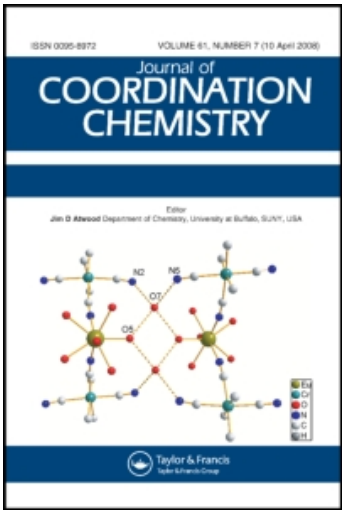

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Synthesis, characterization, electrochemistry, catalytic, and antimicrobial studies of ruthenium(III) complexes containing ONO donor ligands

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Synthesis, characterization, electrochemistry, catalytic, and antimicrobial studies of ruthenium(III) complexes containing ONO donor ligands

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A series of ruthenium(III) complexes $[RuX(EPh_3)_2L]$ (where X = Cl or Br; E = P or As; L = deprotonated dibasic tridentate ligand) were prepared by the reaction of $[RuX_3(EPh_3)_3]$ with Schiff bases (H_2L^1–H_2L^4). The ligands were prepared by the condensation of *N*-4 phenyl/methyl semicarbazide with *o*-vanillin/*o*-hydroxy acetophenone. The complexes were characterized by elemental, physico-chemical, and electrochemical methods. Catalytic studies of these complexes for the oxidation of alcohols and aryl–aryl coupling were carried out. Antimicrobial experiments were also carried out.

Keywords: Ruthenium(III); EPR spectra; Oxidation of alcohols; *N*-methylmorpholine-*N*-oxide; Schiff base

1. Introduction

Controlled oxidation of alcohols is one of the most important reactions in organic chemistry, particularly the conversion of primary alcohols to aldehydes is crucial for the synthesis of fine chemicals such as fragrances or food additives [1]. Numerous oxidizing agents are available to influenace this key reaction; however, these reagents are usually toxic inducing problems [2]. Owing to its central position in the periodic table, ruthenium shows the properties that are common to both early and late transition metals resulting in a confluence of desirable properties. Ru-based oxidation catalysis is being rapidly developed as it affords economic and environmental benefits [3–5]. The utility of the biaryl structural motif has prompted research directed at discovering efficient and high-yield methods for its preparation. Transition metal catalysis has featured prominently in these efforts, leading to a range of useful cross-coupling reactions. Transition-metal catalyzed carbon–carbon bond formation represented a milestone in synthetic organic chemistry allowing the coupling of substrates that would

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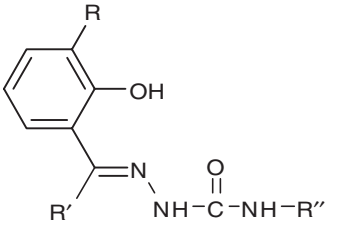
have previously been thought impossible [6, 7]. Semicarbazones have a wide range of biological activities and are versatile ligands. Biological properties of semicarbazones are often related to coordination, constituting an interesting family of ligands for medicinal inorganic research [8]. Ruthenium complexes of such ligands have been well reported in literature [9–11]. In continuation of our work, we report here the synthesis, characterization, catalytic utility, and antimicrobial studies of Ru(III) complexes containing Schiff-base ligands derived from the condensation of *N*-4 phenyl/methyl semicarbazide with *o*-vanillin/*o*-hydroxy acetophenone. The general structure of the Schiff bases are given in scheme 1.

