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# Ruthenium(II) chalconate complexes: Synthesis, characterization, catalytic, and biological studies

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# 1. Introduction

Chalcones bearing non-natural substituents have been synthesized during the recent years in order to develop drugs active against cancer [1,2], malaria [3], leishmaniase [4], tuberculosis [5] and cardiovascular diseases [6]. Apart from its use in medical science, some chalcone derivatives [7] exhibit second harmonic generation (SHG), and hence they are also used in non-linear optical (NLO) applications. 2'-Hydroxychalconate complexes of ruthenium(II) containing triphenylphosphine have been found to show significant catalytic oxidation and biological activities [8]. Many research groups are developing the synthetic chemistry related to ruthenium complexes because of their multiple applications in many different scientific fields [9]. Ruthenium complexes have been used as catalysts or catalyst precursors for a variety of purposes including hydrogenation, oxidation, isomerisation, polymerization, nucleophilic addition to multiple bonds and carbon-carbon bond formation [10].

The oxidation of alcohols into their corresponding aldehydes and ketones is of greater importance in synthetic organic chemistry [11]. Ruthenium complexes have a long pedigree as catalysts for transfer hydrogenation reactions in the presence of isopropanol as hydrogen source [12,13]. Several recent examples of ruthenium *N*-heterocyclic carbene complexes [14–16], Ru(arene)-(diamine) [17], ruthenium(III) amine-bis(phenolate) tripodal complexes [18]

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# ABSTRACT

A series of new hexa-coordinated ruthenium(II) carbonyl complexes of the type [RuCl(CO)(EPh<sub>3</sub>)(B)(L)] (E=P or As; B=PPh<sub>3</sub>, AsPh<sub>3</sub> or Py; L=2'-hydroxychalcones) have been prepared by reacting [RuHCl(CO)(EPh<sub>3</sub>)<sub>2</sub>(B)] (E=P or As; B=PPh<sub>3</sub>, AsPh<sub>3</sub> or Py) with 2'-hydroxychalcones in benzene under reflux. The new complexes have been characterized by analytical and spectral (IR, electronic, <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR) data. Based on the above data, 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 (NMO) as co-oxidant and also found efficient catalyst in the transfer hydrogenation of ketones. The antifungal properties of the complexes have also been examined and compared with standard *Bavistin*.

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and Ru(BINAP)(diamine) [19] have become the most prominent members for the reduction of ketones in high yields. Pincer-type arylruthenium(II) complexes containing the monoanionic terdentate NCN and PCP ligands have been reported by van Koten as active catalysts for the transfer hydrogenation of ketones in the presence of isopropanol and KOH [20]. Even though there are number of reports available on the transfer hydrogenation of ketones by ruthenium complexes, only limited reports are available for catalytic transfer hydrogenation of ketones by ruthenium chalconate complexes.

We, herein report the synthesis of a series of hexa-coordinated ruthenium(II) chalconate complexes containing PPh<sub>3</sub>/AsPh<sub>3</sub>. The characterization of the complexes was accomplished by analytical and spectral (IR, electronic, <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR) methods. Further, some of the synthesized complexes have been effectively used as catalyst in oxidation of alcohols in the presence of NMO and transfer hydrogenation of ketones in the presence of isopropanol and KOH as base. The antifungal properties of the complexes have also been examined and compared with standard *Bavistin*.

# 2. Experimental

#### 2.1. Reagents and materials

All the reagents used were chemically pure and AR grade. The solvents were purified and dried according to standard procedures [21].  $RuCl_3 \cdot 3H_2O$  was purchased from Loba Chemie Pvt. Ltd., and was used without further purification. The starting complexes [RuHCl(CO)(PPh\_3)\_3] [22], [RuHCl(CO)(AsPh\_3)\_3] [23] and

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$L^2$	$4-(OCH_3)C_6H_4$
$L^3$	$4-(Cl)C_6H_4$
$L^4$	3, 4-(OCH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>

Fig. 1. Structure of 2'-hydroxychalcones.

[RuHCl(CO)(Py)(PPh<sub>3</sub>)<sub>2</sub>] [24] were prepared according to the literature methods. The general structure of the 2'-hydroxychalcone ligands used in this study is given below (Fig. 1).

