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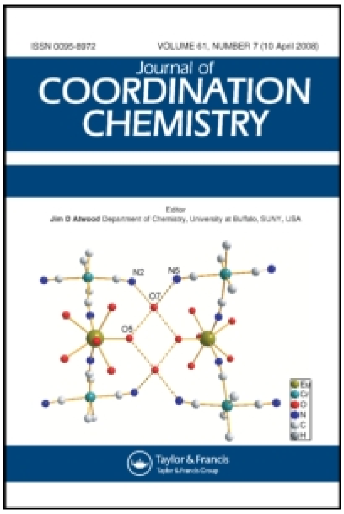

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Ruthenium(III) chalconate complexes containing $PPh_3/AsPh_3$ and their use as catalysts

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Ruthenium(III) complexes of the type $[RuX(EPh_3)(L)_2]$ (X = Cl or Br; E = P or As; L = 2-hydroxychalcone) have been prepared by reacting $[RuX_3(EPh_3)_3]$ with 2-hydroxychalcones in benzene under reflux. The new complexes have been characterized by analytical and spectroscopic (infrared, electronic, electron paramagnetic resonance, and mass) methods. Redox potential studies of the complexes have been carried out to elucidate the electronic structure, geometry, and electrochemical features. On the basis of data obtained, an octahedral structure has been assigned for all the complexes. The new complexes exhibit catalytic activity for the oxidation of primary and secondary alcohols into their corresponding aldehydes and ketones in the presence of *N*-methylmorpholine-*N*-oxide as co-oxidant and they were also found to be efficient catalyst for the transfer hydrogenation of ketones.

Keywords: Ruthenium(III) complexes; Spectroscopic characterization; Cyclic voltammetry; Catalytic activity

1. Introduction

Among the platinum group metals, ruthenium has been extensively studied in terms of its coordination and organometallic chemistry due to their stability, structural novelty [1, 2], and catalytic applications [3, 4]. As coordination environment imparts properties of complexes, complexation of ruthenium by diverse ligands is of importance [5, 6]. Organometallic compounds containing phosphine ligands have catalytic applications in both small-scale organic synthesis and bulk industrial production [7–10].

Selective oxidation of alcohols is one of the most important reactions in organic synthesis [11]. Several metal-based oxidants and halooxoacids have been used for alcohol oxidation [12]. Although these reagents are quite general in scope, the oxidation requires them in stoichiometric amount and produces problematic byproducts. Hence, the development of efficient catalysts for alcohol oxidation is the ongoing research interest [13].

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Ruthenium-mediated transfer hydrogenation (TH) of ketones under basic conditions employing isopropyl alcohol or other hydrogen-donor solvents has emerged as an atom-economical method for the synthesis of secondary alcohols [14]. The reduction of carbonyl compounds to the corresponding alcohols is a fundamental transformation in synthetic organic chemistry. Hydrogen-transfer reactions [15] are advantageous with respect to other reduction methods for several reasons: (a) the hydrogen donor is easy to handle (no gas containment or pressure vessels are necessary), cheap, and environmental friendly (e.g., isopropyl alcohol), (b) possible hazards are minimized, (c) the mild reaction conditions applied can afford enhanced selectivity [16].

To prepare a simple catalyst system for TH as well as oxidation, we, herein, report the synthesis of a series of six-coordinate ruthenium(III) chalconate complexes containing PPh_3/$AsPh_3$. The characterizations of the complexes were accomplished by analytical and spectroscopic (infrared (IR), electronic, mass, electron paramagnetic resonance (EPR), and cyclic voltammetry) methods. Further, some of the synthesized complexes have been effectively used as catalysts in the oxidation of alcohols in the presence of *N*-methylmorpholine-*N*-oxide (NMO) in TH of ketones in the presence of isopropyl alcohol and KOH as the promoter.

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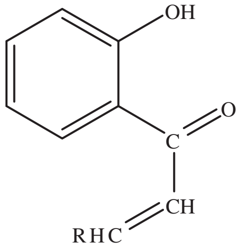
2. Experimental

2.1. *Materials and methods*

All reagents were chemically pure and AR grade. The solvents were purified and dried according to standard procedures [17]. $RuCl_3 \cdot 3H_2O$ was purchased from Loba Chemie Pvt. Ltd. and was used without purification. CHN analyses were performed by using a Carlo Erba 1108 analyzer at Central Drug Research Institute (CDRI), Lucknow, India. MALDI-TOF Mass spectral measurements were performed with a Voyager-De pro instrument. IR spectra of the ligands and complexes were recorded in KBr pellets with a Nicolet FT-IR spectrophotometer from 400 to $4000\,\mathrm{cm^{-1}}$. Electronic spectra of the complexes have been recorded in CH_2Cl_2 using a Shimadzu UV-Vis 1650 PC spectrophotometer from 200 to 800 nm. NMR spectra (^1H and ^{13}C) of the ligands were recorded on a Jeol GSX-400 instrument in $CDCl_3$. NMR spectra were obtained using TMS as the internal standard. EPR spectra of the powder samples of the complexes were recorded with a JEOL JES-FA200 instrument with X-band frequencies at room temperature using 2,2-diphenyl-1-picrylhydrazyl radical (DPPH) as internal standard at Pondicherry University, Pondicherry, India. Cyclic voltammetric measurements of the complexes were carried out with a BAS CV-27 electrochemical analyzer. Results were obtained using acetonitrile solution of $[(n\text{-}C_4H_9)_4N](ClO_4)$ (TBAP) as supporting electrolyte under nitrogen. A three-electrode cell was employed with a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. Melting points were recorded on a Technico micro heating table and are uncorrected. The catalytic yields were determined using an ACME 6000 series GC-FID with a DP-5 column of 30 m length, 0.53 mm diameter, and 5.00 μm film thickness. The starting complexes $[RuCl_3(PPh_3)_3]$ [18], $[RuCl_3(AsPh_3)_3]$ [19], $[RuBr_3(AsPh_3)_3]$ [20], and 2-hydroxychalcone ligands [21] were prepared according