2. Experimental

2.1. *Materials and methods*

All reagents were analytical reagent grade. Solvents were purified and dried according to standard procedures [12]. $RuCl_3{\cdot}3H_2O$ was purchased from Loba Chemie. CHN analyzes were performed in a Vario EL III CHNS analyzer at Cochin University. IR spectra of the complexes were recorded as KBr pellets with a Perkin Elmer 597 infrared spectrophotometer from 4000 to 200 cm^{-1}. Electronic spectra were recorded in dichloromethane with a Systronics double beam UV-Vis Spectrophotometer 2202 with an accuracy of ±0.5 nm. EPR spectra of powdered samples at RT and LNT were recorded with a Bruker model ER-200-D Spectrometer using DPPH as a g-marker at X-band at the Indian Institute of Technology, Chennai. Cyclic voltammetric studies were carried out in acetonitrile using a glassy-carbon working electrode and potentials were referenced to a standard calomel electrode (SCE). $[N(Bu_4)BF_4]$ was used as



Ligand	R	R′	R″
H_2L^1	OCH_3	H	C_6H_5
H_2L^2	OCH_3	H	CH_3
H_2L^3	H	CH_3	C_6H_5
$H2L^4$	H	CH_3	CH_3

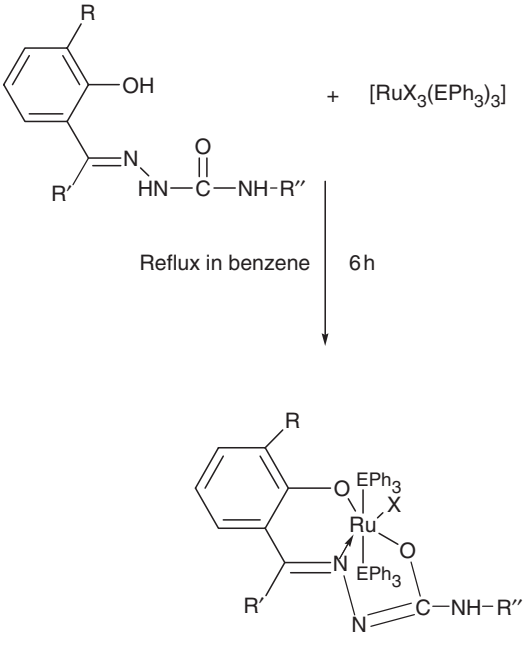
Scheme 1. General structure of the ligands.

supporting electrolyte and the scan rate was 100 mV s^{-1}. Melting points were recorded on a Raaga heating table and are uncorrected. Magnetic susceptibility measurements were made with an EG and G-PARC vibrating sample magnetometer. Molar conductivities of the freshly prepared solutions were measured using an Elico CM 180 conductivity meter. $[RuCl_3(PPh_3)_3]$ [13], $[RuCl_3(AsPh_3)_3]$ [14], $[RuBr_3(AsPh_3)_3]$ [15], and ligands [16] were prepared by the reported methods.

2.2. *Synthesis of [RuCl(PPh$_3$)$_2$L^1]*

The complex $[RuCl(PPh_3)_2L^1]$ was synthesized by refluxing a mixture containing H_2L^1 (0.029 g, 0.1 mmol) and $[RuCl_3(PPh_3)_3]$ (0.099 g, 0.1 mmol) in benzene (25 mL) for 6 h and concentrated to 5 mL. Addition of 10 mL of petroleum ether (60–80 °C) gave the precipitate which was washed with petroleum ether and dried under vacuum. All other complexes which were synthesized using this procedure are given in the following sections (scheme 2).

2.2.1. $[RuCl(PPh_3)_2L^1]$. Yield: 63%. m.p. > 245°C. Elemental Anal. Calcd (%): C, 64.9; H, 4.6; N, 4.4. Found (%): C, 64.2; H, 4.7; N, 4.6. IR (KBr, cm^{-1}): $\nu_{(C=N)}$, 1527; $\nu_{(N=C)}$, 1592; $\nu_{(N-N)}$, 1087; $\nu_{(Ph-C-O)}$, 1297. UV-Vis (dichloromethane) λ, nm (ε; $dm^3\,mol^{-1}\,cm^{-1}$): 587 (767), 486 (2687), 423 (2380).



R = H or OCH_3; R′ = H or CH_3; R″ = C_6H_5 or CH_3; X = Cl or Br; E = P or As

Scheme 2. Preparation of the ruthenium(III) complexes.