# 2.2. Physical measurements

The analysis of carbon, hydrogen and nitrogen were performed on Carlo Erba 1108 model analyzer at the Central Drug Research Institute, Lucknow, India. Infrared spectra were recorded in KBr pellets with a Nicolet FT-IR spectrophotometer in 400–4000 cm<sup>-1</sup> range. Electronic spectra of the complexes have been recorded in CH<sub>2</sub>Cl<sub>2</sub> using a Shimadzu UV-visible 1650 PC spectrophotometer in 200–800 nm range. <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR spectra were recorded in Jeol GSX-400 instrument using CDCl<sub>3</sub> as solvent. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained at room temperature using TMS as the internal standard. <sup>31</sup>P NMR spectra of the complexes were obtained at room temperature using ortho phosphoric acid as a reference. Melting points were recorded on a Technico micro heating table and are uncorrected. The catalytic yields were determined using ACME 6000 series GC-FID with a DP-5 column of 30 m length, 0.53 mm diameter and 5.00  $\mu$ m film thickness.

# 2.3. Synthesis of chalconate ligands

Chalconate ligands were prepared by condensing 4-substituted benzaldehyde (0.6007–0.8309 g, 5 mmol) with 1-acetyl-2-naphthol (0.9311 g, 5 mmol) in presence of 50 cm<sup>3</sup> alcoholic sodium hydroxide solution (20%). After 24 h stirring, the product was precipitated by addition of concentrated hydrochloric acid. Then the product was filtered and recrystallized from ethanol [25].

L<sup>1</sup> is prepared from 1-acetyl-2-naphthol (0.9311 g, 5 mmol) and 4-methyl benzaldehyde (0.6 cm<sup>3</sup>, 5 mmol). m.p. 87 °C (73% yield). Found: C 83.31, H 5.59. C<sub>20</sub>H<sub>16</sub>O<sub>2</sub> requires C 83.26, H 5.54%. IR:  $\nu_{(C=O)}$  1632 s cm<sup>-1</sup>,  $\nu_{(C=C)}$  1565 w cm<sup>-1</sup>,  $\nu_{(C=O)}$  1335 m cm<sup>-1</sup>.

L<sup>2</sup> is prepared from 1-acetyl-2-naphthol (0.9311 g, 5 mmol) and 4-methoxy benzaldehyde (0.61 cm<sup>3</sup>, 5 mmol). m.p. 125 °C (78% yield). Found: C 78.93, H 5.29. C<sub>20</sub>H<sub>16</sub>O<sub>3</sub> requires C 78.91, H 5.24%. IR:  $\nu_{(C=O)}$  1630 s cm<sup>-1</sup>,  $\nu_{(C=C)}$  1555 w cm<sup>-1</sup>,  $\nu_{(C=O)}$  1332 m cm<sup>-1</sup>. L<sup>3</sup> is prepared from 1-acetyl-2-naphthol (0.9311 g, 5 mmol) and

L<sup>3</sup> is prepared from 1-acetyl-2-naphthol (0.9311 g, 5 mmol) and 4-chloro benzaldehyde (0.7029 g, 5 mmol). m.p. 82 °C (68% yield). Found: C 73.91, H 4.24. C<sub>19</sub>H<sub>13</sub>O<sub>2</sub>Cl requires C 73.81, H 4.21%. IR:  $\nu_{(C=0)}$  1633 s cm<sup>-1</sup>,  $\nu_{(C=C)}$  1565 w cm<sup>-1</sup>,  $\nu_{(C=O)}$  1339 m cm<sup>-1</sup>.

L<sup>4</sup> is prepared from 1-acetyl-2-naphthol (0.9311 g, 5 mmol) and 3, 4-dimethoxy benzaldehyde (0.8309 g, 5 mmol). m.p. 95 °C (81% yield). Found: C 75.43, H 5.42. C<sub>21</sub>H<sub>18</sub>O<sub>4</sub> requires C 75.41, H 5.38%. IR:  $\nu_{(C=0)}$  1629 s cm<sup>-1</sup>,  $\nu_{(C=C)}$  1556 w cm<sup>-1</sup>,  $\nu_{(C=0)}$  1340 m cm<sup>-1</sup>.

# 2.4. Synthesis of new ruthenium(II) chalconate complexes

All reactions were carried out under strict anhydrous conditions and were prepared by the following common procedure. To a solution of [RuHCl(CO)(EPh<sub>3</sub>)<sub>2</sub>(B)] (E = P or As; B = PPh<sub>3</sub>, AsPh<sub>3</sub> or Py) (0.1 g, 0.1 mmol) in benzene (20 cm<sup>3</sup>), the appropriate 2'hydroxychalcone (0.0266–0.0435 g, 0.1 mmol) were added in 1:1 molar ratio. The mixture was heated under reflux for 6 h. The reaction mixture gradually changed to deep color and the solvent was removed under reduced pressure. The product was separated by the addition of small amount of petroleum ether (60–80 °C) and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether mixture. The compounds were dried under vacuum and the purity of the complexes was checked by TLC.

