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Ruthenium(II) carbonyl complexes containing chalconates and triphenylphosphine/arsine

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Abstract. A series of new hexa-coordinated ruthenium(II) carbonyl complexes of the type $[RuCl(CO)(EPh_3)(B)(L^{1-4})]$ (4–15) (E = P or As; B = PPh_3, $AsPh_3$ or Py; L = 2′-hydroxychalcone) were synthesized from the reaction of $[RuHCl(CO)(EPh_3)_2(B)]$ (1–3) (E = P or As; B = PPh_3, $AsPh_3$ or Py) with equimolar chalcone in benzene under reflux. The new complexes have been characterized by analytical and spectroscopic (IR, electronic, ^1H, $^{31}P\{^1H\}$, and ^{13}C NMR) methods. On the basis of data obtained, an octahedral structure has been assigned for all the complexes. The 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 were also found to be efficient transfer hydrogenation catalysts. The antifungal properties of the ligands and their complexes have also been examined and compared with standard *Bavistin*.

Keywords. Ruthenium(II) complexes; spectroscopic studies; catalytic oxidation; catalytic transfer hydrogenation, antifungal study.

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 the coordination environment around the central metal ion imparts the properties of complexes, complexation of ruthenium by diverse ligands is of significant importance.[5,6] Organometallic compounds containing phosphine ligands are extensively synthesized due to their structural importance and catalytic applications in both small-scale organic synthesis and bulk industrial production.[7–9]

Oxidation using transition metal complexes is one of the most important and basic reactions in organic synthesis and is being developed as a topic of much current interest.[10–15] Catalytic oxidations may be considered to be one of the more environmentally friendly reactions[16] and most important transformations in industrial chemistry.[17]

Catalytic reduction of ketones to produce secondary alcohols can be carried out using transfer hydrogenation.[18] In view of the low cost of the reducing agent and its operational simplicity, transition-metal catalysed hydrogenation, either with isopropyl alcohol or with a formic acid/triethylamine mixture as a hydride source, has emerged as an attractive alternative to asymmetric hydrogenation with H_2. One of the most efficient systems has been reported by the group of Noyori.[19] Utilizing a ruthenium(II) catalyst, isopropyl alcohol as a donor and potassium hydroxide as a promoter, Noyori and co-workers have demonstrated that transfer hydrogenation reactions of aromatic ketones can occur at room temperature.

The preparation of a new ligand was perhaps the most important step in the development of metal complexes which exhibit unique properties and novel reactivity. Chalcones, an important class of compounds that are widely distributed in nature, have attracted a great deal of interest due to their applications as antibacterial, antiinflammatory and anticancer pharmacological agents.[20–22] Several chalcones are intensively studied, modified and synthesized in order to develop more potential biological and catalytic activities. The search for catalytic oxidations with inexpensive green oxidants such as molecular oxygen or air still plays a key role in the development of industrial processes. In this line triphenylphosphine/arsine complexes of ruthenium have been found to be efficient catalyst for the

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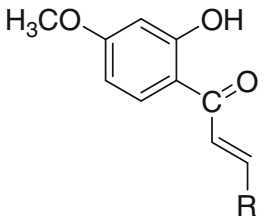
oxidation of alcohols. In addition, ruthenium complexes have long pedigree as catalysts for transfer hydrogenation reactions in the presence of isopropanol as hydrogen source.

In continuation of our effort to synthesize new catalyst system, we report here the synthesis of a series of hexa-coordinated ruthenium(II) complexes with chalcone and other co-ligands. The characterization of the complexes was accomplished by analytical and spectral methods. The synthesized complexes have been effectively used as catalyst in the oxidation of alcohols in the presence of NMO and transfer hydrogenation of ketones in isopropanol with KOH as base. Further, antifungal properties of the synthesized complexes have also been tested.