2.2.2. [RuCl(PPh$_3$)$_2$L^2]. Yield: 61%. m.p. > 245°C. Elemental Anal. Calcd (%): C, 62.6; H, 4.7; N, 4.8. Found: C, 63.0; H, 4.7; N, 4.7. IR (KBr, cm^{-1}): $\nu_{(C=N)}$, 1537; $\nu_{(N=C)}$, 1595; $\nu_{(N-N)}$, 1083; $\nu_{(Ph-C-O)}$, 1296. UV-Vis (dichloromethane) λ, nm (ε; dm^3 mol^{-1} cm^{-1}): 592 (876), 490 (2885), 433 (3591).

2.2.3. [RuCl(PPh$_3$)$_2$L^3]. Yield: 92%. m.p. > 245°C. Elemental Anal. Calcd (%): C, 66.0; H, 4.7; N, 4.5. Found (%): C, 64.8; H, 4.4; N, 4.5. IR (KBr, cm^{-1}): $\nu_{(C=N)}$, 1539; $\nu_{(N=C)}$, 1652; $\nu_{(N-N)}$, 1081; $\nu_{(Ph-C-O)}$, 1288. UV-Vis (dichloromethane) λ, nm (ε; dm^3 mol^{-1} cm^{-1}): 598 (819), 490 (2854), 434 (2904).

2.2.4. [RuCl(PPh$_3$)$_2$L^4]. Yield: 66%. m.p. > 245°C. Elemental Anal. Calcd (%): C, 63.8; H, 4.8; N, 4.9. Found (%): C, 65.0; H, 4.5; N, 4.5. IR (KBr, cm^{-1}): $\nu_{(C=N)}$, 1537; $\nu_{(N=C)}$, 1587; $\nu_{(N-N)}$, 1083; $\nu_{(Ph-C-O)}$, 1288. UV-Vis (dichloromethane) λ, nm (ε; dm^3 mol^{-1} cm^{-1}): 588 (872), 498 (2698), 428 (2874).

2.2.5. [RuCl(AsPh$_3$)$_2$L^1]. Yield: 71%. m.p. = 216°C. Elemental Anal. Calcd (%): C, 59.3; H, 4.2; N, 4.1. Found (%): C, 59.7; H, 4.3; N, 4.5. IR (KBr, cm^{-1}): $\nu_{(C=N)}$, 1525; $\nu_{(N=C)}$, 1595; $\nu_{(N-N)}$, 1091; $\nu_{(Ph-C-O)}$, 1292. UV-Vis (dichloromethane) λ, nm (ε; dm^3 mol^{-1} cm^{-1}): 610 (842), 513 (2753), 424 (2954).

2.2.6. [RuCl(AsPh$_3$)$_2$L^2]. Yield: 81%. m.p. = 209°C. Elemental Anal. Calcd (%): C, 56.9; H, 4.3; N, 4.3. Found (%): C, 57.8; H, 4.5; N, 4.4. IR (KBr, cm^{-1}): $\nu_{(C=N)}$, 1523; $\nu_{(N=C)}$, 1593; $\nu_{(N-N)}$, 1089; $\nu_{(Ph-C-O)}$, 1294. UV-Vis (dichloromethane) λ, nm (ε; dm^3 mol^{-1} cm^{-1}): 613 (704), 513 (2652), 433 (3852).

2.2.7. [RuCl(AsPh$_3$)$_2$L^3]. Yield: 82%. m.p. > 245°C. Elemental Anal. Calcd (%): C, 60.3; H, 4.3; N, 4.1. Found (%): C, 60.2; H, 4.1; N, 4.4. IR (KBr, cm^{-1}): $\nu_{(C=N)}$, 1541; $\nu_{(N=C)}$, 1610; $\nu_{(N-N)}$, 1091; $\nu_{(Ph-C-O)}$, 1290. UV-Vis (dichloromethane) λ, nm (ε; dm^3 mol^{-1} cm^{-1}): 623 (719), 513 (2787), 434 (4450).

2.2.8. [RuCl(AsPh$_3$)$_2$L^4]. Yield: 72%. m.p. > 245°C. Elemental Anal. Calcd (%): C, 57.9; H, 4.3; N, 4.4. Found (%): C, 56.1; H, 4.1; N, 4.4. IR (KBr, cm^{-1}): $\nu_{(C=N)}$, 1541; $\nu_{(N=C)}$, 1605; $\nu_{(N-N)}$, 1089; $\nu_{(Ph-C-O)}$, 1292. UV-Vis (dichloromethane) λ, nm (ε; dm^3 mol^{-1} cm^{-1}): 623 (798), 524 (2851), 432 (4390).