# 2.5. Catalytic oxidation

Catalytic oxidation of primary alcohols to corresponding aldehydes and secondary alcohols to ketones by ruthenium(II) chalconate complexes were studied in the presence of NMO as 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<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) 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 then evaporated from the mother liquor under reduced pressure. The solid residue was extracted with petroleum ether (60–80 °C) (20 cm<sup>3</sup>) and was analyzed by GC. The oxidation products were identified by GC coinjection with authentic samples.

# 2.6. Catalytic transfer hydrogenation of ketones

The catalytic transfer hydrogenation reactions were also studied using ruthenium(II) chalconate complexes as a catalyst, ketone as substrate and KOH as base at 1:300:2.5 molar ratios. The procedure was described as follows. A mixture containing ketone (3.75 mmol), the ruthenium complex (0.0125 mmol) and KOH (0.03 mmol) was heated to reflux in 10 cm<sup>3</sup> of *i*-prOH for 30 min. 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 M HCl. The ether layer was filtered through a short path of silica gel by column chromatography. The filtrate was subjected to GC analysis and the hydrogenated product was identified and determined with authentic samples.

# 3. Results and discussions

Diamagnetic, hexa-coordinated low spin ruthenium(II) complexes of general formula  $[RuCl(CO)(EPh_3)(B)(L)]$  (E=P or As; B=PPh<sub>3</sub>, AsPh<sub>3</sub> or Py; L=2'-hydroxychalcone) were synthesized in good yields from the reaction of  $[RuHCl(CO)(EPh_3)_2(B)]$  (E=P or As; B=PPh<sub>3</sub>, AsPh<sub>3</sub> or Py) with 2'-hydroxychalcone ligands in dry benzene in equal molar ratio (Scheme 1).

In all these reactions, it has been observed that the 2'hydroxychalcones behave as uninegative bidentate chelating ligands by replacing a triphenylphosphine/arsine and a hydride ion 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 sol-



 $(E = P \text{ or } As; B = PPh_3, AsPh_3 \text{ or } PV; R = 4-(CH_3)C_6H_4, 4-(OCH_3)C_6H_4, 4-(Cl)C_6H_4, 3, 4-(OCH_3)2C_6H_3)$ 

Scheme 1. Formation of Ru(II) chalconate complexes.

vents 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.

#### 3.1. Infrared spectral analysis

The important IR absorption bands for the synthesized ligands and complexes are shown in Table 2. The observed bands may be classified into those originating from the ligands and those arising from the bands formed between ruthenium(II) metal ion and the coordinating sites. The free chalconate ligands showed a strong band in the region 1629–1633 cm<sup>-1</sup> due to  $v_{C=0}$ . This band has been shifted to a lower wave number 1605–1623 cm<sup>-1</sup> in the ruthenium complexes indicating the coordination of the ligands to ruthenium through the carbonyl oxygen atom [26]. A strong band observed at 1332–1340 cm<sup>-1</sup> in the free chalconate ligands has been assigned to phenolic  $v_{C-0}$  stretching. This band has been shifted to higher wave number 1378–1384 cm<sup>-1</sup> in the spectra of the complexes due to its coordination to ruthenium ion through the oxygen atom of the phenolic group [27]. This has been further supported by the disappearance of the broad  $v_{OH}$  band around 3400–3600 cm<sup>-1</sup> in

Table 1
Analytical data of ruthenium(II) chalconate cor

Analytical data of ruthenium(II) chalconate complexes.

the complexes, indicating deprotonation of the phenolic proton prior to coordination to ruthenium metal. Hence, from the infrared spectral data, it is inferred that both the carbonyl and phenolic oxygen atoms are involved in the coordination of the chalcones to ruthenium ion in all the complexes. The absence of  $v_{Ru-H}$  vibration around 2010–2020 cm<sup>-1</sup> in the new complexes indicated that the hydride ion in the starting complexes replaced by chalcone ligands during coordination. The absorption due to  $v_{C-C}$  of the free ligands appeared as a separate band in their infrared spectra around 1600 cm<sup>-1</sup>, but the same could not be identified in the spectra of the ruthenium complexes because of their possible merging with  $v_{C=0}$  [28]. In the complexes, the absorption due to the phenyl alkene vibration appeared in the region 1555–1565 cm<sup>-1</sup>, which is slightly lower than that observed in the spectra of the free ligands [8]. A strong band around 1943–1959 cm<sup>-1</sup> indicates the presence of terminally coordinated carbon monoxide [29]. In the IR spectra of the complexes, a medium intensity band is observed in the region 1024–1028 cm<sup>-1</sup> which is characteristic of coordinated nitrogen bases [30]. In addition, the other characteristic bands due to triphenylphosphine or triphenylarsine (around 1440, 1090 and  $700\,\mathrm{cm}^{-1}$ ) were also present in the spectra of all the complexes [31].

