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Synthesis, spectral, electrochemical and catalytic properties of Ru(III) Schiff base complexes containing N, O donors

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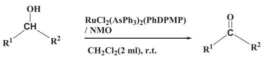
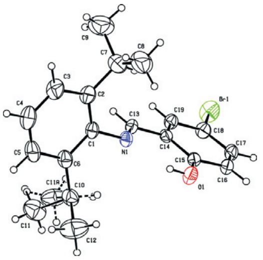
HIGHLIGHTS

- Synthesis, characterization of a new Schiff base and its Ru(III) complexes.
- Ru(III) complexes are paramagnetic with one unpaired electron and octahedral.
- Complexes are redox active based on metal centre.
- New complexes are effective catalyst for the oxidation of alcohols.

GRAPHICAL ABSTRACT





Crystal structure of Br-DPMP

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ABSTRACT

A series of new hexa coordinated ruthenium(III) complexes of the type $[RuY_2(EPh_3)_2(X\text{-}DPMP)]$ (where Y = Br or Cl; E = P or As; DPMP = 2-[(2,6-Diisopropyl-phenylimino)-methyl]-phenol, X = H, Br, Cl, I and Ph) have been synthesized by equimolar $[RuY_3(EPh_3)_3]$ and the Schiff base ligands in benzene. The bidentate Schiff base ligands (X-DPMP) have been derived from condensation of 2,6-diisopropylaniline with mono and multisubstituted salicylaldehyde derivatives. The complexes have been characterized by elemental analysis, magnetic susceptibility, UV–Vis., IR and EPR spectral and electrochemical measurements. All the ruthenium(III) complexes are found to be stable, paramagnetic, low spin, redox active and display either quasi reversible or irreversible redox couples based on metal centre. They have exhibited catalytic activity for the oxidation of wide range of primary and secondary alcohols to corresponding aldehydes or ketones with moderate to high conversion in the presence of *N*-methylmorpholine-*N*-oxide (NMO) as co-oxidant.

1. Introduction

The interest in the synthesis and characterization of transition metal complexes containing a Schiff base with nitrogen and oxygen donor atoms lies in their extensive applications in the fields of catalysis [1,2] and transformations [3,4], which can modify the structural and electronic properties of transition metal centers [5]. Transition metal complexes are powerful catalyst for organic

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transformations both in homogeneous and heterogeneous reactions and the activity of these complexes varied with the type of ligand, coordination site and the metal center [6]. Based on it, they can offer chemo, regio or stereo selectivity with the enhancement of product yield under mild conditions [7]. Transition metal based catalytic conversion of primary and secondary alcohols into their corresponding aldehydes and ketones are essential reaction in organic synthesis [8–10]. Traditional methods for performing such transformation generally involve the use of stoichiometric quantities of inorganic oxidants like Cr (IV) and generate large quantities of waste [11]. The development of effective, greener catalytic system that uses clean and inexpensive oxidants such as NMO, molecular oxygen or hydrogen peroxide for converting alcohols to carbonyl compounds on an industrial scale remains an important challenge [12]. Ruthenium complexes containing triphenylphosphine or triphenylarsine ligands have been extensively investigated and well established [13] as catalyst for alcohol oxidation in combination with various oxidants such as dioxygen [14,15], iodosobenzene [16], *t*-BuOOH [17], H_2O_2 [18], $NaIO_4$ [4] and NMO [19,20].

In contrast to the considerable growth of literature on the chemistry of Schiff base complexes of first row transition metal, the chemistry of ruthenium complexes with multi substituted ligands systems is less well developed. With this in view and continuing interest of our study [21–23], the present report accounts for the synthesis, characterization of new multi substituted Schiff bases and their ruthenium(III) complexes with a special impetus on their spectral and electrochemical investigations. The general structure of Schiff base ligands used in the present work and newly synthesized ruthenium(III) complexes are given in Fig. 1.

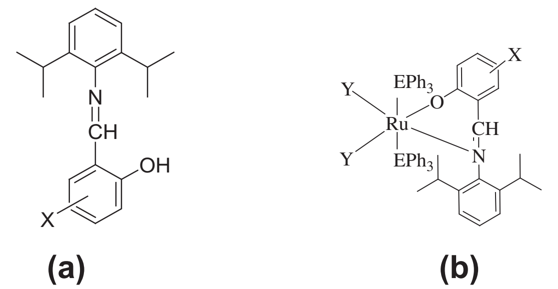
2. Experimental

2.1. Materials

All the reagents used were chemically pure and AR grade. Solvents were purified and dried according to standard procedure. $RuCl_3{\cdot}3H_2O$ was purchased from Loba Chemical Pvt. Ltd., Bombay, India and was used without further purification. $RuCl_3(PPh_3)_3$ [24] $RuCl_3(AsPh_3)_3$ [25] $RuBr_3(AsPh_3)_3$ [26] and the Schiff bases were prepared according to literature procedures. The supporting electrolyte, tertiary-butyl ammonium perchlorate (TBAP) was dried in vacuum before use.