2.2.9. [RuBr(AsPh$_3$)$_2$L^1]. Yield: 69%. m.p. = 210°C. Elemental Anal. Calcd (%): C, 56.9; H, 4.0; N, 3.9. Found (%): C, 57.9; H, 4.2; N, 4.3. IR (KBr, cm^{-1}): $\nu_{(C=N)}$, 1515; $\nu_{(N=C)}$, 1596; $\nu_{(N-N)}$, 1081; $\nu_{(Ph-C-O)}$, 1290. UV-Vis (dichloromethane) λ, nm (ε; dm^3 mol^{-1} cm^{-1}): 618 (876), 519 (2856), 441 (4298).

2.2.10. [RuBr(AsPh$_3$)$_2$L^2]. Yield: 75%. m.p. = 185°C. Elemental Anal. Calcd (%): C, 54.5; H, 4.1; N, 4.1. Found (%): C, 53.9; H, 4.0; N, 4.5. IR (KBr, cm^{-1}): $\nu_{(C=N)}$, 1515; $\nu_{(N=C)}$, 1600; $\nu_{(N-N)}$, 1081; $\nu_{(Ph-C-O)}$, 1294. UV-Vis (dichloromethane) λ, nm (ε; dm^3 mol^{-1} cm^{-1}): 639 (412), 529 (2397), 444 (6412).

2.2.11. [RuBr(AsPh$_3$)$_2$L^3]. Yield: 84%. m.p. = 200°C. Elemental Anal. Calcd (%): C, 57.7; H, 4.1; N, 4.0. Found (%): C, 57.6; H, 4.0; N, 4.0. IR (KBr, cm^{-1}): $\nu_{(C=N)}$, 1539; $\nu_{(N=C)}$, 1612; $\nu_{(N-N)}$, 1081; $\nu_{(Ph-C-O)}$, 1290. UV-Vis (dichloromethane) λ, nm (ε; dm^3 mol^{-1} cm^{-1}): 626 (387), 525 (2965), 418 (3564).

2.2.12. [RuBr(AsPh$_3$)$_2$L^4]. Yield: 71%. m.p. = 190°C. Elemental Anal. Calcd (%): C, 55.3; H, 4.1; N, 4.2. Found (%): C, 56.5; H, 4.3; N, 4.3. IR (KBr, cm^{-1}): $\nu_{(C=N)}$, 1541; $\nu_{(N=C)}$, 1608; $\nu_{(N-N)}$, 1083; $\nu_{(Ph-C-O)}$, 1292. UV-Vis (dichloromethane) λ, nm (ε; dm^3 mol^{-1} cm^{-1}): 624 (497), 524 (2123), 439 (3476).

2.3. *Catalytic oxidation experiments*

2.3.1. NMO as oxidant. To a solution of the alcohol (0.07–0.13 mL, 1 mmol) in dichloromethane (20 mL), *N*-methylmorpholine-*N*-oxide (NMO) (0.35 g, 3 mmol), and the ruthenium complex (0.009 g, 0.01 mmol) were added and the solution was heated under reflux for 3 h. The mixture was then filtered and the filtrate was dried over anhydrous Na_2SO_4, evaporated to dryness, and extracted with diethyl ether. The diethyl ether extract was filtered and evaporated to give the corresponding carbonyl compound which was quantified as its 2,4-dinitrophenylhydrazone [12, 17].

2.3.2. Molecular oxygen as oxidant. To a solution of alcohol (0.07–0.13 mL, 1 mmol) in dichloromethane (20 mL) a solution of the ruthenium complex in dichloromethane (0.009 g, 0.01 mmol) was added, 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 (60–80°C). The combined extracts were filtered and evaporated to give the corresponding carbonyl compound, which was then quantified as its 2,4-dinitrophenylhydrazone [12, 18].