Complex	Formula	Yield (%)	m.p. (°C)	Calculated (found) (%)		
				С	Н	N
$[RuCl(CO)(PPh_3)_2(L^1)]$	C57H45O3P2ClRu	53	153	70.11(69.92)	4.64(4.68)	-
$RuCl(CO)(PPh_3)_2(L^2)$ ]	C57H45O4P2ClRu	61	133	68.98(67.88)	4.57(4.68)	-
$RuCl(CO)(PPh_3)_2(L^3)$ ]	C <sub>56</sub> H <sub>42</sub> O <sub>3</sub> P <sub>2</sub> Cl <sub>2</sub> Ru	58	167	66.25(65.96)	4.41(4.39)	-
$RuCl(CO)(PPh_3)_2(L^4)]$	C58H47O5P2ClRu	62	152	66.97(66.92)	4.80(4.72)	-
$RuCl(CO)(AsPh_3)_2(L^1)]$	C57H45O3As2ClRu	56	151	63.07(63.12)	4.41(4.43)	-
$RuCl(CO)(AsPh_3)_2(L^2)]$	C57H45O4AS2ClRu	49	143	62.11(62.08)	4.34(4.28)	-
$RuCl(CO)(AsPh_3)_2(L^3)]$	C56H42O3As2Cl2Ru	52	142	60.70(60.68)	4.07(3.97)	-
$RuCl(CO)(AsPh_3)_2(L^4)]$	C58H47O5AS2ClRu	55	139	61.49(61.50)	4.41(4.39)	-
$RuCl(CO)(Py)(PPh_3)(L^1)]$	C44H35O3PNCIRu	48	160	65.03(65.24)	4.66(4.46)	1.85(1.79)
$RuCl(CO)(Py)(PPh_3)(L^2)$ ]	C44H35O4PNClRu	51	121	63.69(63.58)	4.56(4.58)	1.81(1.92)
$RuCl(CO)(Py)(PPh_3)(L^3)]$	C43H32O3PNCl2Ru	63	155	61.78(61.86)	4.15(4.11)	1.80(1.84)
$RuCl(CO)(Py)(PPh_3)(L^4)]$	C45H37O5PNCIRu	68	141	65.41(65.22)	4.83(4.79)	1.82(1.78)

Table 2

IR absorption frequencies (cm<sup>-1</sup>) and electronic spectral data (nm) of ruthenium(II) chalconate complexes.

Compound	$v_{C=0}$	ν <sub>C=0</sub>	$\nu_{C-O}$	v <sub>c=c</sub>	$\lambda_{\max}(\varepsilon) (\mathrm{dm^3  mol^{-1}  cm^{-1}})$
L <sup>1</sup>	-	1632	1335	1565	_
L <sup>2</sup>	-	1630	1332	1555	-
L <sup>3</sup>	-	1633	1339	1565	-
L <sup>4</sup>	-	1629	1340	1556	-
$[RuCl(CO)(PPh_3)_2(L^1)]$	1954	1618	1384	1555	326(19,523), 212(31,648)
$[RuCl(CO)(PPh_3)_2(L^2)]$	1943	1605	1383	1550	672(548), 323(19,638), 236(22,523), 202(33,425)
$[RuCl(CO)(PPh_3)_2(L^3)]$	1955	1617	1383	1555	670(542), 210(31,256),
$[RuCl(CO)(PPh_3)_2(L^4)]$	1954	1617	1384	1551	328(19,916), 235(27,141), 213(32,040), 205(34,374)
$[RuCl(CO)(AsPh_3)_2(L^1)]$	1959	1618	1382	1560	678(476), 239(28,498)
$[RuCl(CO)(AsPh_3)_2(L^2)]$	1959	1621	1383	1549	676(512), 237(27,980), 210(31,256)
$[RuCl(CO)(AsPh_3)_2(L^3)]$	1958	1619	1380	1542	677(493), 238(28,252), 203(33,625)
$[RuCl(CO)(AsPh_3)_2(L^4)]$	1959	1623	1378	1548	682(442), 236(27,523)
$[RuCl(CO)(Py)(PPh_3)(L^1)]$	1945	1614	1381	1553	638(592), 278(25,916), 271(26,328), 236(27,523)
$[RuCl(CO)(Py)(PPh_3)(L^2)]$	1945	1606	1383	1550	672(548), 618(708), 330(19,142), 238(28,252)
$[RuCl(CO)(Py)(PPh_3)(L^3)]$	1947	1615	1382	1553	668(562), 278(28,920), 236(27,523), 210(31,256)
$[RuCl(CO)(Py)(PPh_3)(L^4)]$	1945	1615	1383	1553	675(532), 278(28,920), 271(29,563), 236(27,523)

The observed bands in the regions  $460-475 \text{ cm}^{-1}$  in the monouclear complexes are tentatively assigned to the  $v_{\text{Ru-Cl}}$  vibrations [32].