2.2. Physical measurements

The magnetic susceptibilities of the complexes in the solid state were measured on a Gouy balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant. The IR spectra of the ligands and complexes in KBr (4000–400 cm^{-1}) were recorded on a Perkin Elmer 577 grating spectrophotometer. The electronic spectra in MeCN were obtained on a Shimadzu-160 UV–Vis. Spectrophotometer. Microanalyses for the carbon, hydrogen and nitrogen content of the new complexes were carried out by the CDRI, Lucknow, India. The metal contents of the complexes were estimated by incinerating them to their oxides in the presence of ammonium oxalate. ^1H NMR spectra were recorded in $CDCl_3$ with TMS as an internal standard on a Brucker 300 MHz spectrometer. X-band EPR spectra were recorded on a Varian-E-12 spectrometer with a quartz Dewar for measurements at the liquid N_2 temperature and the spectra were calibrated with DPPH. Cyclic voltammetric measurements were made in MeCN (HPLC grade) using BAS-CV50 electrochemical analyzer. The three electrode cell comprised a reference Ag/AgCl, auxillary Pt and the working glassy carbon electrodes. Bu_4NClO_4 was used as supporting electrolyte. The single crystal XRD data collection have been obtained using APEX2 (Bruker, 2004), IIT Madras, Chennai, India.



E = P or As; Y = Br or Cl; X = H, Br, Cl, I, Ph for Ruthenium (III) complexes

Fig. 1. The chemical structure of (a) substituted Schiff base ligand [X-DPMP] (b) Ru(III) – Schiff base complexes.

2.3. Synthesis of ligands

The monobasic bidentate Schiff base ligands were prepared by condensation of 2,6-diisopropylaniline [2 mmol] with salicylaldehyde and substituted salicyaldehydes [2 mmol] in 1:1 M ratio in ethanol. The reaction mixture was then refluxed for 3 h. Upon cooling to 0 °C, the product separated out as yellow solid precipitated which was filtered, washed with ice cold ethanol and dried in vacuum over anhydrous $CaCl_2$. Yellow crystals suitable for X-ray diffraction were obtained directly from the reaction mixture, by slow evaporation of the solvent at room temperature.

2.3.1. 2-[(2,6-diisopropylphenylimino)methyl] phenol [DPMP]

Overall yield 70%. Anal. Calc. $C_{19}H_{23}ON$: C, 81.10, H, 8.24; N, 4.98. Found: C, 81.20%; H, 8.21%; N, 4.88%. δ ppm: 15.23 (s, 1H), 9.07 (s, 1H), 7.96–7.99 (d, 1H), 7.84–7.87 (d, 1H), 7.75–7.77 (d, 1H), 7.46–7.51 (m, 2H), 7.31–7.36 (m, 2H), 7.17–7.24 (m, 2H), 3.05 (m, 2H), 1.21–1.23 (d, 12H). The expanded ^1H NMR spectrum is shown in Fig. 2.

2.3.2. 4-Chloro-2-[(2,6-diisopropyl-phenylimino)-methyl]-phenol [Cl-DPMP]

^1H NMR ($CDCl_3$) 410 MHz: δ ppm 13.12 (s, 1H), 8.27 (s, 1H), 7.12 (d, 1H), 7.22–7.49 (m, 5H), 2.98 (m, 2H), 1.19–1.23 (d, 12H).

^{13}C NMR ($CDCl_3$): δ 165.33 (Azomethine), 159.64 (Ar—C—OH), 145.62 (Ar—C—Azomethine—N), 138.45 Ar—C—Isopropyl), 132.95 (Ar), 131.13 (Ar), 125.67 (Ar—C—Cl), 123.61 (Ar), 123.25 (Ar), 119.29 (Ar—C—Azomethine—C), 118.86 (Ar), 28.22 (Aliphatic CH_3), 23.58 (Aliphatic CH).

2.3.3. 1-[(2,6-diisopropylphenylimino)methyl] naphthalen-2-ol [Ph-DPMP]

Overall yield 75%. Anal. Calc. $C_{23}H_{25}ON$: C, 83.34, H, 7.60; N, 4.23. Found: C, 83.23%; H, 7.64%; N, 4.21%. δ ppm: 13.11 (s, 1H), 8.30 (s, 1H), 7.34–7.44 (m, 2H), 7.18 (s, 3H), 7.05–7.08 (d, 1H), 6.94–6.99 (m, 2H), 1.16–1.19 (d, 12H).

2.3.4. 4-Bromo-2-[(2,6-diisopropyl-phenylimino)-methyl]-phenol [Br-DPMP]

Overall yield 70%. Anal. Calc. $C_{19}H_{22}BrON$: C, 63.35; H, 6.11; N, 3.89. Found: C, 63.25%; H, 6.25%; N, 3.99%. δ ppm: 12.95 (s,1H), 8.28 (s, 1H), 7.03 (d, 1H), 7.23–7.41 (m, 5H), 2.95–3.02 (m, 2H), 1.20–1.23 (d, 12H).