Ligand	R
L^1	C_6H_5
L^2	4-$(OCH_3)C_6H_4$
L^3	4-$(Cl)C_6H_4$
L^4	4-$(CH_3)C_6H_4$

Figure 1. Structure of 2-hydroxychalcones.

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to the literature methods. The general structure of the 2-hydroxychalcones used in this study is given in figure 1.

2.2. *Synthesis of ruthenium(III) chalconate complexes*

All the reactions were carried out under anhydrous conditions by following common procedure. To a solution of $[RuX_3(EPh_3)_3]$ ($X = Cl$ or Br; $E = P$ or As) (0.1 mmol) in benzene (20 cm^3), the appropriate 2-hydroxychalcone (0.2 mmol) was added in 1 : 2 molar ratio. The mixture was heated under reflux for 6 h on a water bath, during which the reaction mixture gradually changed to deep color. After the reaction time, the contents were concentrated to around 3 cm^3 by removing the solvent under reduced pressure. The contents are cooled and then the product was separated by the addition of 10 cm^3 of petroleum ether (60–80°C). The product was recrystallized from CH_2Cl_2/petroleum ether. The compounds were dried under vacuum over fused calcium chloride and the purity of the complexes was checked by TLC.

2.3. *Procedure for catalytic oxidation of alcohols*

Catalytic oxidation of primary alcohols to corresponding aldehydes and secondary alcohols to ketones by ruthenium(III) chalconate complexes were studied in the presence of NMO as the co-oxidant. A typical reaction using the complex as a catalyst and primary or secondary alcohol, as substrates at 1 : 100 molar ratio was described as follows. A solution of ruthenium complex (0.01 mmol) in CH_2Cl_2 (20 cm^3) was added to the mixture containing substrate (1 mmol), NMO (3 mmol), and molecular sieves. The solution mixture was refluxed for 3 h and the solvent was evaporated from the mother liquor under reduced pressure. The solid residue was then extracted with diethyl ether (20 cm^3) and analyzed by GC. The oxidation products were identified by GC co-injection with authentic samples.

2.4. *Procedure for catalytic TH of ketones*

The catalytic TH reactions were also studied using ruthenium(III) chalconate complexes as catalysts, ketone as substrate, and KOH as promoter at 1 : 300 : 2.5 molar ratios. The procedure is as follows. A mixture containing ketone (3.75 mmol), ruthenium complex (0.0125 mmol), and KOH (0.03 mmol) was heated to reflux in 10 cm^3 of isopropyl alcohol for 2 h. After completion of reaction the catalyst was removed from the reaction mixture by the addition of diethyl ether followed by filtration and subsequent neutralization with 1 mol L^{-1} HCl. The ether layer was filtered through a short path of silica gel by column chromatography. The filtrate was subjected to GC analyses and the hydrogenated product was identified and determined with authentic samples.

3. Results and discussion

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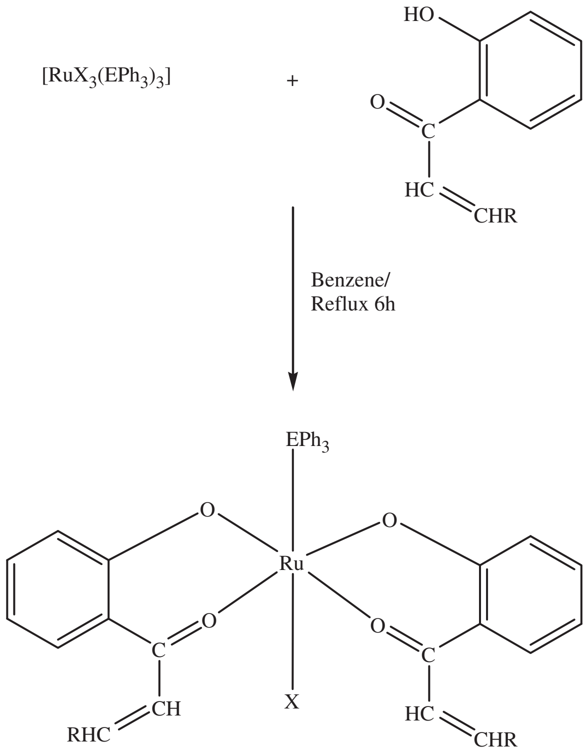
Paramagnetic, six-coordinate, low-spin ruthenium(III) complexes of general formula $[RuX(EPh_3)(L)]$ (X = Cl or Br; E = P or As; L = 2-hydroxychalcone) were synthesized in good yields from the reaction of $[RuX_3(EPh_3)_3]$ (X = Cl or Br; E = P or As) with 2-hydroxychalcone in dry benzene in 1 : 2 molar ratio (scheme 1).

