(III), which has relatively high oxidizing properties, the charge transfer bands $L_{\pi y} \rightarrow t_{2g}$ are prominent in the low-energy region and obscure weaker bands due to d–d transitions [27]. We have assigned these bands as charge-transfer transitions $L_{\pi y} \rightarrow t_{2g}$ based on the extinction coefficients ($\epsilon = 343$–$3370\ dm^3\ mol^{-1}$), which are characteristic of Ru(III) octahedral complexes [28–30]. The complexes show d–d transitions in the range 512–520 nm.

3.1.3. ^{1}H-NMR and ^{13}C-NMR spectra of Schiff-base ligands. ^{1}H-NMR spectra (Supplementary material) of the Schiff base have been recorded in DMSO.d_6. The H_2L^1 and H_2L^2 ligands show multiplets and a singlet at 6.8–8.4 and 9.1 ppm for the presence of aromatic and –NH-protons, respectively. The enolic OH, methyl, and methyne protons appear as a singlet at 11.5–12.6, 1.9, and 4.3–4.9 ppm. The =N–CH_2 protons for all ligands appear as triplets in the range 3.3–4.6 ppm. For H_2L^2 ligand, the aromatic methyl protons are singlet at 2.1 ppm. For H_2L^3 ligand, the ethoxy methyl and methylene protons are triplet and quartet at 1.1 and 3.9 ppm, respectively.

The ^{13}C-NMR data for the ligands have been recorded in $CDCl_3$ (Supplementary material). The chemical shifts for carbons of aromatic rings for H_2L^1 and H_2L^2 are at 110–137 ppm. The methyl, N–CH_2, and methyne carbons are at 19–20, 42–44, and 48–58 ppm. For all the ligands, the C–OH carbon is at 72–85 ppm. In H_2L^2 ligand, the aromatic methyl carbon is at 18 ppm. In H_2L^3 ligand, the ethoxy methyl and methylene carbons are at 15 and 50 ppm, respectively.

3.1.4. EPR spectra. The RT and LN EPR spectra of powder samples at X-band frequencies have spectroscopic data as in table 2. EPR spectra of Ru(III) complexes at LNT showed no indication of hyperfine interaction. The complexes exhibited spectra

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Table 2. EPR and cyclic voltammetry[a] data for the Ru(III) complexes.

					Ru(IV)–Ru(III)				Ru(III)–Ru(II)			
Complexes	g_x	g_y	g_z	$\langle g\rangle$*	E_{pa}(V)	E_{pc}(V)	E_f(V)	ΔE_p(mV)	E_{pa}(V)	E_{pc}(V)	E_f(V)	ΔE_p(mV)
[RuCl(PPh$_3$)L^1]	1.90	1.90	2.17	1.99	–	0.94	–	–	−0.67	−0.47	−0.57	200
[RuCl(PPh$_3$)L^1]LNT	1.8	1.8	2.06	1.89	–	–	–	–	–	–	–	–
[RuCl(AsPh$_3$)L^1]	1.88	1.88	2.22	2.0	0.41	–	–	–	−0.74	−0.67	−0.71	70
[RuBr(PPh$_3$)L^1]	1.7	1.7	1.94	1.8	0.24	0.07	0.16	170	−0.72	−0.57	−0.65	150
[RuBr(PPh$_3$)L^1]LNT	1.7	1.7	2.0	1.81	–	–	–	–	–	–	–	–
[RuBr(AsPh$_3$)L^1]	1.7	–	–	0.98	0.85	0.52	0.67	330	−0.69	−0.47	−0.58	220
[RuCl(PPh$_3$)L^2]	1.91	1.91	2.19	2.0	1.11	–	–	–	–	−0.54	–	–
[RuCl(PPh$_3$)L^2]LNT	1.8	1.8	2.05	1.9	–	–	–	–	–	–	–	–
[RuCl(AsPh$_3$)L^2]	1.7	1.7	1.98	1.8	0.12	–	–	–	−0.80	−0.67	−0.74	130
[RuBr(PPh$_3$)L^2]	1.7	1.7	1.93	1.8	0.14	0.02	0.08	120	−0.79	−0.64	−0.72	150
[RuBr(AsPh$_3$)L^2]	1.62	1.62	1.95	1.73	1.07	0.87	0.97	200	−0.64	−0.49	−0.57	150
[RuCl(PPh$_3$)L^3]	2.2	–	–	1.27	0.13	–	–	–	−0.75	−0.59	−0.67	160
[RuCl(AsPh$_3$)L^3]	1.82	1.82	2.20	1.95	1.3	1.28	1.29	20	−0.62	−0.51	−0.57	110
[RuBr(PPh$_3$)L^3]	1.7	1.7	1.94	1.80	0.22	0.06	0.14	160	−0.63	−0.56	−0.60	70
[RuBr(AsPh$_3$)L^3]	1.61	1.61	1.76	1.7	0.92	0.48	0.70	440	−0.82	−0.70	−0.76	120