# 3.2. Electronic spectral analysis

All the chalconate ruthenium complexes are diamagnetic, indicating the presence of ruthenium in the +2 oxidation state. The ground state of ruthenium(II) in an octahedral environment is  ${}^{1}A_{1g}$ , arising from the  $t_{2g}^{6}$  configuration, and the excited states corresponding to the  $t_{2g}^{5}$  eg configuration are  ${}^{3}T_{1g}$ ,  ${}^{3}T_{2g}$  and  ${}^{1}T_{1g}$ . Hence, four bands corresponding to the transitions  ${}^{1}A_{1g} \rightarrow {}^{3}T_{1g}$ ,  ${}^{1}A_{1g} \rightarrow {}^{3}T_{2g}$ ,  ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$  and  ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$  are possible in order of increasing energy.

The electronic spectra of all the complexes in dichloromethane showed two to four bands in the region 682–202 nm (Table 2). The bands around 682–618 nm have been assigned to spin allowed  ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$  transition [33] and the other high intensity bands in the visible region around 330–323 nm have been assigned to charge transfer transition based on their extinction coefficient values (Table 2) [34]. The bands that appeared below 300 nm are characterized by intra-ligand charge transfer. The nature of the observed electronic spectra and the position of absorption bands are consistent with those of other similar ruthenium(II) octahedral complexes [35].

#### 3.3. <sup>1</sup>H NMR spectral analysis

The <sup>1</sup>H NMR spectra of the ruthenium(II) complexes were recorded in  $CDCl_3$  to conform the binding of chalcone to ruthenium ion. All the complexes exhibit multiplet in the region 6.73–7.99 ppm in their <sup>1</sup>H NMR spectra (Table 3), which has been assigned to the protons of phenyl groups present in the PPh<sub>3</sub> or AsPh<sub>3</sub> or pyridine

**Table 3** <sup>1</sup>H NMR data ( $\delta$  in ppm) of ruthenium(II) chalconate complexes.

Complex	<sup>1</sup> H NMR (ppm)
$[\operatorname{RuCl}(\operatorname{CO})(\operatorname{PPh}_3)_2(L^3)]$	7.03–7.48 (m, –CH=CH– and aromatic)
$[RuCl(CO)(Py)(PPh_3)(L^2)]$	7.05–7.91 (m, –CH=CH– and aromatic),
	3.83 (s, OCH <sub>3</sub> )
$[RuCl(CO)(Py)(PPh_3)(L^4)]$	6.73–7.99 (m, –CH=CH– and aromatic),
	3.86, 3.83 (s, OCH <sub>3</sub> )
$[RuCl(CO)(AsPh_3)_2(L^1)]$	6.86–7.69 (m, -CH=CH- and aromatic),
	1.58 (s, CH <sub>3</sub> )
$[RuCl(CO)(Py)(PPh_3)(L^3)]$	6.95–7.37 (m, –CH=CH– and aromatic)
$[RuCl(CO)(Py)(PPh_3)(L^1)]$	7.14-7.82 (m, -CH=CH- and aromatic),
	1.52 (s, CH <sub>3</sub> )

and 2'-hydroxychalcone ligands [36]. The signal due to two alkene protons also appeared in the region 6.9–7.1 ppm and hence, merged with the multiplet of aromatic protons. This clearly revealed the absence of alkene coordination to the metal. If alkene carbons were coordinated to the metal, the resonance due to the protons on the alkene carbon would have been shifted to lower  $\delta$  value at least by 2 ppm [37]. The signal for methyl protons appear as a singlet in the region 1.52–1.58 ppm. In addition, a singlet around 3.8 ppm was assigned to methoxy proton. No peak was observed for the OH proton, supporting the fact that the phenolic group is deprotonated, suggesting coordination through the phenolic oxygen of chalcone to the ruthenium. The new complexes did not show any signal in the up-field region (–5 to –12 ppm) for the hydride ligand, thus proving its substitution by the chalcone ligands.