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.[23] $RuCl_3.3H_2O$ was purchased from Loba Chemie Pvt. Ltd., and was used without further purification. The starting complexes $[RuHCl(CO)(PPh_3)_3]$ (1),[24] $[RuHCl(CO)(AsPh_3)_3]$ (2)[25] and $[RuHCl(CO)(Py)(PPh_3)_2]$ (3)[26] were prepared according to the literature methods. The general structure of the chalcone ligands used in this study is given below (figure 1).



Ligand	R
L^1	4-$(CH_3)C_6H_4$
L^2	4-$(OCH_3)C_6H_4$
L^3	4-$(Cl)C_6H_4$
L^4	3, 4-$(OCH_3)_2C_6H_3$

Figure 1. Structure of chalcone.

2.2 *Instrumentation*

Analyses of carbon, hydrogen and nitrogen were performed in Carlo Erba 1108 analyzer at Central Drug Research Institute (CDRI), Lucknow, India. FT-IR spectra were recorded in KBr pellets with a Nicolet FT-IR spectrophotometer in 400–4000 cm^{-1} range. Electronic spectra of the complexes have been recorded in CH_2Cl_2 on a Shimadzu UV-visible 1650 PC spectrophotometer in 200–800 nm range. The NMR spectra (^1H, $^{31}P\{^1H\}$ and ^{13}C) were recorded in Jeol GSX- 400 instrument. The samples were dissolved in $CDCl_3$ and ^1H NMR and ^{13}C NMR spectra were obtained using TMS as the internal standard. $^{31}P\{^1H\}$ NMR spectra of the complexes were obtained using ortho phosphoric acid as a reference. The catalytic yields were determined using ACME 6000 series Gas chromatography instrument equipped with a flame ionization detector (FID) using a DP-5 column of 30 m length, 0.53 mm diameter and 5.00 μm film thickness. Melting points were recorded on a Technico micro heating table and are uncorrected.

2.3 *Synthesis of chalcone ligands*

Chalcone ligands were synthesized by stirring 2-hydroxy-4-methoxy acetophenone (0.8309 g, 5 mmol) with corresponding substituted benzaldehyde (0.6007–0.8309 g, 5 mmol) in the presence of 50 mL alcoholic sodium hydroxide solution (20%). After 24 h stirring, the reaction mixture was treated with conc. HCl (5 mL, 5 M), resulting in the formation of precipitate. The precipitate was filtered, dried under vacuum. Yield = 80% (0.6601 g, 5 mmol, L^1), 75% (0.6200 g, 5 mmol, L^2), 88% (0.7302 g, 5 mmol, L^3), 78% (0.6503 g, 5 mmol, L^4). The compounds are purified by crystallization from ethanol solution.

2.4 *Synthesis of new ruthenium(II) chalconate complexes (4–15)*

All complexes were synthesized by the following common procedure. To a solution of $[RuHCl(CO)(EPh_3)_2$ (B)](1-3) (E = P or As; B = PPh_3, $AsPh_3$ or Py) (0.1 g) in benzene (20 mL), the appropriate chalcone (0.0247–0.0409 g) were added in 1:1 molar ratio. The mixture was heated under reflux for 6 h. After the reaction time, the reaction mixture was concentrated to around 3 mL. The reaction mixture was cooled and then treated with 10 mL of petroleum ether (60–80°C), resulting in the formation of new ruthenium chalconate complex. The complex was filtered, dried under vacuum. Yield = 76%

(4), 65% (5), 72% (6), 68% (7), 67% (8), 79% (9), 81% (10), 72% (11), 74% (12), 82% (13), 76% (14), 79% (15). The complexes were purified by crystallization from CH_2Cl_2/petroleum ether mixture. The purity of the complexes was checked by NMR.

2.5 *Procedure for catalytic oxidation of alcohols*

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 substrate at 1:100 molar ratio was described as follows. A solution of ruthenium complex (0.01 mmol) in CH_2Cl_2 (20 mL) was added to the mixture containing substrate (1 mmol), NMO (3 mmol) and molecular sieves. The reaction mixture was refluxed for 1 h, and the solvent was then evaporated from the mother liquor under reduced pressure. The solid residue was then extracted with diethyl ether (20 mL), concentrated to ≈1 mL and was analysed by GC. The oxidation products were identified by GC co-injection with authentic samples.