In all these reactions, 2-hydroxychalcones behave as monobasic bidentate chelating ligands by replacing two triphenylphosphine/arsine and chloride/bromide from the starting complexes.

All the complexes are stable in air at room temperature, brown in color, non-hygroscopic, and highly soluble in common organic solvents such as dichloromethane, acetonitrile, chloroform, and DMSO. The analytical data are listed in table 1 and are in good agreement with the general molecular formula proposed for all the complexes. Mass spectrum of the representative complex $[RuCl(AsPh_3)(L^1)_2]$ displayed molecular ion isotopic cluster $[RuCl(AsPh_3)(L^1)_2]^+$ at *m*/*z* 889, another isotopic dominant fragment ($[Ru(L^1)]^+$) at *m*/*z* 322. This is consistent with the proposed molecular formulas of new ruthenium(III) chalconate complexes.

3.1. *IR spectroscopic analysis*

The important IR absorption bands for the ligands and complexes are shown in table 2. The free chalcones showed a strong band at 1634–1640 cm^{-1} due to $\nu_{C=O}$. This band has been shifted to lower wave number 1599–1626 cm^{-1} in the ruthenium complexes indicating coordination of the ligands to ruthenium through carbonyl oxygen [22]. A strong band at 1303–1316 cm^{-1} in the free chalcone has been assigned to phenolic $\nu_{C–O}$. This band shifts to higher wave number 1310–1319 cm^{-1} in spectra of the complexes due to its coordination to ruthenium ion through oxygen [23]. This has been further supported by the disappearance of the broad ν_{OH} band around 3400–3600 cm^{-1} in the complexes, indicating deprotonation of the phenol prior to coordination to ruthenium metal. Hence, from the IR spectroscopic data, it is inferred that both the carbonyl and phenolic oxygens are involved in the coordination of chalcones to ruthenium ion in all the complexes.



(X = Cl or Br; E = P or As; R = C_6H_5, 4-$(OCH_3)C_6H_4$, 4-$Cl(C_6H_4)$ or 4-$CH_3(C_6H_4)$)

Scheme 1. Formation of ruthenium(III) chalconate complexes.

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Table 1. Analytical data of ruthenium(III) chalconate complexes

Complex	Formula	Yield (%)	D.Pt (°C)	Calculated (found) (%)	
				C	H
$[RuCl(PPh_3)(L^1)_2]$	$C_{48}H_{37}O_4PClRu$	56	108	68.20(67.98)	4.41(4.42)
$[RuCl(PPh_3)(L^2)_2]$	$C_{50}H_{41}O_6PClRu$	62	162	66.33(66.10)	4.56(4.60)
$[RuCl(PPh_3)(L^3)_2]$	$C_{48}H_{35}O_4PCl_3Ru$	59	168	63.06(63.16)	3.86(3.78)
$[RuCl(PPh_3)(L^4)_2]$	$C_{50}H_{41}O_4PClRu$	64	120	68.76(68.62)	4.73(4.72)
$[RuCl(AsPh_3)(L^1)_2]$	$C_{48}H_{37}O_4AsClRu$	58	146	64.83(64.82)	4.19(4.21)
$[RuCl(AsPh_3)(L^2)_2]$	$C_{50}H_{41}O_6AsClRu$	55	141	63.46(63.48)	4.35(4.28)
$[RuCl(AsPh_3)(L^3)_2]$	$C_{48}H_{35}O_4AsCl_3Ru$	62	140	60.17(60.09)	3.68(3.67)
$[RuCl(AsPh_3)(L^4)_2]$	$C_{50}H_{41}O_4AsClRu$	65	150	65.47(65.41)	4.50(4.49)
$[RuBr(AsPh_3)(L^1)_2]$	$C_{48}H_{37}O_4AsBrRu$	68	138	61.74(61.64)	3.99(4.00)
$[RuBr(AsPh_3)(L^2)_2]$	$C_{50}H_{41}O_6AsBrRu$	71	142	60.43(60.48)	4.16(4.18)
$[RuBr(AsPh_3)(L^3)_2]$	$C_{48}H_{35}O_4Cl_2AsBrRu$	63	133	57.50(57.56)	3.52(3.46)
$[RuBr(AsPh_3)(L^4)_2]$	$C_{50}H_{41}O_4AsBrRu$	68	125	62.44(62.36)	4.30(4.27)

Table 2. IR absorption frequencies (cm^{-1}) and electronic spectroscopic data[a] (nm) of free ligands and their ruthenium(III) chalconate complexes