# 3.4. <sup>31</sup> P NMR spectral analysis

<sup>31</sup>P NMR spectra of some of the complexes were recorded to confirm the presence of triphenylphosphine groups and to determine the geometry of the complexes (Table 4, Fig. 2). In the case of the complexes containing two triphenylphosphine ligands, a sharp singlet was observed around 29.03–29.13 ppm due to presence of magnetically equivalent phosphorus atoms suggesting the presence of two triphenylphosphine groups in a position trans to each other [36]. The spectrum of all other complexes exhibited a singlet around 28.53–28.65 ppm corresponding to the presence of triphenylphosphine group in a position trans to heterocyclic nitrogen base [15].

# 3.5. <sup>13</sup>C NMR spectral analysis

The <sup>13</sup>C NMR spectra of some of the complexes were recorded to confirm the formation of new ruthenium(II) chalconate complexes (Table 4). The spectrum shows multiplets around 113.69–135.72 ppm region assigned to aromatic carbons. The alkene carbons appeared in the region 115.45–130.58 ppm, and hence merged with the aromatic carbons. The appearance of a peak at 160.84–168.52 ppm region in the spectrum is due to carbonyl

Table 4
$^{13}$ C NMR and $^{31}$ P NMR data ( $\delta$ in ppm) of ruthenium(II) chalconate complexes.

Complex	<sup>13</sup> C NMR (ppm)	<sup>31</sup> P NMR (ppm)
$[RuCl(CO)(PPh_3)_2(L^1)]$	127.60-134.61(m), 165.96(s), 20.71(s)	29.13
$[RuCl(CO)(PPh_3)_2(L^2)]$	120.69–134.66(m), 160.84(s), 55.43(s)	29.03
$[RuCl(CO)(Py)(PPh_3)(L^2)]$	113.79–134.54(m), 168.52(s), 55.43(s)	28.53
$[RuCl(CO)(Py)(PPh_3)(L^4)]$	115.13-135.72(m), 162.89(s), 55.96(s)	28.65



 $(E = P \text{ or } As; B = PPh_3, AsPh_3 \text{ or } Py; R = 4-(CH_3)C_6H_4, 4-(OCH_3)C_6H_4, 4-(Cl)C_6H_4, 3, 4-(OCH_3)_2C_6H_3)$ 

Fig. 3. Proposed structure of new ruthenium(II) chalconate complexes.

carbon. In addition, sharp singlets appeared at 55.43–55.96 and 20.71 ppm region assigned to methoxy and methyl carbon, respectively.

Based on the analytical and spectral (IR, electronic, <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR) data, an octahedral structure (Fig. 3) has been tentatively proposed for all the ruthenium(II) chalconate complexes.

#### 3.6. Catalytic oxidation

Catalytic oxidation of primary alcohols and secondary alcohols by the synthesized ruthenium(II) carbonyl chalconate complexes were carried out in  $CH_2Cl_2$  in the presence of NMO, and the byproduct water was removed by using molecular sieves. All the complexes oxidize primary alcohols to the corresponding aldehydes and secondary alcohols to ketones (Scheme 2) with high yields and the results are listed in Table 5. 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.



R, R' = alkyl (or) aryl (or) H

Scheme 2. Catalytic oxidation of alcohols.

The oxidation of benzylalcohol to benzaldehyde resulted in 73-99% yield and cyclohexanol to cyclohexanone resulted in 50–98% yield. The relatively higher product yield obtained for the oxidation of benzylalcohol as compared to cyclohexanol is due to the fact that the  $\alpha$ -CH unit of benzylalcohol is more acidic than cyclohexanol [38]. It has been observed that the triphenylarsine ruthenium(II) chalconate complexes possess greater catalytic activity than triphenylphosphine complexes. The catalytic activity of new ruthenium(II) chalconate complexes is comparable with that of corresponding starting complexes for the oxidation of benzyl alcohol whereas the activity is tremendously improved to the new complexes for the oxidation of cyclohexanol. The conversion of primary and secondary alcohols to corresponding aldehydes and ketones increases with increase in reaction time up to 3 h (Fig. 4). It has also been observed that the ruthenium(II) chalconate complexes have better catalytic efficiency in the case of oxidation of primary and secondary alcohols when compared to an earlier report [26] on similar ruthenium complexes as catalysts in the presence of NMO.

Results of the present investigations suggest that the complexes are able to react efficiently with NMO to yield a high valent ruthenium-oxo species [39] capable of oxygen atom transfer to alcohols. This was further supported by spectral changes that occur by addition of NMO to a dichloromethane solution of the ruthenium(II) complexes. The appearance of a peak at 390 nm is attributed to the formation of Ru<sup>IV</sup>=O species, which is in conformity with other oxo ruthenium(IV) complexes [40,41]. Further support in favor of the formation of such species was

#### Table 5

Catalytic oxidation data of ruthenium(II) chalconate complexes.