$\langle g\rangle^* = \left(\frac{1}{3}g_x^2 + \frac{1}{3}g_y^2 + \frac{1}{3}g_z^2\right)^{1/2}$. $\Delta E_p = E_{pa} - E_{pc}$; $E_f = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potential in volts, respectively.
[a]Supporting electrolyte [NBu$_4$]ClO$_4$ (0.1 mol).

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with two different '*g*' values ($g_x = g_y \neq g_z$) in the range 1.7–2.0 indicative of tetragonal distortion in these octahedral complexes. [RuBr(AsPh$_3$)L^1] and [RuCl(PPh$_3$)L^3] have a single isotropic resonance with 'g' values in the range 0.98–1.27, indicating very high symmetry around ruthenium. Such isotropic lines are usually observed either due to intermolecular spin exchange, which can broaden the lines or due to unpaired electrons in a degenerate orbital [31]. EPR spectra recorded for [RuCl(PPh$_3$)L^1], [RuBr(PPh$_3$)L^1], and [RuCl(PPh$_3$)L^2] at LNT did not show much variation from that observed at RT [32].

3.2. *Electrochemistry*

Complexes were electrochemically examined at a glassy-carbon working electrode in dichloromethane solution using a cyclic voltammetry. A respective voltammogram of the complexes is provided in "Supplementary material" and data are given in table 2. The oxidation and reduction of each complex were characterized by the well-defined waves with E_f values in the range from 0.08 to 1.29 V (oxidation) and from −0.57 to−0.74 V (reduction) against Ag/AgCl. Complexes showed redox couples with peak-to-peak separation values (ΔE_p) ranging from 110 to 440 mV revealing that this process is at best quasi-reversible. This is attributed to show electron transfer and adsorption of the complex onto the electrode surface. [RuCl(PPh$_3$)L^2] is irreversible due to oxidative degradation or short-lived state of the metal. The oxidation and reduction potentials of [RuCl(AsPh$_3$)L^3], [RuCl(AsPh$_3$)L^1], and [RuBr(PPh$_3$)L^3] are reversible with ΔE_p values from 20 to 70 mV. The reversibility is due to one-electron transfer [33]. The complexes [RuCl(PPh$_3$)L^1], [RuCl(AsPh$_3$)L^1], [RuCl(AsPh$_3$)L^2], and [RuCl(PPh$_3$)L^3] showed only reduction potential [34].