2.6 *Procedure for catalytic transfer hydrogenation of ketone*

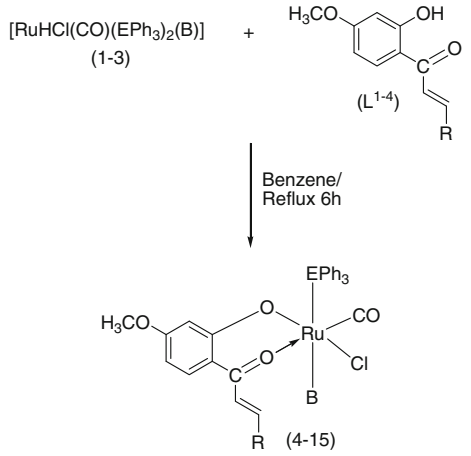
The catalytic transfer hydrogenation reactions were studied using ruthenium(II) chalconate complex as a catalyst, ketone as substrate and KOH as promoter at 1:300:2.5 molar ratios. The procedure was described as follows. A mixture containing ketone (3.75 mmol), the ruthenium complex (0.0125 mmol) and KOH (0.03 mmol) in 10 mL of isopropyl alcohol was reacted under reflux in water bath for different time period. 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 concentrated to ≈1 mL and 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 [Ru(CO)-$(EPh_3)(B)(L^{1-4})$] (4–15) (E = P or As; B = PPh_3, $AsPh_3$ or Py; L = chalcone) were synthesized in good yields from the reaction of $[RuHCl(CO)(EPh_3)_2(B)]$ (1–3) (E = P or As; B = PPh_3, $AsPh_3$ or Py) with chalcone ligands in dry benzene in equal molar ratio (scheme 1).

In all these reactions, it has been observed that the chalcones behave as monoanionic 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 colour, non-hygroscopic and



(E = P or As; B = PPh_3, $AsPh_3$ or Py; L^1 = R = 4-$(CH_3)C_6H_4$, L^2 = R = 4-$(OCH_3)C_6H_4$, L^3 = R = 4-$(Cl)C_6H_4$,

L^4 = R = 3, 4-$(OCH_3)_2C_6H_3$)

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

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

Complex	Yield (%)	D.Pt (°C)	Calculated (found) (%)		
			C	H	N
[RuCl(CO)(PPh_3)$_2$(L^1)] (4)	76	171	67.82(67.68)	4.74(4.76)	–
[RuCl(CO)(PPh_3)$_2$(L^2)] (5)	65	138	66.70(66.58)	4.66(4.63)	–
[RuCl(CO)(PPh_3)$_2$(L^3)] (6)	72	178	65.17(64.98)	4.33(4.35)	–
[RuCl(CO)(PPh_3)$_2$(L^4)] (7)	68	143	65.90(66.02)	4.73(4.72)	–
[RuCl(CO)($AsPh_3$)$_2$(L^1)](8)	67	144	62.11(62.16)	4.34(4.32)	–
[RuCl(CO)($AsPh_3$)$_2$(L^2)] (9)	79	115	61.17(61.18)	4.28(4.26)	–
[RuCl(CO)($AsPh_3$)$_2$(L^3)] (10)	81	138	59.79(59.72)	3.98(4.02)	–
[RuCl(CO)($AsPh_3$)$_2$(L^4)] (11)	72	134	60.59(60.61)	4.34(4.37)	–
[RuCl(CO)(Py)(PPh_3)(L^1)] (12)	74	195	63.69(63.54)	4.56(4.58)	1.81(1.89)
[RuCl(CO)(Py)(PPh_3)(L^2)] (13)	82	142	62.39(62.33)	4.47(4.51)	1.77(1.72)
[RuCl(CO)(Py)(PPh_3)(L^3)] (14)	76	136	60.54(60.56)	4.06(4.10)	1.76(1.73)
[RuCl(CO)(Py)(PPh_3)(L^4)] (15)	79	132	61.58(61.46)	4.55(4.57)	1.71(1.67)

highly soluble in common organic solvents such as dichloromethane, acetonitrile, chloroform, benzene 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 spectroscopic analysis*