Complex	Substrate	Product	Yield (%) <sup>a</sup>	TONb
$[RuCl(CO)(PPh_3)_2(L^1)]$	Benzyl alcohol	A	81	81
	Cyclohexanol	B	79	79
$[RuCl(CO)(PPh_3)_2(L^2)]$	Benzyl alcohol	A	93	93
	Cyclohexanol	B	90	90
$[RuCl(CO)(PPh_3)_2(L^4)]$	Benzyl alcohol	A	92	92
	Cyclohexanol	B	71	71
$[RuCl(CO)(AsPh_3)_2(L^1)]$	Benzyl alcohol	A	89	89
	Cyclohexanol	B	85	85
$[RuCl(CO)(AsPh_3)_2(L^2)]$	Benzyl alcohol	A	90	90
	Cyclohexanol	B	88	88
[RuCl(CO)(AsPh <sub>3</sub> ) <sub>2</sub> (L <sup>3</sup> )]	Benzyl alcohol	A	99	99
	Cyclohexanol	B	98	98
[RuCl(CO)(AsPh <sub>3</sub> ) <sub>2</sub> (L <sup>4</sup> )]	Benzyl alcohol	A	85	85
	Cyclohexanol	B	79	79
$[RuCl(CO)(Py)(PPh_3)(L^2)]$	Benzyl alcohol	A	84	84
	Cyclohexanol	B	75	75
[RuCl(CO)(Py)(PPh <sub>3</sub> )(L <sup>3</sup> )]	Benzyl alcohol	A	73	73
	Cyclohexanol	B	70	70
[RuCl(CO)(Py)(PPh <sub>3</sub> )(L <sup>4</sup> )]	Benzyl alcohol	A	93	93
	Cyclohexanol	B	71	71
[RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub> ]	Benzyl alcohol	A	81	81
	Cyclohexanol	B	37	37
[RuHCl(CO)(AsPh <sub>3</sub> ) <sub>3</sub> ]	Benzyl alcohol	A	87	87
	Cyclohexanol	B	52	52
[RuHCl(CO)(Py)(PPh <sub>3</sub> ) <sub>2</sub> ]	Benzyl alcohol	A	81	81
	Cyclohexanol	B	46	46

A: benzaldehyde; B: cyclohexanone.

<sup>a</sup> Yield determined by GC and comparing with the analyses of authentic samples.

<sup>b</sup> Ratio of moles of product obtained to the moles of the catalyst used.

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<sup>-1</sup>, characteristic of Ru<sup>IV</sup>=O species [39,41] (Scheme 3).

#### 3.7. Catalytic transfer hydrogenation

The catalytic transfer hydrogenation of ketones in the presence of ruthenium chalconate complexes has been studied in



Fig. 4. Catalytic oxidation of benzylalcohol (A) and cyclohexanol (B) in different time intervals.



Scheme 3. Proposed catalytic cycle for the oxidation of alcohols by the Ru(II) chalconate complexes.



Scheme 4. Catalytic transfer hydrogenation of ketones.

isopropanol–KOH medium using a molar ratio 1:2.5:300 for the catalyst, KOH and the ketone in 10 cm<sup>3</sup> of isopropanol (Scheme 4).

Typical results are shown in Table 6. The catalyst performed efficiently for both aliphatic and aromatic ketones with high conversion and turnover. Cyclohexanone was converted into cyclohexanol in 96–99% yield. Acetophenone was converted into corresponding alcohol in 73-89% yield. Similarly, isobutyl methyl ketone underwent transfer hydrogenation to afford the corresponding alcohol in 75–78% yield, and found that all type of the catalysts performed efficiently for reduction of cyclohexanone to cyclohexanol. The catalytic efficiency of new ruthenium(II) chalconate complexes is moderately increased for conversion of cyclohexanone to cyclohexanol whereas the activity is tremendously improved for reduction of acetophenone and isobutyl methyl ketone when compared to corresponding starting complexes. In the absence of base no transfer hydrogenation of ketones was observed. The role of KOH is to generate the catalyst from the chloro precursor and the reaction mediates through the hydride species. The base facilitated the formation of the ruthenium alkoxide by abstracting the proton of the alcohol and subsequently, the alkoxide underwent β-elimination to give a ruthenium hydride which is the active species in this reaction.