Complex	$\nu_{C=O}$	$\nu_{C–O}$	$\nu_{C=C}$	λ_{max} (ε) ($dm^3\,mol^{-1}\,cm^{-1}$)
L^1	1639	1308	1572	234(31,468), 223(30,240)
L^2	1639	1303	1564	236(30,856), 224(30,210)
L^3	1640	1316	1585	233(31,040), 222(30,240)
L^4	1634	1305	1562	238(30,460), 225(30,380)
$[RuCl(PPh_3)(L^1)_2]$	1626	1313	1544	341(23,750), 231(31,040), 219(31,653), 216(33,845)
$[RuCl(PPh_3)(L^2)_2]$	1599	1311	1542	380(21,958), 231(31,040), 215(32,985)
$[RuCl(PPh_3)(L^3)_2]$	1618	1319	1544	341(23,750), 231(31,040), 215(32,985)
$[RuCl(PPh_3)(L^4)_2]$	1609	1318	1543	357(22,562), 231(31,040), 220(31,964)
$[RuCl(AsPh_3)(L^1)_2]$	1622	1312	1543	341(23,750), 231(31,040), 215(32,985)
$[RuCl(AsPh_3)(L^2)_2]$	1602	1311	1540	371(21,496), 341(23,750), 231(31,040), 221(31,867)
$[RuCl(AsPh_3)(L^3)_2]$	1621	1312	1542	441(20,385), 341(23,750), 231(31,040), 215(32,985)
$[RuCl(AsPh_3)(L^4)_2]$	1617	1311	1541	341(23,750), 231(31,040), 216(33,845)
$[RuBr(AsPh_3)(L^1)_2]$	1619	1312	1542	441(20,385), 341(23,750), 231(31,040), 224(31,238)
$[RuBr(AsPh_3)(L^2)_2]$	1600	1310	1539	341(23,750), 232(31,180), 220(31,964), 214(33,653)
$[RuBr(AsPh_3)(L^3)_2]$	1620	1312	1541	341(23,750), 231(31,040), 220(31,964), 210(32,179)
$[RuBr(AsPh_3)(L^4)_2]$	1616	1312	1541	441(20,385), 231(31,040), 219(31,653), 215(32,985)

[a] Solvent used: CH_2Cl_2.

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The $\nu_{C–C}$ of the free ligands appeared as a separate band in their IR spectra around 1600 cm^{-1}, but could not be identified in spectra of the ruthenium complexes because of their possible merging with $\nu_{C=O}$ [24]. In the complexes, the absorption due to the phenyl alkene vibration appeared at 1539–1544 cm^{-1}, slightly lower than that observed in the spectra of the free ligands [25]. In addition, characteristic bands due to triphenylphosphine or triphenylarsine (around 1440, 1090, and 700 cm^{-1}) were also present in the spectra of all the complexes [26].

3.2. *Electronic spectroscopic analysis*

Electronic spectra of the ligands and their complexes were recorded in CH_2Cl_2 from 200 to 800 nm. For a low-spin d^5 system in an octahedral environment, the ground state is $^2T_{2g}$ arising from a t^5_{2g} configuration. The next higher energy configuration $t^4_{2g}\,e^1_g$ gives rise to four states, namely $^2A_{2g}$, $^2A_{1g}$, $^2T_{1g}$, and $^2T_{2g}$, and so four bands are expected. In most of the ruthenium(III) complexes, the absorption spectra show only charge transfer (CT) bands [27]. In a d^5 system, and especially in ruthenium(III) which is a relatively good oxidizing agent, the CT bands of the type $L_{\pi y} \rightarrow T_{2g}$ are prominent in the low-energy region and the weaker bands are obscure due to d–d transitions. It, therefore, becomes difficult to conclusively assign bands of ruthenium(III) complexes which appear in the visible region [28].

The electronic spectroscopic data of the free ligands and their complexes are listed in table 2. The spectra of the free ligands showed two types of transitions. The peak at 225–222 nm was assigned to π–π^* transitions involving molecular orbitals located on the phenol. These peaks shift in the spectra of the complexes due to the donation of a lone pair of electrons by oxygen of the phenoxy to ruthenium [25]. The second type of

Table 3. ^{1}H NMR and ^{13}C NMR data (δ in ppm) of 2-hydroxychalcone ligands

Ligand	^{1}H NMR	^{13}C NMR
L^1	12.79 (s, –OH), 7.94–6.92 (m, aromatic)	193.74 (s, –C=O), 163.61 (s, –C–OH), 145.45–118.64 (m, aromatic)
L^2	12.92 (s, –OH), 7.91–6.88 (m, aromatic), 3.85 (s, $–OCH_3$)	193.65 (s, –C=O), 163.54 (s, –C–OH), 145.31–114.51 (m, aromatic), 55.41 (s, $–OCH_3$)
L^3	12.81 (s, –OH), 7.89–6.90 (m, aromatic)	193.71 (s, –C=O), 163.58 (s, –C–OH), 145.42–116.52 (m, aromatic)
L^4	12.90 (s, –OH), 7.93–6.94 (m, aromatic), 1.25 (s, $–CH_3$)	193.73 (s, –C=O), 163.56 (s, –C–OH), 145.40–114.84 (m, aromatic), 20.52 (s, $–CH_3$)

transitions at 238–233 nm are assigned to n–π^* transitions involving molecular orbitals of the –C=N and the benzene ring. These bands also shift upon complexation indicating that the imine nitrogen coordinates to the metal [29].

The spectra of all the complexes show other types of transitions. Broad bands at 441–341 nm can be assigned to CT transitions [23]. The pattern of the electronic spectra of all the complexes indicate an octahedral environment around ruthenium(III) ion.