The important IR absorption bands for the synthesized ligands and complexes are shown in table 2. The free chalcone ligands showed a strong band in the region 1631–1642 cm^{-1} due to υ_{C-O}. This band has been shifted to a lower wave number 1603–1623 cm^{-1} in the ruthenium complexes indicating the coordination of the ligands to ruthenium through the carbonyl oxygen atom.[27] A strong band observed at 1358–1365 cm^{-1} in the free chalcone ligands has been assigned to phenolic υ_{C-O} stretching. This band has been shifted to higher wave number 1372–1384 cm^{-1} in the spectra of the complexes due to its coordination to ruthenium ion through the oxygen atom of the phenolic group.[28] This has been further supported by the disappearance of the broad υ_{OH} band around 3400–3600 cm^{-1} in the complexes, indicating deprotonation of the phenolic proton prior to coordination to ruthenium metal. Hence, from the infrared spectroscopic data, it is inferred that both the carbonyl and phenolic oxygen atoms are involved in the coordination of the chalcone to ruthenium ion in all the complexes. The absorption due to

Table 2. IR absorption frequencies (cm^{-1}) of free ligands and their ruthenium(II) chalconate complexes.

Compound	$\nu_{C\equiv O}$	$\nu_{C=O}$	$\nu_{C=C}$	ν_{C-O}	PPh_3/$AsPh_3$
L^1	-	1631	1568	1358	-
L^2	-	1634	1574	1363	-
L^3	-	1642	1582	1361	-
L^4	-	1636	1565	1365	-
4	1955	1606	1543	1380	1435, 1093, 696
5	1952	1603	1542	1382	1434, 1093, 695
6	1952	1603	1542	1382	1434, 1093, 695
7	1950	1605	1542	1384	1436, 1094, 696
8	1960	1618	1549	1373	1434, 1075, 692
9	1959	1612	1549	1382	1435, 1076, 692
10	1960	1623	1545	1372	1434, 1076, 692
11	1959	1623	1548	1381	1435, 1076, 693
12	1945	1605	1541	1380	1446, 1095, 694
13	1943	1603	1542	1382	1438, 1094, 695
14	1944	1606	1544	1380	1438, 1092, 694
15	1945	1604	1543	1381	1437, 1092, 696

υ_{C-C} of the free ligands appeared as a separate band in their infrared spectra around 1600 cm^{-1}, but the same could not be identified in the spectra of the ruthenium complexes because of their possible merging with υ_{C-O}.[29] In the complexes, the absorption due to the phenyl alkene vibration appeared in the region 1565–1582 cm^{-1}, which is slightly lower than that observed in the spectra of the free ligands.[30] A strong band around 1943–1960 cm^{-1} indicates the presence of terminally coordinated carbon monoxide[31] in all the complexes. In the IR spectra of the complexes containing pyridine, a medium intensity band is observed in the region of 1017–1023 cm^{-1} which is characteristic of coordinated nitrogen bases.[32] In addition, the other characteristic bands due to triphenylphosphine or triphenylarsine (around 1440, 1090 and 700 cm^{-1}) were also present in the spectra of all the complexes.[33] The observed bands in the regions 454–476 cm^{-1} in the mononuclear complexes are tentatively assigned to the υ_{Ru-Cl} vibrations.[34]

Table 3. Electronic spectroscopic data (nm) of free ligands and their ruthenium(II) chalconate complexes.