3.3. *Study of catalytic activities*

3.3.1. Oxidation of alcohols. Transition metals play a vital role in activation of the molecular oxygen for catalytic oxidation [24, 35, 36]. Catalytic oxidation of primary alcohols by Schiff-base ligands, metal starting complexes, and new Ru(III) Schiff-base complexes were carried out in CH_2Cl_2 under oxygen at ambient temperature (table 3). Benzaldehyde, cyclohexanone, and propionaldehyde were formed from benzyl alcohol, cyclohexanol, and propan-1-ol, respectively, after stirring for 6 h, and then the carbonyl compounds were quantified as 2,4-dinitrophenylhydrazone derivatives. Only an insignificant amount of carbonyl compound is formed when the reaction is carried out without the catalyst. The relatively higher product yield obtained for oxidation of benzyl alcohol compared with the cyclohexanol and propan-1-ol was due to the α-CH unit of benzyl alcohol being more acidic than the cyclohexanol and propan-1-ol [37]. The yields obtained from the reactions catalyzed by Ru–PPh_3 complexes are greater than those of Ru–$AsPh_3$ complexes [38]. Higher yields were obtained for new Ru(III) complexes compared with the Schiff-base ligands and the Ru(III) starting complexes. When the reaction was repeated three times, the corresponding carbonyl compound was quantitatively produced at the same rate as in the first-run. The error limit was found to be 0.1–0.3%.

3.3.2. Aryl–aryl coupling. The ligands, Ru(III) starting complexes and new Ru(III) complexes have also been used as catalysts for aryl–aryl coupling. The system chosen

Table 3. Catalytic activities of the Ru(III) complexes.

	Aryl–aryl coupling reaction		Oxidation of alcohols					
	Yield of biphenyl		Benzyl alcohol		Cyclohexanol		Propan-1-ol	
Complexes	In gram	Yield (%)	Yield (%)	Turnover number[a]	Yield (%)	Turnover number[a]	Yield (%)	Turnover number[a]
$[RuCl_3(PPh_3)_3]$	0.511	53.1	55.9	57.9	20.9	21.8	29.8	49.5
$[RuCl_3(AsPh_3)_3]$	0.352	36.6	42.1	43.6	10.6	11.1	24.4	40.6
$[RuBr_3(PPh_3)_3]$	0.469	48.7	46.1	47.9	20.2	21.1	26.8	44.6
$[RuBr_3(AsPh_3)_3]$	0.423	44.0	38.7	40.2	19.9	20.8	21.9	36.6
H_2L^1	0.187	19.4	37.1	38.4	10.3	10.7	18.5	30.8
H_2L^2	0.201	20.9	16.5	17.1	4.5	4.7	14.7	24.5
H_2L^3	0.139	14.4	28.6	29.7	7.9	8.2	13.7	22.8
$[RuCl(PPh_3)L^1]$	0.658	68.4	79.8	82.8	38.7	40.5	55.8	92.8
$[RuCl(AsPh_3)L^1]$	0.603	62.7	73.8	76.5	22.9	23.9	51.4	85.5
$[RuBr(PPh_3)L^1]$	0.686	71.3	86.6	89.7	41.8	43.7	57.9	96.5
$[RuBr(AsPh_3)L^1]$	0.634	65.9	68.4	70.9	32.2	33.6	50.4	83.9
$[RuCl(PPh_3)L^2]$	0.666	69.2	78.5	81.0	38.4	40.1	58.9	98.2
$[RuCl(AsPh_3)L^2]$	0.611	63.5	72.8	75.4	36.3	38.0	49.1	81.7
$[RuBr(PPh_3)L^2]$	0.649	67.4	78.1	80.9	42.5	44.4	52.5	87.5
$[RuBr(AsPh_3)L^2]$	0.627	65.1	74.4	77.2	34.6	36.2	50.0	83.0
$[RuCl(PPh_3)L^3]$	0.635	66.0	80.5	83.4	36.0	37.6	52.0	86.6
$[RuCl(AsPh_3)L^3]$	0.619	64.3	64.0	66.4	35.7	37.2	51.2	85.2
$[RuBr(PPh_3)L^3]$	0.644	67.0	85.6	88.7	37.0	38.7	53.1	88.4
$[RuBr(AsPh_3)L^3]$	0.622	64.6	75.8	78.3	36.3	37.9	50.9	84.8

Error limit: 0.1–0.3% for oxidation of alcohols and 0.4–0.6% for aryl–aryl coupling.
[a]Moles per catalyst.

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Table 4. Antibacterial and antifungal activities of Ru(III) complexes.