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3.3. *^{1}H and ^{13}C NMR spectra of 2-hydroxychalcone ligands*

The ^{1}H NMR spectra of the 2-hydroxychalcone ligands were recorded in $CDCl_3$ to confirm the formation of the ligands. The OH signal of all chalcone ligands appeared as a sharp singlet at 12.79–12.92 ppm (table 3). All the ligands showed peaks at 6.88–7.94 ppm, assigned to protons of phenyl in the 2-hydroxychalcone. The signal due to two alkene protons appeared at 6.9–7.9 ppm, and hence merged with the multiplet of aromatic protons. The signal for methoxy proton appeared as a singlet at 3.85 ppm in L^2 and the signal for methyl proton appeared as a singlet at 1.25 ppm in L^4.

^{13}C NMR spectra of the ligands exhibit a sharp singlet at 193.65–193.74 ppm (table 3), assigned to –C=O carbon. The signal for phenolic –C–OH carbon appeared at 163.54–163.61 ppm. Multiplets around 114.51–145.45 ppm have been assigned to aromatic carbons. The alkene carbons appeared at 115.45–140.58 ppm, and hence merged with the aromatic carbons. A sharp singlet at 55.41 ppm was assigned to methoxy carbon in L^2. In addition, a sharp singlet at 20.52 ppm was assigned to methyl carbon in L^4.

3.4. *EPR spectroscopic analysis*

The solid-state EPR spectra of all the ruthenium(III) chalconate complexes (a representative spectrum given in figure 2) were recorded in X-band frequencies at room temperature.

Most of the complexes showed a single isotropic line with 'g' values in the range 2.23–2.43, indicating high symmetry (O_h) around ruthenium. Such isotropic lines are either due to the intermolecular spin exchange which can broaden the lines or due to the occupancy of the unpaired electron in a degenerate orbital. Few of the complexes (table 4, $[RuCl(AsPh_3)(L^{1-3})_2]$) showed spectra characteristics of an axially symmetric

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Figure 2. EPR spectrum of [RuCl(AsPh$_3$)(L^4)$_2$].

Table 4. EPR spectroscopic data of ruthenium(III) chalconate complexes

Complex	g_x	g_y	g_z	$\langle g\rangle$*
[RuCl(PPh$_3$)(L^1)$_2$]	–	2.39	–	–
[RuCl(PPh$_3$)(L^2)$_2$]	–	2.41	–	–
[RuCl(PPh$_3$)(L^3)$_2$]	–	2.43	–	–
[RuCl(PPh$_3$)(L^4)$_2$]	–	2.36	–	–
[RuCl(AsPh$_3$)(L^1)$_2$]	2.40	2.40	1.97	2.26
[RuCl(AsPh$_3$)(L^2)$_2$]	2.28	2.28	2.03	2.19
[RuCl(AsPh$_3$)(L^3)$_2$]	2.32	2.32	2.04	2.23
[RuCl(AsPh$_3$)(L^4)$_2$]	2.34	2.09	1.98	2.14
[RuCl(AsPh$_3$)(L^4)$_2$] LNT	2.32	2.12	1.96	2.14
[RuBr(AsPh$_3$)(L^1)$_2$]	–	2.39	–	–
[RuBr(AsPh$_3$)(L^2)$_2$]	–	2.42	–	–
[RuBr(AsPh$_3$)(L^3)$_2$]	–	2.23	–	–
[RuBr(AsPh$_3$)(L^4)$_2$]	–	2.32	–	–

$\langle g\rangle^* = [1/3(g_x)^2 + 1/3(g_y)^2 + 1/3(g_z)^2]^{1/2}$.

system with $g_\perp$ around 2.28–2.40 and $g_\parallel$ around 1.97–2.04. For an octahedral field with tetragonal distortion ($g_x = g_y \neq g_z$), and hence, two values for 'g' indicate tetragonal distortion in these complexes. However, [RuCl(AsPh$_3$)(L^4)$_2$] showed three lines with three different 'g' values ($g_x \neq g_y \neq g_z$), indicating rhombic distortion. The spectra of

Table 5. Electrochemical data for some ruthenium(III) chalconate complexes

	Ru(IV)–Ru(III)				Ru(III)–Ru(II)			
Complex	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	ΔE_p (mV)	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	ΔE_p (mV)
$[RuCl(PPh_3)(L^1)_2]$	–	1.08	–	–	−1.13	−0.74	−0.94	390
$[RuCl(PPh_3)(L^2)_2]$	–	1.09	–	–	−1.12	−0.77	−0.95	350
$[RuCl(AsPh_3)(L^1)_2]$	–	1.02	–	–	−1.18	−0.63	−0.91	550
$[RuCl(AsPh_3)(L^3)_2]$	–	1.05	–	–	−1.15	−0.71	−0.93	440
$[RuCl(AsPh_3)(L^4)_2]$	–	0.79	–	–	−1.10	−0.64	−0.87	460
$[RuBr(AsPh_3)(L^3)_2]$	–	0.88	–	–	−1.04	−0.59	−0.82	450
$[RuBr(AsPh_3)(L^4)_2]$	–	0.77	–	–	−1.06	−0.61	−0.84	450

Supporting electrolyte, NBu_4ClO_4 (0.05 mol L^{-1}); complex, 0.001 mol L^{-1}; solvent, CH_3CN; $\Delta E_p = E_{pa} - E_{pc}$, where E_{pa} and E_{pc} are anodic and cathodic potentials, respectively; $E_{1/2} = 0.5(E_{pa} + E_{pc})$; scan rate: 100 mV s^{-1}.