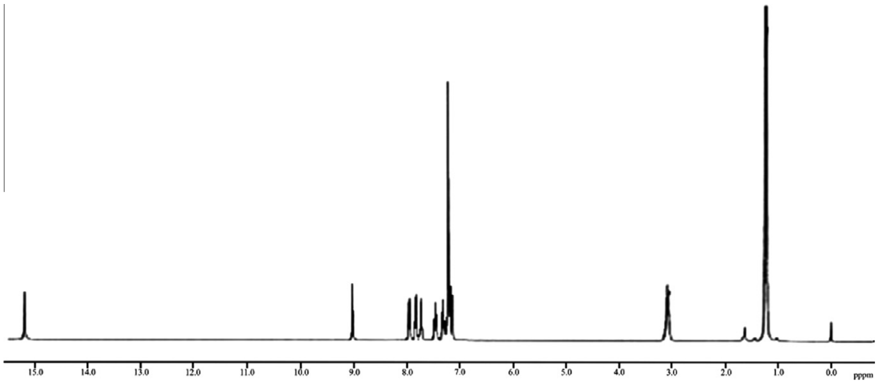


Fig. 2. Expanded ^{1}H NMR spectrum of Schiff base ligand 2-[2,6-diisopropylphenylimino)-methyl]-phenol [DPMP].

2.3.5. 2-[(2,6-Diisopropyl-phenylimino)-methyl]-4-iodo-phenol [I-DPMP]

Overall yield 70%. Anal. Calc. $C_{19}H_{22}ION$: C, 56.03, H, 5.41; N, 3.44. Found: C, 56.23%; H, 5.60%; N, 3.63%. δ ppm: 13.19 (s, 1H), 8.25 (s, 1H), 7.68–7.71 (m, 2H), 7.28 (s, 3H), 6.86–6.91 (d, 1H), 2.90–3.04 (m, 2H), 1.18–1.22 (d, 12H).

2.4. Synthesis of Ru(III) complexes

All the complexes were prepared under anhydrous conditions using the following general procedure. To a solution of $[RuY_3(EPh_3)_3]$ (where Y = Br or Cl; E = P or As) (0.1 mmol) in benzene (20 ml) was purged the nitrogen gas for 15 min. and the appropriate Schiff base ligand (0.1 mmol) in benzene was added. The solution was refluxed for 4–5 h and the resulting solution was concentrated to 3 ml under reduced pressure and cooled. The complex separated out upon the addition of petroleum ether (60–80 °C). The solid was filtered off, washed with petroleum ether and recrystallised from 1:1 benzene–petroleum ether mixture and dried under vacuum.

2.5. Typical procedure for alcohol oxidation

The reaction mixture of Primary or secondary alcohol (1 mmol), $Ru^{III}Cl_2(AsPh_3)_2$ (Ph-DPMP) Schiff base complex (0.1 mmol), NMO (1.1 mmol) and dichloromethane (2 mL) was stirred at room temperature. The filtrate obtained was evaporated under reduced pressure and the residual mass was dissolved in a mixture of ethyl acetate/hexane (1:4) and then passed through a short column of silica gel using hexane/ethyl acetate (4:1) as eluent. Removal of solvent and usual workup gave the corresponding aldehydes and ketones, which were identified by comparing their physical and spectral data with those of authentic compounds reported in literature [27].

3. Results and discussion

The Ruthenium(III) complexes having general formula $[RuY_2(EPh_3)_2(X\text{-}DPMP)]$ (where Y = Br or Cl; E = P or As; DPMP = 2-[(2,6-Diisopropyl-phenylimino)-methyl]-phenol, X = H, Br, Cl, I and Ph) are paramagnetic and the metal to ligand ratio of all the complexes were 1:1 in benzene. All the new Schiff base ruthenium(III) complexes are highly coloured, stable in air, non-hygroscopic in nature and highly soluble in common solvents such as CH_3CN, DMSO and $CHCl_3$ but insoluble in water. The analytical data listed in Table 1, are in good agreement with the calculated values thus confirming the general molecular formula proposed for all the complexes. Mass spectrometry chemical ionization of the representative $RuCl_2(PPh_3)_2$(Cl-DPMP) complex shows m/z at 1012 along with various fragments and isotopic peaks.

3.1. Spectral Characterization

All the Ru(III) complexes are uniformly paramagnetic with magnetic moments in the range of 1.78–2.15 B.M which corresponds to one unpaired electron with non-interacting low-spin d^5 configuration at 298 K in an octahedral environment. These values are consistent with the +3 oxidation state of the metal ions [28].

The electronic spectra of all the Ru(III) – Schiff base complexes in $CHCl_3$ solution showed two or four bands in the region 250–400 nm. The assortment of intense bands exhibited by the complexes in the region 250–360 nm are believed to be ligand centered transitions. In addition, the other bands at 400 and 460 nm have been assigned to charge transfer bands. This is in conformity with the assignments made for other similar Ru (III) octahedral complexes [29].