	Diameter of inhibition zone (mm)															
	Antibacterial activity								Antifungal activity							
	S. albus				*E. coli*				*C. albicans*				*A. niger*			
Complexes	0.25	0.5	1.0	2.0	0.25	0.5	1.0	2.0	0.25	0.5	1.0	2.0	0.25	0.5	1.0	2.0
$[RuCl_3(PPh_3)_3]$	7	7	8	9	9	9	9	10	5	6	6	7	6	6	7	8
$[RuCl_3(AsPh_3)_3]$	9	10	10	11	8	10	11	12	6	7	7	7	7	8	9	9
$[RuBr_3(PPh_3)_3]$	6	8	9	9	9	10	11	12	6	7	8	9	8	8	9	9
$[RuBr_3(AsPh_3)_3]$	10	10	11	11	7	9	11	11	7	8	8	8	7	9	9	10
H_2L^1	4	4	5	5	5	5	6	6	–	–	1	2	–	–	–	1
H_2L^2	2	3	4	4	–	4	6	6	1	2	2	3	1	2	2	2
H_2L^3	1	2	3	4	4	4	4	5	–	1	1	2	2	3	3	3
$[RuCl(PPh_3)L^1]$	16	16	17	19	17	17	18	18	10	11	12	12	–	11	13	14
$[RuCl(AsPh_3)L^1]$	15	16	19	20	18	18	18	19	12	13	15	15	13	16	16	17
$[RuBr(PPh_3)L^1]$	17	18	18	19	14	14	16	16	14	16	16	17	13	14	14	14
$[RuBr(AsPh_3)L^1]$	13	13	15	16	13	13	14	15	15	15	15	16	14	15	15	15
$[RuCl(PPh_3)L^2]$	14	15	16	17	15	16	16	17	12	12	12	14	–	13	14	14
$[RuCl(AsPh_3)L^2]$	18	19	20	22	19	19	21	22	10	12	12	13	11	13	14	15
$[RuBr(PPh_3)L^2]$	20	20	21	23	20	20	20	21	16	17	17	17	15	15	15	17
$[RuBr(AsPh_3)L^2]$	17	18	18	18	16	19	19	20	15	17	18	19	14	16	17	17
Standard	19	19	20	22	20	20	21	21	15	17	19	20	16	16	17	18
Dichloromethane	No activities															

Error limit, 0.2–0.5 mm.

for the study is coupling of phenylmagnesium bromide with bromobenzene to give biphenyl. Bromobenzene was first converted into the corresponding Grignard reagent. Then bromobenzene followed by the complex chosen for investigations was added to the above reagent and the mixture was heated under reflux for 6 h. After the workup, the mixture yielded biphenyl. Only an insignificant amount of biphenyl was formed when the reaction was carried out without the catalyst. The experiment was repeated twice and the error limits were 0.4–0.6%.

3.4. *Antibacterial and antifungal activities*

The *in vitro* antimicrobial screenings of the free ligand and its Ru(III) complexes were tested for bacteria and fungi by the disc diffusion method (table 4). Variation in the effectiveness of the different compounds against different organisms depends on their impermeability of the microbial cells or on the difference in the ribosome of the microbial cells [24, 39–42]. All the complexes show superior antifungal and antibacterial activities compared to the free ligands and starting Ru(III) complexes.

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4. Conclusion

Ruthenium(III) complexes have been synthesized using Schiff bases formed by condensing ethylenediamine with acetoacetanilide/acetoacetotoluidide/ethylacetoacetate with Ru(III) precursors. An octahedral structure has been tentatively proposed for all the complexes. Ru(III) Schiff-base complexes show higher catalytic and biological activity when compared with the Schiff-base ligands or the metal starting precursors. Some of the complexes reached the effectiveness of the standards ciprofloxacin and co-trimazine. We carried out catalysis using the molecular oxygen as an oxidizing agent. On comparison with previous literature, our Schiff-base complexes show greater oxidation activities [43]. In antimicrobial studies also, our complexes show greater effectiveness than the standard ones. Many Schiff-base complexes did not reach the effectiveness of the standard [20, 26, 44]. So, our complexes are better at oxidation and bioactivities when compared with previous literature.

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