$[RuCl(AsPh_3)(L^4)_2]$ at liquid nitrogen temperature did not show much variation from that observed at room temperature, indicating rhombic distortion in the complex. Overall, the position of the lines and the nature of the EPR spectra are characteristic of the octahedral ruthenium(III) complexes [30, 31].

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3.5. *Cyclic voltammetry*

Redox behavior of some of the complexes was studied by cyclic voltammetry under N_2 atmosphere at glassy carbon working electrode in acetonitrile solution (0.05 mol L^{-1}: NBu_4ClO_4) and the redox potentials are expressed with reference to Ag/AgCl. The complexes display irreversible oxidative (RuIV/RuIII) and quasireversible reductive response (RuIII/RuII) at 100 mV s^{-1}. The potentials are summarized in table 5.

The complexes exhibit quasireversible reduction with $E_{1/2}$ in the range −0.82 to −0.94 V (RuIII/RuII). The reduction observed is quasireversible in nature, characterized by large peak-to-peak separation (ΔE_p) of 350–550 mV, suggestive of a single-step one-electron transfer process [32]. The quasireversible reduction waves with large peak-to-peak separation values (ΔE_p) are attributed to slow electron transfer and adsorption of the complexes on the electrode surface [33–35]. The complexes showed an irreversible oxidation process, which may be ascribed to the short-lived oxidized state of the metal ion.

The potentials of both the oxidation (RuIV/RuIII) and reduction (RuIII/RuII) have been found to be sensitive to the nature of the substituent (R) in the chalcone ligands. The formal potentials $E_{1/2}$ increase with the increase in electron-withdrawing nature of the substituent (R). The plot of $E_{1/2}$ *versus* σ (σ – the Hammet constant of R: $OCH_3 = -0.27$, $CH_3 = -0.17$, $Cl = 0.23$, $H = 0.00$) [36] is linear for reduction (figure 3) with slopes of 0.33 V (RuIII/RuII) for complexes $[RuCl(PPh_3)(L^1)_2]$, $[RuCl(PPh_3)(L^2)_2]$, $[RuCl(AsPh_3)(L^3)_2]$, and $[RuCl(AsPh_3)(L^4)_2]$. The linear correlation of the redox potentials and electronic nature (σ) of the substituents clearly shows that a single substituent on the chalcone ligand, which is four bonds away from the metal center, can influence metal-centered potentials in a predictable manner. Hence, it is clear that the present ligand system is suitable for stabilizing the higher oxidation state of ruthenium ions. Further, reduction potentials do not show any systematic variation with the change in chloride or bromide present in the ruthenium complexes.

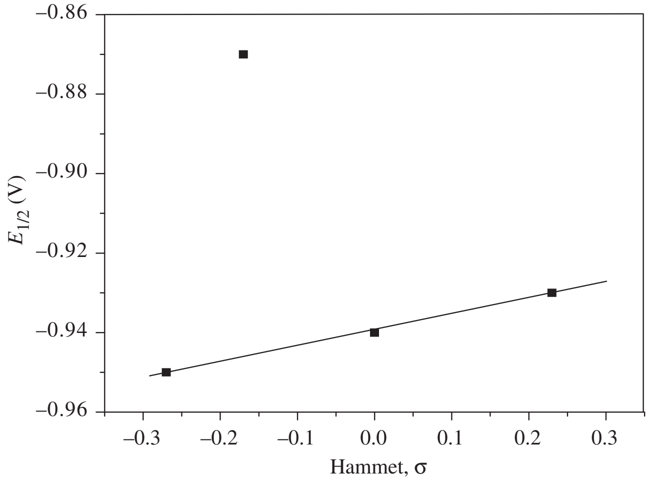

Figure 3. Least-squares plot of (RuIII/RuII) potentials *vs.* σ.

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3.6. *Catalytic oxidation*

Catalytic oxidations of primary alcohols and secondary alcohols by the ruthenium(III) chalconate complexes were carried out in CH_2Cl_2 in the presence of NMO, and the by-product water was removed by using molecular sieves. All the complexes oxidize primary alcohols to the corresponding aldehydes and secondary alcohols to ketones with high yields (table 6). The aldehydes or ketones formed after 3 h of reflux were determined by GC and there was no detectable oxidation in the absence of ruthenium complex.

The oxidation of benzyl alcohol to benzaldehyde resulted in 71–99% yield and cyclohexanol to cyclohexanone resulted in 47–93% yield. The higher product yield obtained for the oxidation of benzyl alcohol compared to cyclohexanol is due to the fact that the α-CH unit of benzyl alcohol is more acidic than cyclohexanol [37]. Triphenylarsine ruthenium(III) chalconate complexes possess greater catalytic activity than triphenylphosphine complexes. The catalytic activity of new ruthenium(III) chalconate complexes is compared with that of corresponding starting complexes $[RuCl_3(PPh_3)_3]$, $[RuCl_3(AsPh_3)_3]$, and $[RuBr_3(AsPh_3)_3]$; the activities are comparable for the oxidation of benzyl alcohol and tremendously improved for the oxidation of cyclohexanol. The conversion is higher than the conventional catalyst $K_2Cr_2O_7$ [26, 38]. There is no correlation between the redox potential with catalytic activity of the complexes. The conversion of primary and secondary alcohols to corresponding aldehydes and ketones increases with the increase in reaction time up to 3 h (figure 4).