The IR spectrum of the free Schiff base ligands is shown in Fig. 3 and the spectral bands of the Schiff base ligand and the complexes are listed in Table 2. The IR spectra of the free Schiff bases showed a very strong absorption band around 1624 cm^{-1} characteristic of azomethine ($>C{=}N$) group [30]. Coordination of the Schiff bases to the ruthenium ion through the azomethine nitrogen atom is expected to reduce the electron density in the azomethine frequency. The band due to azomethine nitrogen $\nu_{(C=N)}$ showed a modest decrease in the stretching frequency for the complexes and is shifted to lower frequencies, appearing around 1618–1524 cm^{-1} after complexation [bathochromic shift], indicating the coordination of the azomethine nitrogen [31–33]. The free ligands exhibit a broad band at 3444–3435 cm^{-1}, which may be assigned to the $\nu_{(OH)}$ and this band is absent in the spectra of all the complexes. This fact is further supported by an upward shift in the stretching frequency of phenolic oxygen in the complex $\nu_{(C=O)}$ = 1320–1276 cm^{-1} [32,33], indicating the subsequent deprotonation of the phenolic proton prior to the coordination [34]. This is further substantiated by the absence of a ^{1}H NMR signal for the OH group around δ 11.3 ppm for all the complexes [35]. The binding of the metal to the ligand through azomethine nitrogen and oxygen atom is further supported by the appearance of new band in 623–522 cm^{-1} and 460–400 cm^{-1} ranges due to $\upsilon_{(M-N)}$ and $\upsilon_{(M-O)}$ respectively, in the spectra of all the complexes [36]. In addition, the Schiff base complexes show strong vibrations band near 690, 745 and 1550 cm^{-1}, which are attributed to the triphenylphosphine or arsine fragments [37].

The representative EPR spectra of newly synthesized ruthenium complex in Liquid Nitrogen Temperature is shown in Fig. 4 and the spectral data are listed in Table 3. All the Ru(III) – Schiff base

Table 1
Colour, magnetic moment and absorption maxima of Ruthenium(III) complexes.

Complexes	Colour	Mol. wt.	Found (calculated) (%)				$\mu_{eff.}$ (B.M.)	$\lambda_{max.}$ (cm^{-1})
			C	H	N	M		
1. $RuBr_2(AsPh_3)_2$ (DPMP)	Brown	991.7					1.99	46,511
			52.03	3.53	1.41	10.19		38,461
			52.15	3.65	1.55	10.30		21,739
								18,018
2. $RuBr_2(AsPh_3)_2$ (Br-DPMP)	Green	1070.6					2.01	46,948
			48.19	3.18	1.31	9.44		38,910
			48.29	3.30	1.42	9.55		31,152
								20,325
								17,889
3. $RuBr_2(AsPh_3)_2$ (Cl-DPMP)	Black	1026.15					1.97	46,511
			50.29	3.31	1.36	9.85		36,231
			50.39	3.20	1.48	9.72		20,576
								18,018
4. $RuBr_2(AsPh_3)_2$ (I-DPMP)	Brown	1117.6					2.02	46,728
			46.17	3.04	1.25	9.04		37,313
			46.29	3.24	1.36	9.20		20,242
								18,115
5. $RuBr_2(AsPh_3)_2$ (Ph-DPMP)	Brown	1041.7					2.01	46,082
			54.14	3.55	1.34	9.70		38,461
			54.26	3.65	1.44	9.82		20,325
								17,953
6. $RuCl_2(PPh_3)_2$ (DPMP)	Brown	976.9	63.32	4.29	1.72	12.40	1.87	46,296
			63.52	4.49	1.86	12.53		24,691
7. $RuCl_2(PPh_3)_2$ (Br-DPMP)	Brown	1055					1.90	45,662
			57.67	3.79	1.56	11.29		36,900
			57.77	3.89	1.75	11.39		27,932
								25,188
8. $RuCl_2(PPh_3)_2$ (Cl-DPMP)	Brown	1011.5					1.95	46,511
			60.68	3.99	1.65	11.89		28,248
			60.79	3.79	1.85	11.79		24,630
9. $RuCl_2(PPh_3)_2$ (I-DPMP)	Black	1102					1.99	48,076
			54.79	3.61	1.49	10.73		24,449
			54.69	3.71	1.59	10.86		
10. $RuCl_2(PPh_3)_2$ (Ph-DPMP)	Black	1026.9	65.13	4.27	1.62	11.67	2.00	47,169
			65.26	4.38	1.73	11.79		24,630
11. $RuCl_2(AsPh_3)_2$ (DPMP)	Brown	902.8					2.03	45,045
			57.16	3.77	1.55	11.19		31,545
			57.39	3.86	1.45	11.09		25,000
								21,645
12. $RuCl_2(AsPh_3)_2$ (Br-DPMP)	Black	981.7					1.87	46,082
			52.56	3.46	1.43	10.29		31,545
			52.46	3.36	1.56	10.39		25,062
13. $RuBr_2(PPh_3)_2$ (Cl-DPMP)	Brown	937.25					1.89	46,082
			55.05	3.63	1.49	10.78		32,573
			55.25	3.73	1.59	10.89		25,062
14. $RuBr_2(PPh_3)_2$ (I-DPMP)	Black	1028.7	50.16	3.31	1.36	9.83	1.95	44,444
			50.26	3.52	1.22	9.70		24,813
15. $RuBr_2(PPh_3)_2$ (Ph-DPMP)	Brown	952.8					1.99	46,082
								37,313
			59.19	3.88	1.47	10.61		32,573
			59.09	3.78	1.57	10.83		24,570
								13,888

complexes are paramagnetic, exhibiting a low-spin d^5 system, the $^2T_{2g}$ (octahedral) ground state [38]. All the complexes exhibit three lines with different ‘g’ values, indicating the presence of magnetic anisotropy with axial distortion. The average ‘g’ values lie in the 1.93–2.35 range, which indicate the rhombic distortion [4,31,39,40]. These values are in the range that are obtained for similar Ru(III) complexes [41].