Addition of bases like NaOH or Na-(iOPr) also leads to similar final conversion, but the highest rate was observed when KOH was employed [42]. Pamies and Backvall [43] studied the mechanism for a number of bisphosphineruthenium(II) complexes by monitoring the racemization of monodeuterated S-phenylethylalcohol with acetophenone and found that the catalysts under study in most of the cases followed the monohydride pathway. Since our catalysts are similar to those studied by Pamies and Backvall we assumed that the reactions followed the monohydride pathway.

#### 3.8. Antifungal activity

The *in vitro* antifungal screening against *Aspergillus niger* and *Mucor Sp.* for the ligands and some of their ruthenium(II) complexes have been carried out by disc diffusion method [44]. The results (Table 7) showed that the new ruthenium(II) chalconate complexes are more toxic than their parent ligands and starting complexes against the same microorganisms and under identical experimental conditions. The increase in the antifungal activity of the metal chelates may be due to the effect of the metal ion on the normal cell

process. A possible mode for toxicity increase may be considered in the light of Tweedy's chelation theory [45]. 'Chelation reduces the polarity of the metal ion because of partial sharing of its positive charge with the donor groups and possible  $\pi$ -electron delocalization over the whole chelate ring. Such chelation could enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the lipid layers of the cell membrane' [46]. Further, the toxicity of the compounds increases with increase in concentration. Though the complexes possess activity, it could not reach the effectiveness of the standard drug *Bavistin*. The

# Table 6

Catalytic transfer hydrogenation of ketones by ruthenium(II) chalconate complexes<sup>a</sup>.

Complex	Substrate	Product	Conversion (%)	TON <sup>b</sup> (TOF) <sup>c</sup>
[RuCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> (L <sup>2</sup> )]	C <sup>°</sup>	OH	89	267(534)
		OH OH	78	234(468)
	Ŭ		99	297(594)
[RuCl(CO)(AsPh <sub>3</sub> ) <sub>2</sub> (L <sup>3</sup> )]		OH	73	219(438)
		OH OH	75	225(450)
	Ŭ		96	288(576)
[RuCl(CO)(Py)(PPh <sub>3</sub> )(L <sup>4</sup> )]		OH	77	231(462)
	> î	OH	76	228(456)
		OH	99	297(594)
[RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub> ]		OH	18	54(108)
	X	OH	16	48(96)
	Ů	OH	88	264(528)
[RuHCl(CO)(AsPh <sub>3</sub> ) <sub>3</sub> ]	Ů	OH	38	114(228)
		OH	26	78(156)
	ů –	OH	87	261(522)

#### Table 6 (Continued)



<sup>a</sup> Conditions: reactions were carried out at 80 °C using 3.75 mmol of ketone (10 cm<sup>3</sup> isopropanol); catalyst/ketone/KOH ratio 1:300:2.5.

<sup>b</sup> 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. TON = ratio of moles of product obtained to the moles of the catalyst used.

<sup>c</sup> TOF (TON h<sup>-1</sup>).

#### Table 7

Fungicidal activity data for some ruthenium(II) chalconate complexes.

Compound	Diameter of inhibition zone (mm)					
	Aspergillus	niger	Mucor Sp.	Mucor Sp.		
	50 ppm	100 ppm	50 ppm	100 ppn		
L <sup>2</sup>	6	8	8	9		
[RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub> ]	9	11	9	11		
[RuHCl(CO)(AsPh <sub>3</sub> ) <sub>3</sub> ]	7	9	8	11		
[RuHCl(CO)(Py)(PPh <sub>3</sub> ) <sub>2</sub> ]	8	11	10	11		
$[RuCl(CO)(PPh_3)_2(L^2)]$	14	17	14	16		
$[RuCl(CO)(AsPh_3)_2(L^2)]$	9	11	9	12		
$[RuCl(CO)(Py)(PPh_3)(L^2)]$	11	16	12	14		
Bavistin	38	56	42	53		

variation in the effectiveness of the different compounds against different organisms depends either on the impermeability of the cells of the microbes or differences in ribosomes of microbial cells.

# 4. Conclusions

Several new ruthenium(II) chalconate complexes were synthesized using chalconate formed from derivatives of benzaldehyde and 1-acetyl-2-naphthol. The new complexes have been characterized by analytical and spectral data. An octahedral structure has been tentatively proposed for all the complexes. The complexes showed efficient catalytic property for the oxidation of both primary and secondary alcohols to the corresponding carbonyl compounds with excellent yields in the presence of *N*methylmorpholine-*N*-oxide, and also for transfer hydrogenation of aliphatic and aromatic ketones with high conversions (>99%).

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