The complexes are able to react efficiently with NMO to yield high-valent ruthenium-oxo species [38], capable of oxygen atom transfer to alcohols. This was further supported by spectroscopic changes that occur by the addition of NMO to a dichloromethane solution of the ruthenium(III) complexes. The appearance of a peak at 390 nm in UV-Vis spectra is attributed to the formation of $Ru^V=O$, in conformity with

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Table 6. Catalytic oxidation data of ruthenium(III) chalconate complexes

Complex	Substrate	Product	Yield (%)[a]	TON[b]
$[RuCl(PPh_3)(L^2)_2]$	Benzyl alcohol	A	88	88
	Cyclohexanol	B	69	69
$[RuCl(PPh_3)(L^3)_2]$	Benzyl alcohol	A	71	71
	Cyclohexanol	B	61	61
$[RuCl(PPh_3)(L^4)_2]$	Benzyl alcohol	A	96	96
	Cyclohexanol	B	77	77
$[RuCl(AsPh_3)(L^2)_2]$	Benzyl alcohol	A	98	98
	Cyclohexanol	B	91	91
$[RuCl(AsPh_3)(L^3)_2]$	Benzyl alcohol	A	98	98
	Cyclohexanol	B	87	87
$[RuCl(AsPh_3)(L^4)_2]$	Benzyl alcohol	A	97	97
	Cyclohexanol	B	93	93
$[RuBr(AsPh_3)(L^2)_2]$	Benzyl alcohol	A	98	98
	Cyclohexanol	B	47	47
$[RuBr(AsPh_3)(L^3)_2]$	Benzyl alcohol	A	99	99
	Cyclohexanol	B	55	55
$[RuBr(AsPh_3)(L^4)_2]$	Benzyl alcohol	A	98	98
	Cyclohexanol	B	60	60
$[RuCl_3(PPh_3)_3]$	Benzyl alcohol	A	68	68
	Cyclohexanol	B	56	56
$[RuCl_3(AsPh_3)_3]$	Benzyl alcohol	A	87	87
	Cyclohexanol	B	77	77
$[RuBr_3(AsPh_3)_3]$	Benzyl alcohol	A	88	88
	Cyclohexanol	B	45	45
$K_2Cr_2O_7/H_2SO_4$	Benzyl alcohol	A	07	07
	Cyclohexanol	B	04	04

A: benzaldehyde; B: cyclohexanone.

[a] Yield determined by GC and comparing with the analyses of authentic samples.

[b] Ratio of moles of product obtained to the moles of the catalyst used.

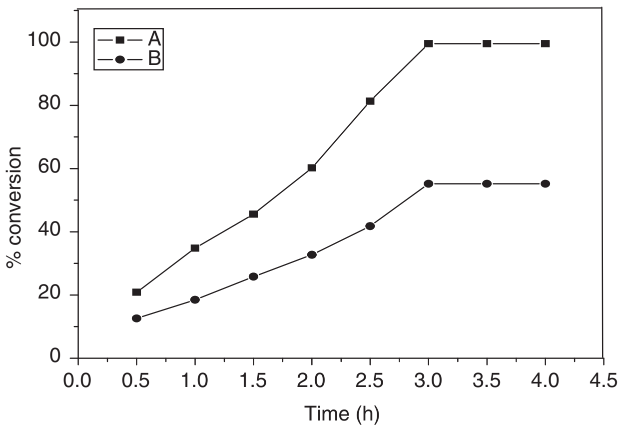

Figure 4. Catalytic oxidation of benzyl alcohol (A) and cyclohexanol (B) in different time intervals $[RuBr(AsPh_3)(L^3)_2]$.

other oxo ruthenium(V) complexes [39, 40]. The formation of such species was identified from the IR spectrum of the solid mass (obtained by evaporation of the resultant solution to dryness), which showed a band at 860 cm^{-1}, characteristic of $Ru^V{=}O$ species [40, 41].

Table 7. Catalytic TH of ketones by ruthenium(III) chalconate complexes.[a]

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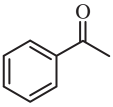
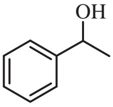
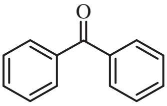
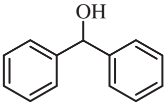
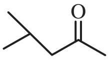
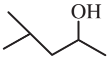
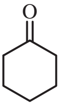
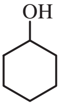
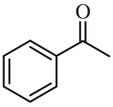
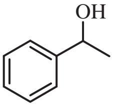
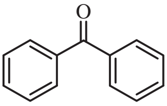
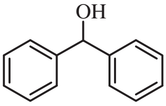
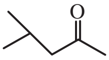
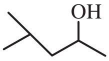
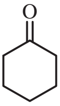
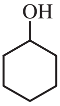
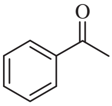
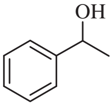
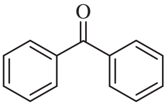
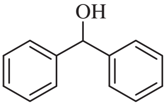
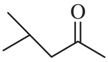
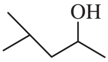
[RuCl(PPh$_3$)(L^2)$_2$]			80	240
			74	222
			61	183
			94	282
[RuCl(AsPh$_3$)(L^1)$_2$]			33	99
			43	129
			41	123
			84	252
[RuBr(AsPh$_3$)(L^1)$_2$]			40	120
			52	156
			63	189