Compound	λ_{max}	Assignments
L^1	301, 246, 204	n - π^*, π - π^*
L^2	307, 247, 206	n - π^*, π - π^*
L^3	298, 245, 205	n - π^*, π - π^*
L^4	289, 245, 209	n - π^*, π - π^*
4	358, 234, 205	n - π^*, π - π^*, C.T
5	371, 338, 240, 204	n - π^*, π - π^*, C.T
6	362, 334, 238, 208	n - π^*, π - π^*, C.T
7	401, 373, 246, 207	n - π^*, π - π^*, C.T
8	332, 244, 209	n - π^*, π - π^*, C.T
9	368, 336, 246, 207	n - π^*, π - π^*, C.T
10	334, 249, 208	n - π^*, π - π^*, C.T
11	334, 258, 248, 218	n - π^*, π - π^*, C.T
12	365, 240, 209	n - π^*, π - π^*, C.T
13	368, 243, 208	n - π^*, π - π^*, C.T
14	338, 239, 209	n - π^*, π - π^*, C.T
15	389, 374, 236, 209	n - π^*, π - π^*, C.T

3.2 *Electronic spectroscopic 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 $^1A_{1g}$, arising from the t_{2g}^6 configuration, and the excited states corresponding to the $t_{2g}^5 e_g^1$ configuration are $^3T_{1g}$, $^2T_{2g,}^1$ T_{1g} and $^1T_{2g}$. Hence, four bands corresponding to the transitions $^1A_1 \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ are possible in the order of increasing energy.

The electronic spectral data of the free ligands and their complexes in dichloromethane are listed in table 3. The spectra of all the free ligands showed two types of transitions. The peak appeared at 204–247 nm range was assigned to $\pi - \pi^*$ transitions involving molecular orbital located on the phenolic chromophore. These peaks have been shifted in the spectra of the complexes; this may be due to the donation of a lone pair of electrons by the oxygen of the phenoxy group to the central metal atom.[35] The second type of transitions appeared at 289–307 nm range assigned to n – π^* transitions involving molecular orbital of the −C=O chromophore and the benzene ring. These bands have also been shifted upon complexation indicated that, the carbonyl group oxygen atom appears to be coordinated to the metal ion.[36] The spectra of all the complexes show another type of transition different from the free ligands. The bands appeared at range 332–401 nm, which can be assigned to charge transfer transitions.[37] The nature of the observed electronic spectra and the position of absorption bands are consistent with those of other similar ruthenium(II) octahedral complexes.[37]

3.3 ^1H *NMR Spectroscopic analysis*

The ^1H NMR spectra of the ruthenium(II) chalconate complexes were recorded in $CDCl_3$ to confirm the binding of chalcone to ruthenium ion. All the complexes exhibit series of overlapping multiplet in the region 6.54–7.75 ppm in their ^1H NMR spectra (table 4), which have been assigned to the protons of phenyl groups present in the PPh_3 or $AsPh_3$ or Py and chalcone.[30] The signal for alkene protons also appeared in the region 6.5–7.5 ppm and hence, merged with the multiplet of aromatic protons. The signal for $(-OCH_3)C_6H_4$ methoxy proton was observed as a singlet at 3.90–4.07 ppm region and $(-OCH_3)C_6H_3$ methoxy protons appeared as a singlet at 3.53–3.62 ppm region.

Further, the signal for methyl protons appeared as a singlet at 1.25–1.26 ppm region. No peak was observed for the OH protons, supporting the assumption that the phenolic hydroxyl group is deprotonated and coordinated through the oxygen of chalcone to the ruthenium.

3.4 $^{31}P\{^1H\}$ *NMR spectroscopic analysis*

$^{31}P\{^1H\}$ NMR spectra of some of the complexes were recorded to confirm the presence of triphenylphosphine

Table 4. ^{1}H NMR data (δ in ppm) of free ligands and their ruthenium(II) chalconate complexes.