3.2. X-ray crystallography

The representative crystal structure of the ligand Br-DPMP is shown in Fig. 5 and it has the dihedral angle between the benzene rings is 76.17 (14)° and an intramolecular O—H···N hydrogen bond with an S(6) graph-set motif is present. One methyl group is disordered over two sets of sites with site occupancies of 0.66 (3) and 0.34 (3). A weak intermolecular C—H···π interaction is observed in the crystal structure [42].

3.3. Electrochemical studies

The redox properties of all the Ru(III) complexes were investigated in acetonitrile solution by cyclic voltammetry and the redox potentials are expressed with reference to Ag/AgCl. The voltammetric data are presented in Table 4 and a representative cyclic

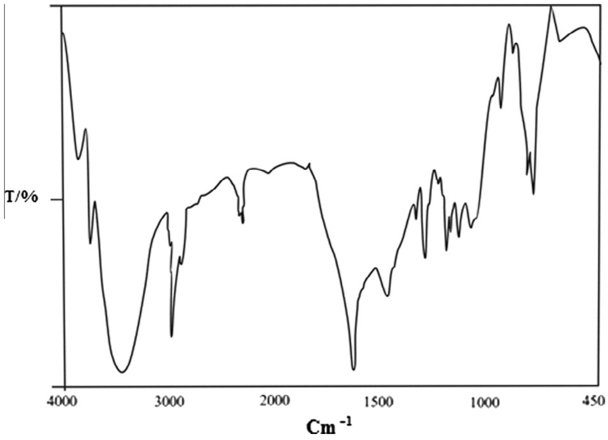


Fig. 3. IR spectrum of the Schiff base ligand DPMP.

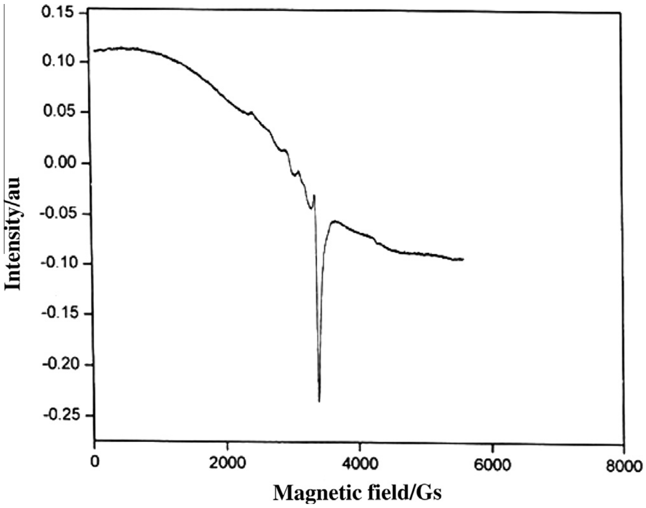


Fig. 4. Representative ESR spectra of $Ru^{III}Cl_2(AsPh_3)_2$(IDPMP) in LNT.

voltammogram Ru(III) complexes are shown in Fig. 6. Cyclic Voltammogram of the $Ru^{III}Y_2(EPh_3)_2$ (X-DPMP) complexes exhibit the half wave potentials in −688 to −1036 mV range. The corresponding separations between the reduction and oxidation peaks are in the 228–1143 mV range for scanning rates of 100 mV s^{-1}. The Ru(III)/Ru(II) reductions in every case suggest the irreversible one electron transfer process with respect to the central metal atom [31,43].

$$Ru^{III}Y_2(EPh_3)_2(Cl\text{-}DPMP) + e^- \leftrightarrow [Ru^{II}Y_2(EPh_3)_2(Cl\text{-}DPMP)]$$

There is no much variation in the redox potentials due to the replacement of triphenylphosphine by triphenylarsine [4,18]. The redox behaviour of Ru(III) complexes at glassy carbon electrode surface follows a diffusion-controlled process which is evident from the plot of $\sqrt{SR}$ vs peak current (Fig. 7). A straight line was obtained for lower scanning rates (25–200 mV s^{-1}).

Table 2
IR spectral data of ligands and their Ruthenium(III) complexes.

S.No.	Ligands and complexes	υ(OH)	υ(CH=N)	υ(C—O)	υ(M—N)/υ(M—O)
Free ligand					
1	DPMP	3444	1625	1271	–
2	Br-DPMP	3444	1624	1272	–
3	Cl-DPMP	3444	1624	1277	–
4	I-DPMP	3435	1623	1272	–
5	Ph-DPMP	3444	1623	1172	–
Ruthenium (III) complex					
1	$RuBr_2(AsPh_3)_2$ (DPMP)	–	1574	1311	567 474
2	$RuBr_2(AsPh_3)_2$ (Br-DPMP)	–	1572	1311	600 475
3	$RuBr_2(AsPh_3)_2$ (Cl-DPMP)	–	1576	1334	565 474
4	$RuBr_2(AsPh_3)_2$ (I-DPMP)	–	1572	1313	544 474
5	$RuBr_2(AsPh_3)_2$ (Ph-DPMP)	–	1583	1309	563 474
6	$RuCl_2(PPh_3)_2$ (DPMP)	–	1524	1323	536 466
7	$RuCl_2(PPh_3)_2$ (Br-DPMP)	–	1568	1373	534 467
8	$RuCl_2(PPh_3)_2$ (Cl-DPMP)	–	1577	1285	532 468
9	$RuCl_2(PPh_3)_2$ (I-DPMP)	–	1618	1335	522 461
10	$RuCl_2(PPh_3)_2$ (Ph-DPMP)	–	1574	1398	521 474
11	$RuCl_2(AsPh_3)_2$ (DPMP)	–	1574	1309	617 474
12	$RuCl_2(AsPh_3)_2$ (Br-DPMP)	–	1572	1315	542 474
13	$RuCl_2(AsPh_3)_2$ (Cl-DPMP)	–	1574	1311	623 474
14	$RuCl_2(AsPh_3)_2$ (I-DPMP)	–	1572	1309	621 473
15	$RuCl_2(AsPh_3)_2$ (Ph-DPMP)	–	1582	1375	565 474