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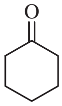
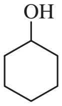
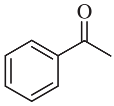
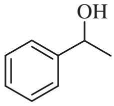
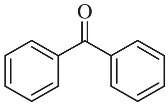
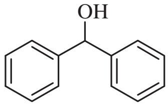
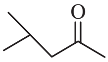
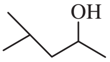
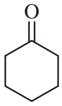
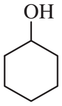
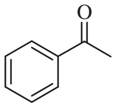
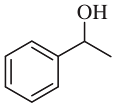
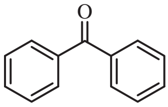
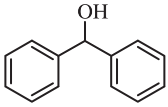
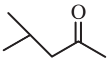
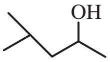
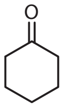
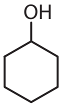
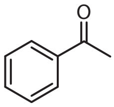
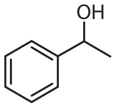
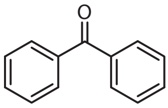
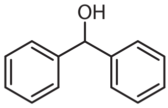
			99	297
[RuCl$_3$(PPh$_3$)$_3$]			42	126
			34	102
			38	114
			83	249
[RuCl$_3$(AsPh$_3$)$_3$]			23	69
			25	75
			33	99
			72	216
[RuBr$_3$(AsPh$_3$)$_3$]			30	90
			27	81

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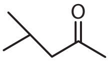
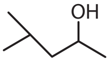
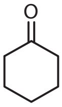
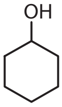
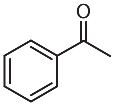
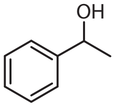
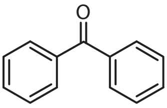
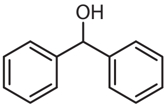
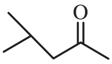
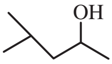
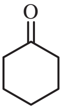
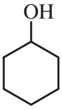
			36	108
			86	258
NaBH$_4$			20	60
			32	96
			28	84
			34	102

[a] Conditions: reactions were carried out heated to reflux using 3.75 mmol of ketone (10 cm^3 isopropyl alcohol); catalyst/ketone/KOH ratio 1 : 300 : 2.5.
[b] Yield of product was determined using a ACME 6000 series GC-FID with a DP-5
column of 30 m length, 0.53 mm diameter, and 5.00 µm film thickness and by comparison with authentic samples.
[c] TON = ratio of moles of product obtained to the moles of the catalyst used.

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3.7. *Catalytic TH*

The catalytic TH of ketones in the presence of ruthenium chalconate complexes has been studied in isopropyl alcohol-KOH using a molar ratio 1 : 2.5 : 300 for the catalyst, KOH, and the ketone in 10 cm^3 of isopropyl alcohol. The ruthenium(III) chalconate complexes showed excellent catalytic activity. Typical results are shown in table 7. Cyclohexanone converted into cyclohexanol in 84–99% yield. Acetophenone was converted into 1-phenyl ethanol in 33–80% yield and benzophenone was converted into benzhydrol in 43–74% yield. Similarly, iso-butylmethylketone underwent TH to afford the corresponding alcohol in 41–63% yield. The catalytic efficiency of the new ruthenium(III) chalconate complexes is moderately increased for the conversion of cyclohexanone to cyclohexanol, but tremendously improved for the reduction of acetophenone, benzophenone, and isobutyl methyl ketone when compared to the corresponding starting complexes. The conversion is higher than the conventional catalyst NaBH$_4$. In the absence of base, no TH of ketone was observed. The base facilitated the formation of the ruthenium alkoxide by abstracting the proton of the

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alcohol and subsequently, the alkoxide underwent β-elimination to give a ruthenium hydride which is an active species in this reaction [42]. There is no correlation between the redox potential with catalytic activity of the complexes.

4. Conclusions

Some new ruthenium(III) chalconate complexes were synthesized using chalconate produced from the derivatives of benzaldehyde and 2-hydroxyacetophenone. The new complexes have been characterized by analytical and spectroscopic (IR, electronic, mass, EPR, and cyclic voltammetry) methods. An octahedral structure has been tentatively proposed for all the complexes. The complexes showed efficient catalytic activity for the oxidation of both primary and secondary alcohols with excellent yields in the presence of NMO, and also for TH of aliphatic and aromatic ketones with high conversions in the presence of isopropyl alcohol and KOH. Although some ruthenium complexes have been found in recent literature [43, 44], ruthenium(III) chalconate complexes have been rarely seen as catalysts for the oxidation and TH. In our system, the presence of triphenylphosphine/arsine may allow the activity to be tuned by changing the electronic environment around the metal.

Supplementary material

Representative mass spectrum and cyclic voltammogram of ruthenium(III) chalconate complexes have been provided as supplementary materials.

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