2.4. *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, hydrolyzed with a saturated solution of aqueous NH_4Cl and the ether extract on evaporation gave a crude product which was chromatographed to get pure biphenyl and compared with an authentic sample [19] (m.p.: 69–72°C).

2.5. *Antibacterial activity*

The ligands and their complexes were tested for *in vitro* growth inhibitory activity against *Escherichia coli* and *Bacillus subtilis* using the disc diffusion method.

The bacteria were cultured in nutrient agar medium and used as inoculum for the study. Bacterial cells were swabbed onto nutrient agar medium in Petri plates. Two different concentrations of the ligands and the complexes (0.5 and 1.0 g of the substances in 100 mL of the solvent) were prepared in DMSO and soaked in filter paper discs (5 mm diameter, 1 mm thick). These discs were placed on the already seeded plates and incubated at $35 \pm 2^{\circ}C$ for 24 h. The diameter (mm) of the inhibition zone around each disc was measured after 24 h. A common standard antibiotic, Ampicillin, was used as a standard in the same solvent and at the same concentration [20]. A control test with the solvent was also carried out under identical conditions.

3. Results and discussion

All complexes are quite stable in air and light. Analytical data for the complexes are in good agreement with proposed formulas. The complexes are soluble in common organic solvents, such as DMSO, dichloromethane, and chloroform. The molar conductivities for complexes in DMSO (1.0×10^{-3} mol) are in the range of 10.5–13.4 $ohm^{-1}\,cm^2\,mol^{-1}$. It is clear from conductivity measurements that the complexes are non-electrolytes [21].

3.1. *IR spectra*

Considerable shift in the band positions of $\nu_{(C=N)}$, $\nu_{(N-N)}$, and phenolic $\nu_{(C-O)}$ of the complexes from the IR spectra of the ligands and the absence of phenolic $\nu_{(O-H)}$ in all the complexes indicate azomethine nitrogen and deprotonated phenolic oxygen coordination to ruthenium. Absence of amide $\nu_{(C=O)}$ and $\nu_{(N-H)}$ vibrations and also the absence of the enolic $\nu_{(O-H)}$ vibrations in the spectra of the complexes confirm enolate oxygen coordination after deprotonation. Coordination modes of the ligands were further confirmed by the presence of the characteristic peaks due to Ru–O, Ru–N, Ru–PPh_3, and Ru–$AsPh_3$ [21–24]. In all complexes, the Schiff bases coordinate to ruthenium as dibasic tridentate (ONO) donors that are in line with the recently reported work involving a similar type of ligand [25].

3.2. *Electronic spectra*

Electronic spectra of the complexes show five types of bands assigned on the basis of the wavelength of absorption and molar absorption coefficient. Bands in the UV region were assigned to intraligand, $\pi \rightarrow \pi^*$, and $n \rightarrow \pi^*$ transitions [26, 27]; less intense shoulders observed in the visible region were assigned to d–d transitions. Ligand field parameters confirm octahedral geometry around ruthenium [28].

3.3. *Magnetic moment and EPR spectra*

Effective magnetic moments of the ruthenium(III) complexes are from 1.78 to 1.96 BM, indicating one unpaired electron and confirming that ruthenium is +3 [23]. The room

temperature and liquid nitrogen temperature EPR spectra of powder samples (Supplementary material) show two signals with $g_{\perp} = 2.41$–2.69 and $g_{||} = 2.05$–2.22, indicating axial distortion. Axial distortion splits the t_2 level into a and e and the energy levels are in the order $d_{xy} > d_{xz}, d_{yz}$ with the unpaired electron in d_{xy}. The *trans* binding of the two PPh_3 ligands is primarily responsible for the axial distortion [29, 30]. The EPR spectra of ruthenium(III) complexes showed no indication of hyperfine interaction of Ru with N, As, P, Cl, and Br. Further, there exist no significant variation in the EPR spectra of the complexes recorded at room temperature and liquid nitrogen temperature, indicating octahedral geometry around ruthenium.