Table 3
ESR spectral data of ruthenium complexes.

S. No.	Ruthenium(III) complexes	g_{11}	g_{12}	g_{13}	$\langle g_{ave} \rangle$
1	$RuBr_2(AsPh_3)_2$ (DPMP)	2.8257	2.1841	1.9613	2.2317
2	$RuBr_2(AsPh_3)_2$ (Br-DPMP)	2.7957	2.2011	2.0102	2.3595
3	$RuBr_2(AsPh_3)_2$ (Cl-DPMP)	2.8023	2.2083	2.0150	2.2442
4	$RuBr_2(AsPh_3)_2$ (I-DPMP)	2.8051	2.1799	1.9120	2.2096
5	$RuBr_2(AsPh_3)_2$ (Ph-DPMP)	2.7725	2.3452	1.9732	2.2636
6	$RuCl_2(AsPh_3)_2$ (I-DPMP)	2.3959	2.2938	2.0629	2.1394
7	$RuCl_2(AsPh_3)_2$ (Ph-DPMP)	2.3508	2.0235	1.6808	1.9342

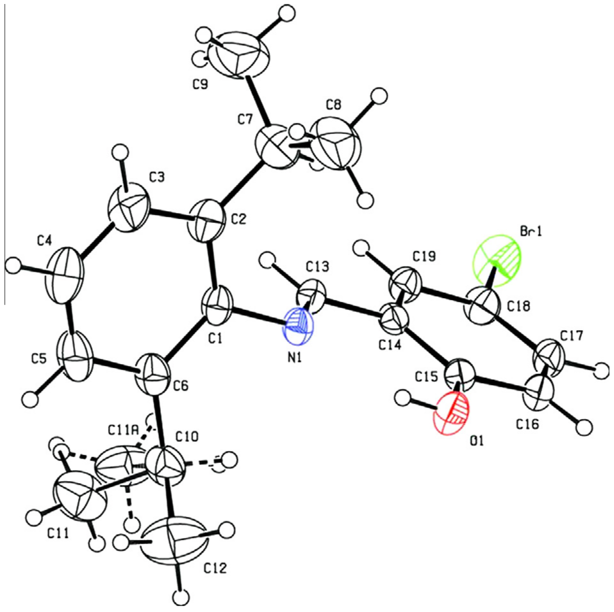


Fig. 5. Representative crystal structure of Br-DPMP.

Table 4
Electrochemical data of Ruthenium(III) complexes.

S. No.	Ruthenium (III) complexes	E_p^a (mV)	E_p^c (mV)	ΔE_p	$E_{1/2}$
1	$RuBr_2(AsPh_3)_2$ (DPMP)	−548	−991	443	−770
2	$RuBr_2(AsPh_3)_2$ (Br-DPMP)	−488	−1191	703	−840
3	$RuBr_2(AsPh_3)_2$ (Cl-DPMP)	−555	−978	423	−767
4	$RuBr_2(AsPh_3)_2$ (I-DPMP)	−566	−1036	470	−801
5	$RuBr_2(AsPh_3)_2$ (Ph-DPMP)	−546	−1033	487	−790
6	$RuCl_2(PPh_3)_2$ (DPMP)	−487	−1268	781	−878
7	$RuCl_2(PPh_3)_2$ (Br-DPMP)	−592	−820	228	−706
8	$RuCl_2(PPh_3)_2$ (Cl-DPMP)	−383	−1336	953	−860
9	$RuCl_2(PPh_3)_2$ (I-DPMP)	−494	−1022	528	−758
10	$RuCl_2(PPh_3)_2$ (Ph-DPMP)	−537	−838	301	−688
11	$RuCl_2(AsPh_3)_2$ (DPMP)	−520	−1552	1032	−1036
12	$RuCl_2(AsPh_3)_2$ (Br-DPMP)	−478	−1386	908	−932
13	$RuCl_2(AsPh_3)_2$ (Cl-DPMP)	−396	−1539	1143	−968
14	$RuCl_2(AsPh_3)_2$ (I-DPMP)	−494	−1029	535	−762
15	$RuCl_2(AsPh_3)_2$ (Ph-DPMP)	−500	−1343	843	−922