3.4. *Electrochemical properties*

All the complexes showed only a reversible oxidation wave in the anodic side of SCE. A representative cyclic voltammogram and the data are provided in the "Supplemental material". Redox potentials were observed from 1.13 to 1.23 V with peak to peak separations within the range of 50–120 mV. The observed oxidation is assigned from ruthenium(III) to ruthenium(IV). The peak-to-peak separation value ($\Delta Ep = 50$–90 mV) for all the complexes except $[RuCl(PPh_3)_2L^3]$ and $[RuCl(AsPh_3)_2L^3]$ indicates that the oxidation in these complexes are reversible and the corresponding values for the above-mentioned complexes are 100 and 120 mV, respectively, indicating quasi-reversible oxidation. The stability of the +3 oxidation state and the accessibility of +4 state are mainly attributed to phenolate-O coordination. For electron-withdrawing substituents, oxidation of the metal occurs at higher potentials and for electron-releasing substituents, it occurs at lower potentials [31, 32].

3.5. *Catalytic oxidation of alcohols*

Oxidation of primary/secondary alcohols was carried out using the ruthenium complexes as catalysts and NMO/molecular oxygen as the oxidant. Alcohols were converted into their corresponding aldehydes/ketones (table 1). Among phosphine complexes, the order of catalytic activity in terms of yield and turnover number was $[RuCl(PPh_3)_2L^3] > [RuCl(PPh_3)_2L^4] > [RuCl(PPh_3)_2L^1]$. In terms of substituents present in the Schiff-base moiety, the order of activity is $CH_3, C_6H_5 > CH_3, CH_3 > OCH_3, C_6H_5$. Hence, it is inferred that inductive ($-CH_3$ and $-OCH_3$) and mesomeric effects ($-C_6H_5$) of the substituents play a major role in catalytic activity of their corresponding complexes. Electron releasing substituents, $-CH_3$ and $-C_6H_5$ in H_2L^3 make the complex more active. In the complex with two $-CH_3$ groups, the one which is directly attached to the azomethine nitrogen contributes more to the electronic effect and hence to the catalytic activity. Contribution from the other $-CH_3$ group is less, owing to the short distance of the inductive effect. With one $-OCH_3$ and one $-C_6H_5$ as substituents, the resultant contribution from the +M effect of the $-C_6H_5$ group and the – I effect of the $-OCH_3$ group makes this complex less active than the other two complexes. When the activities of $[RuCl(PPh_3)_2L^1]$ and $[RuCl(AsPh_3)_2L^1]$ are compared, triphenylarsine complex was more active, perhaps due to the high donor ability of the arsine. Hence, electron-releasing groups increase the catalytic activity and electron-withdrawing groups decrease the catalytic activity [33]. Oxidation of primary aliphatic alcohols was moderate in conversion. When the results are compared with recently reported work,

Table 1. Oxidation of alcohols by Ru(III) complexes.

Complex	Substrate	Product	NMO oxidant		Molecular oxygen oxidant	
			Yield (%)[a]	TON[b]	Yield (%)[a]	TON[b]
$[RuCl(PPh_3)_2L^1]$	Benzyl alcohol	Benzaldehyde	79	80	41	42
	Cyclohexanol	Cyclohexanone	81	83	42	43
	Cinnamyl alcohol	Cinnamaldehyde	75	76	39	40
	n-Butanol	Butyraldehyde	58	60	30	31
	Isobutyl alcohol	Ethyl methyl ketone	68	69	35	36
	n-Propanol	Propionaldehyde	69	71	35	37
$[RuCl(AsPh_3)_2L^1]$	Benzyl alcohol	Benzaldehyde	81	82	43	44
	Cyclohexanol	Cyclohexanone	84	85	45	46
	Cinnamyl alcohol	Cinnamaldehyde	79	80	43	44
	n-Butanol	Butyraldehyde	59	61	35	36
	Isobutyl alcohol	Ethyl methyl ketone	69	71	36	37
	n-Propanol	Propionaldehyde	71	73	36	37
$[RuCl(PPh_3)_2L^3]$	Benzyl alcohol	Benzaldehyde	83	84	44	45
	Cyclohexanol	Cyclohexanone	85	87	44	45
	Cinnamyl alcohol	Cinnamaldehyde	79	80	41	41
	n-Butanol	Butyraldehyde	62	63	35	36
	Isobutyl alcohol	Ethyl methyl ketone	70	72	38	39
	n-Propanol	Propionaldehyde	73	76	39	40
$[RuCl(PPh_3)_2L^4]$	Benzyl alcohol	Benzaldehyde	80	81	41	42
	Cyclohexanol	Cyclohexanone	82	84	44	44
	Cinnamyl alcohol	Cinnamaldehyde	77	78	41	42
	n-Butanol	Butyraldehyde	58	60	32	33
	Isobutyl alcohol	Ethyl methyl ketone	68	70	31	32
	n-Propanol	Propionaldehyde	70	72	37	38

TON = Turn over number.
[a]Yield based on substrate.
[b]Moles of product per mole of catalyst.

involving a series of ruthenium(II) complexes containing similar donors, ruthenium(III) complexes are better catalysts than ruthenium(II) complexes [34].

We tested the catalytic efficiency of our complexes with molecular oxygen as oxidant, but the yields and turnover numbers were moderate when compared with NMO and other currently employed oxidants. The new complexes react more efficiently with NMO than with molecular oxygen. This is indicated by the low-product yield when molecular oxygen is employed as the oxidant as previously observed [35, 36]. It has been established that the oxidation of alcohols by the ruthenium(III)/molecular oxygen system is quite slow, requiring high pressure and temperature [32].

Though many catalytic systems have been reported for the oxidation of alcohols, most of them suffer from limitations. Chromium-based oxidations are effective but have serious drawbacks generating stoichiometric amounts of heavy-metal waste, and Cr(VI) is a proven carcinogen [37]. Despite being an effective oxidant, practical applications of iodosylbenzene as oxidant are hampered by its low solubility in non-reactive media, as well as low thermal stability and explosive properties upon moderate heating [38]. As reported earlier, TEMPO-bleach oxidation did not work well with unsaturated alcohols [39]. Ionic liquids, which are excellent clean solvents, suffer from reduced activity due to residual chloride [40] and not effective for the oxidation of aliphatic alcohols [36]. TPAP, the most widely used ruthenium catalyst, requires low-temperature storage to retain its activity [41]. Other catalytic systems

Table 2. Aryl–aryl coupling of Ru(III) complexes.

Complex	Biphenyl yield (g)	Biphenyl yield (%)
$[RuCl(PPh_3)_2L^1]$	0.42	28.51
$[RuCl(PPh_3)_2L^2]$	0.32	21.72
$[RuCl(PPh_3)_2L^3]$	0.42	28.51
$[RuCl(PPh_3)_2L^4]$	0.50	33.94
$[RuCl(AsPh_3)_2L^1]$	0.49	33.26
$[RuCl(AsPh_3)_2L^2]$	0.50	33.94
$[RuCl(AsPh_3)_2L^3]$	0.40	27.15
$[RuCl(AsPh_3)_2L^4]$	0.41	27.83
$[RuBr(AsPh_3)_2L^1]$	0.39	26.47
$[RuBr(AsPh_3)_2L^2]$	0.44	29.86
$[RuBr(AsPh_3)_2L^3]$	0.38	25.79
$[RuBr(AsPh_3)_2L^4]$	0.41	27.83

(*N*-halo reagents) either require a longer reaction time or special conditions such as very low temperatures or highly volatile solvent [42]. The complexes reported in this article possess comparable catalytic activity with the currently employed catalytic systems such as supported gold nanoparticles in aqueous H_2O_2 [43], $Pd(OAc)_2$ oxygen/toluene [44], and electrochemical oxidation [45] in terms of yield and selectivity. Dichloromethane used in this study was reported to be a better solvent than the other common organic solvents in terms of yield and it requires less reaction time [39].

3.6. *Aryl–aryl coupling*

The ruthenium complexes were used as catalysts for the coupling of phenyl magnesium bromide with bromobenzene to give biphenyl as the product. The yield of biphenyl is moderate (table 2). This may be due to the fact that the active species (d^7 configuration) derived from ruthenium complexes are less stable [46].