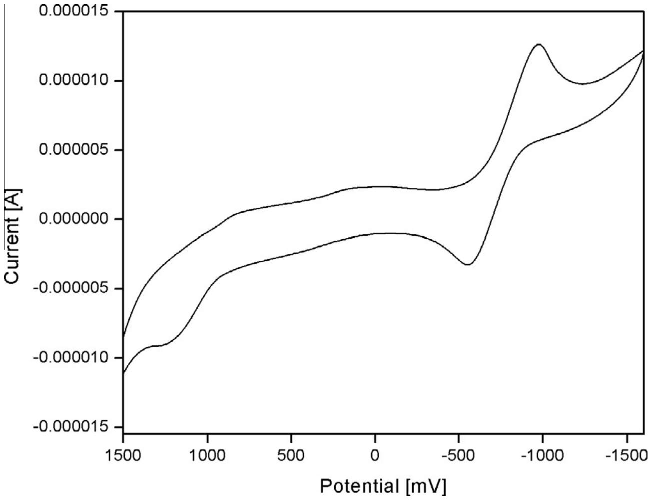


Fig. 6. Cyclic voltamogram of $RuBr_2$ $(AsPh_3)_2$ (Np-DPMP)complexes.

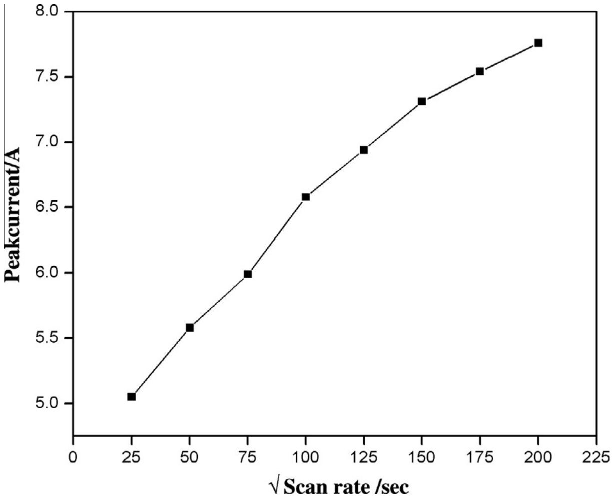


Fig. 7. √Scan rate vs Peak current for $RuCl_2$ $(AsPh_3)_2$ (Cl-DPMP) complex.

Table 5
Oxidation of benzyl alcohol (1 mmol) under various conditions by using $RuCl_2(AsPh_3)_2$(Ph-DPMP)/NMO system in CH_2Cl_2.

Entry	Catalyst (mol%)	Oxidant	Solvent	Time (min)	Yield (%)[a]
1	5	NMO	CH_2Cl_2	75	80
2	10	NMO	CH_2Cl_2	45	87
3	10	NMO	CH_3CN	120	70
4	10	$NaIO_4$	CH_2Cl_2	90	78
5	–	NMO	CH_2Cl_2	120	Trace

[a] Isolated yield.

Table 6
Oxidation of *sec*-phenylethanol under various conditions by using $RuCl_2(AsPh_3)_2$(Ph-DPMP)/NMO system in CH_2Cl_2.

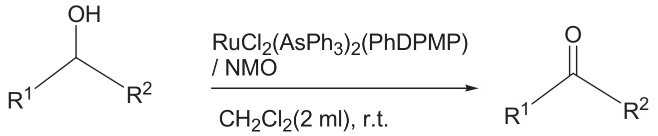
Entry	Catalyst (mol%)	Oxidant	Solvent	Time (min)	Yield (%)[a]
1	5	NMO	CH_2Cl_2	120	65
2	10	NMO	CH_2Cl_2	70	82
3	10	NMO	CH_3CN	150	60
4	10	PPNO	CH_2Cl_2	110	70
5	–	NMO	CH_2Cl_2	180	Trace

[a] Isolated yield.

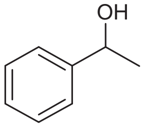
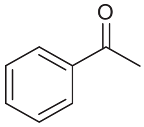
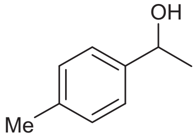
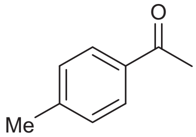
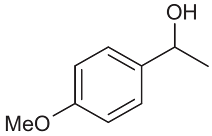
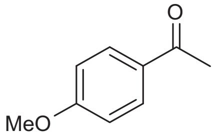
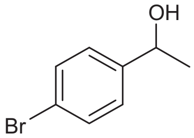
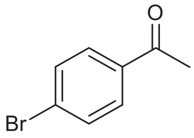
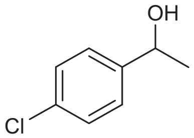
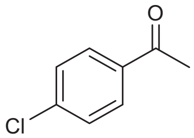
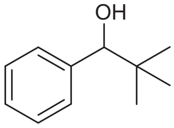
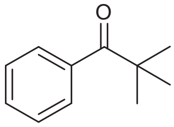
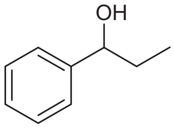
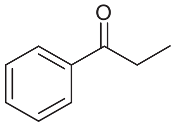
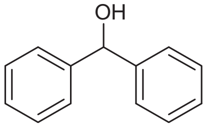
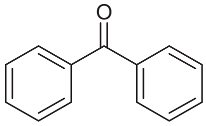
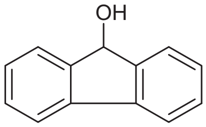
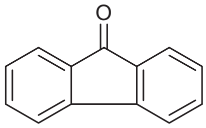
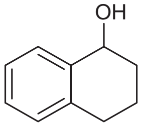
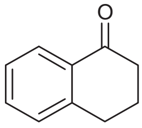
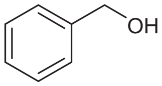
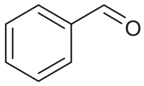
3.4. Oxidation of alcohols by Ru(III) Schiff base complex