3.7. *Biocidal studies*

Inhibition activity of the test compounds was assessed from the zones of inhibition. Error in the measurement is given in parentheses (table 3). Antimicrobial activities show that the ruthenium chelates are more toxic than their parent ligands against the same micro-organisms under identical experimental conditions. The four Schiff-base ligands had the same activity against the organisms and the magnitude of their influence in their corresponding complexes was also same. The inhibition activity was found to be slightly augmented by bromide than the more electronegative chloride. The inhibition activity was increased with the concentration. Though the complexes possess inhibition activity, it did not reach the effectiveness of Ampicillin.

4. Conclusion

A series of ruthenium(III) complexes $[RuX(EPh_3)_2L]$ were prepared by the reaction of $[RuX_3(EPh_3)_3]$, with Schiff bases prepared by condensation of *N*-4 phenyl/methyl

Table 3. Antibacterial activity of Ru(III) complexes.

	Zone of inhibition (mm)			
	B. subtilis		*E. coli*	
Ligand/complex	0.5%	1.0%	0.5%	1.0%
H_2L^1	7 (±0.02)	10 (±0.05)	10 (±0.02)	12 (±0.04)
$[RuCl(PPh_3)_2L^1]$	11 (±0.06)	15 (±0.03)	13 (±0.05)	16 (±0.05)
$[RuCl(AsPh_3)_2L^1]$	10 (±0.04)	13 (±0.05)	12 (±0.00)	15 (±0.03)
$[RuBr(AsPh_3)_2L^1]$	14 (±0.03)	18 (±0.03)	15 (±0.03)	18 (±0.05)
H_2L^2	7 (±0.03)	11 (±0.05)	9 (±0.05)	12 (±0.05)
$[RuCl(PPh_3)_2L^2]$	10 (±0.02)	14 (±0.02)	11 (±0.05)	14 (±0.05)
$[RuCl(AsPh_3)_2L^2]$	12 (±0.00)	17 (±0.05)	13 (±0.03)	17 (±0.03)
$[RuBr(AsPh_3)_2L^2]$	15 (±0.05)	18 (±0.05)	16 (±0.05)	20 (±0.05)
H_2L^3	6 (±0.05)	9 (±0.05)	7 (±0.05)	11 (±0.05)
$[RuCl(PPh_3)_2L^3]$	9 (±0.03)	13 (±0.05)	10 (±0.04)	13 (±0.05)
$[RuCl(AsPh_3)_2L^3]$	9 (±0.03)	14 (±0.05)	11 (±0.05)	15 (±0.05)
$[RuBr(AsPh_3)_2L^3]$	12 (±0.04)	16 (±0.00)	13 (±0.00)	16 (±0.05)
H_2L^4	7 (±0.05)	9 (±0.05)	8 (±0.05)	12 (±0.05)
$[RuCl(PPh_3)_2L^4]$	10 (±0.05)	14 (±0.02)	11 (±0.04)	15 (±0.05)
$[RuCl(AsPh_3)_2L^4]$	12 (±0.02)	17 (±0.03)	12 (±0.04)	15 (±0.05)
$[RuBr(AsPh_3)_2L^4]$	14 (±0.05)	19 (±0.05)	15 (±0.05)	19 (±0.05)
Ampicillin	20 (±0.04)	24 (±0.00)	22 (±0.05)	26 (±0.00)

0.5% and 1.0% indicate 0.5 and 1.0 g of the substance in 100 mL of DMSO, respectively.

semicarbazide with *o*-vanillin/*o*-hydroxy acetophenone. The complexes were characterized by analytical, spectral, magnetic moment, and electrochemical data. The complexes are catalysts for the oxidation of primary/secondary alcohols, better catalytic activity in the presence of NMO than molecular oxygen as oxidant and moderate activity in the case of aryl–aryl coupling. All the complexes possess better antibacterial activity against *B. subtilis* and *E. coli* than their parent ligands.

We have introduced a new mild reagent for the oxidation of different types of alcohols in refluxing dichloromethane. The stability, easy preparation, mild reaction conditions, high-yields of products, and reaction under non-aqueous conditions make this reagent useful for the oxidation of alcohols. The scope of our catalyst is illustrated by the highly selective oxidation of non-activated aliphatic alcohols as well as activated benzyl alcohol and also secondary alcohols in excellent yields.

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