$RuCl_2(AsPh_3)_2$(Ph-DPMP) was tested with or without additive for the oxidative process of primary and secondary alcohols. Results of Tables 5 and 6 indicate that the yield of isolated product increases with the increase of catalytic load (entry 1 and 2). Further, the nature of the terminal oxidant plays an important role in the oxidation process (entry 2 and 4). The solvent system also affects the reaction time and yields (entry 2 and 3). The observed results show that NMO is the best oxidant when compare with

Table 7
Oxidation of 1° and 2° alcohol to corresponding carbonyl compounds

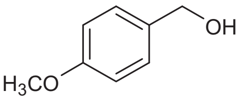
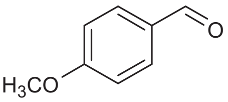
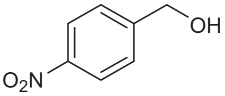
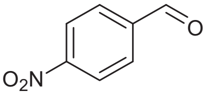
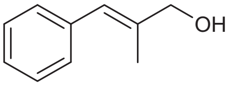
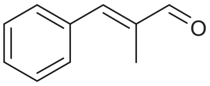
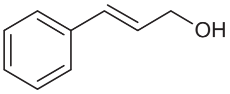
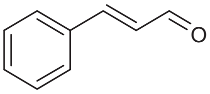


.

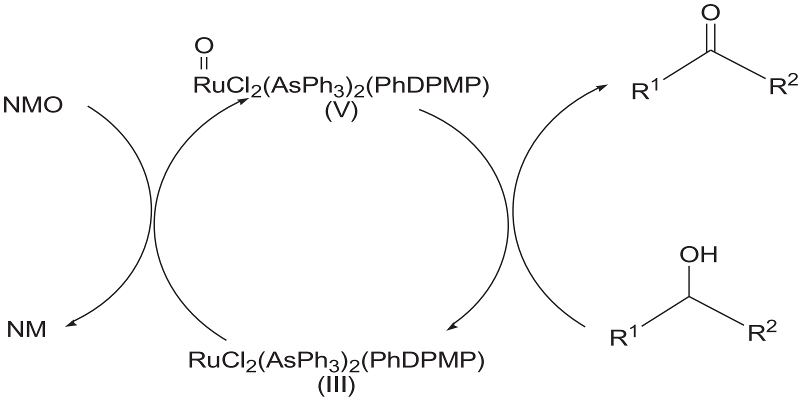
Entry	Substrate	Product	Time (min.)	Yield (%)[a]
1			70	82
2			70	75
3			65	80
4			75	78
5			75	75
6			75	70
7			85	65
8			80	75
9			85	68
10			85	73
11			45	87

(*continued on next page*)

Table 7 (*continued*)

Entry	Substrate	Product	Time (min.)	Yield (%)[a]
12			45	85
13			60	80
14			60	75
15			55	75

[a] Isolated yield.



Scheme 1. Proposed scheme for the oxidation of 1° and 2° alcohol to corresponding carbonylcompounds.

$NaIO_4$. Control experiments were carried out without ruthenium catalyst under the same reaction conditions and there is no detectable oxidation of alcohols (entry 5). An efficient oxidative condition is described with entry 2.

Investigations of oxidation of various phenols under optimized condition are given in Table 7. Unsubstituted and substituted *sec*-phenylethanols (entries 1–6) were efficiently oxidized to corresponding ketones with excellent yield. The change of methyl group of 1-phenylethanol into larger groups prolongs the reaction time (entries 7–10).

Simple benzyl alcohols are smoothly converted into their corresponding aldehydes (entry 11, 12 and 13). Allylic alcohols could be vulnerable to oxidation through the formation of carbonyl compound or epoxide. In the present system allylic alcohols (entry 10 and 11) undergo oxidation to give carbonyl compounds in good yield for relatively shorter reaction period. The formed product has been confirmed through NMR spectral study.

In comparison, the results of the present investigation suggest that the ruthenium(III) Schiff base complexes are able to react efficiently with NMO to yield a high valent ruthenium species [19,44]. Further, the catalytic oxidation could occur through hydrogen extraction. The yield of carbonyl compounds obtained is significantly higher than those obtained from similar reported Ru(III)-PPh_3/NMO catalytic system [44]. On the basis of previous oxidation studies [6,19,44], the following mechanism has been proposed as indicated in Scheme 1.

4. Conclusions

Ruthenium (III) complexes of multisubstituted Schiff base ligands have been prepared and characterized. The magnetic and spectral evidences show that the complexes are formed through the coordination of phenolic oxygen and the azomethine nitrogen atoms. Newly synthesized complexes are found to be octahedral. The complexes are redox active and display either quasi reversible or irreversible redox couples based on metal centre. In comparison, the ruthenium(III) complexes were found to be effective catalyst for the oxidation of alcohols under mild conditions. Further, the yield of carbonyl compounds obtained is significantly higher than those obtained from similar reported catalytic system.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2013.12.048.

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