Complex	δ(ppm)
4	6.92–7.56 (m, aromatic and -CH=CH-), 3.54 (OCH_3), 1.26 (s,CH_3)
7	7.07–7.66 (m, aromatic and -CH=CH-), 4.07, 3.96, 3.58 (OCH_3)
9	6.99–7.74 (m, aromatic and -CH=CH-), 3.90, 3.62 (OCH_3)
10	6.89–7.65 (m, aromatic and -CH=CH-), 3.59 (OCH_3)
12	7.21–7.68 (m, aromatic and -CH=CH-), 3.53 (OCH_3), 1.25 (s,CH_3)
14	6.54–7.75 (m, aromatic and -CH=CH-), 3.62 (OCH_3)

groups and to determine the geometry of the complexes (table 5). In the case of the complexes containing two triphenylphosphine ligands, a sharp singlet was observed around 30.05–30.12 ppm due to presence of magnetically equivalent phosphorus atoms suggesting the presence of two triphenylphosphine groups in a position *trans* to each other.[35] The spectrum of all other complexes exhibited a singlet around 30.05 ppm corresponding to the presence of triphenylphosphine group in a position *trans* to heterocyclic nitrogen base.[14]

3.5 ^{13}*C NMR Spectroscopic analysis*

The ^{13}C NMR spectra of ruthenium(II) chalconate complexes (table 5) exhibit a resonance at 208.25–204.98 ppm region and are assigned to CO carbon. A sharp singlet appeared at 179.26–177.83 ppm region. This band was assigned to phenolic –C–O carbon. The appearance of a peak at 167.58–163.73 ppm region in the spectra is due to coordinated carbonyl carbon. Multiplets appeared around 135.52–124.27 ppm region have been assigned to aromatic carbons. The alkene carbons appeared in the region 134.58–125.45 ppm, and hence merged with the aromatic carbons. The two singlet appeared around 55.38 and 54.96–54.86 ppm region assigned to methoxy carbon of $(-OCH_3)C_6H_4$ and $(-OCH_3)C_6H_3$ groups. In addition, methyl carbon appeared at 20.34 ppm region.

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 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 and the results are listed in table 6. The aldehydes or ketones formed after 1 h of reflux were determined by GC and there was no detectable oxidation in the absence of ruthenium complex. The catalytic activity of new ruthenium(II) chalconate complexes is comparable with that of corresponding starting complexes in the case of oxidation of benzyl alcohol. The new complexes exhibit greater catalytic activities for the oxidation of cyclohexanol.

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] which is capable of oxygen atom transfer to alcohols. This was further supported by spectroscopic changes that occur by addition of NMO to a dichloromethane solution of the ruthenium(II) complexes. The appearance of a peak at 390 nm in UV-Vis spectra is attributed to the formation of $Ru^{IV} = O$ species, which was also found for other oxo ruthenium(IV) complexes.[40,41] Further support in favour of the formation of such species was identified from the IR spectra of the solid mass (obtained by

Table 5. ^{13}C NMR and ^{31}P{^{1}H} NMR data (δ in ppm) of ruthenium(II) chalconate complexes.

Complex	^{13}C NMR (ppm)	^{31}P{^{1}H} NMR (ppm)
4	206.34(s), 178.68(s), 167.49(s), 124.27–132.73(m), 54.93(s), 20.34(s)	30.12
6	205.92(s), 177.83(s), 163.73(s), 127.75–134.36(m), 54.89(s)	30.05
13	208.25(s), 179.26(s), 167.58(s), 127.76–134.51(m), 55.36(s), 54.86(s)	30.05
14	204.98(s), 178.18(s), 165.74(s), 127.13–135.52(m), 54.96(s)	30.05

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

Complex	Substrate	Product	Yield (%)[a]
5	Benzyl alcohol	A	98
	Cyclohexanol	B	89
6	Benzyl alcohol	A	86
	Cyclohexanol	B	81
9	Benzyl alcohol	A	99
	Cyclohexanol	B	80
10	Benzyl alcohol	A	97
	Cyclohexanol	B	76
11	Benzyl alcohol	A	94
	Cyclohexanol	B	74
12	Benzyl alcohol	A	99
	Cyclohexanol	B	53
13	Benzyl alcohol	A	94
	Cyclohexanol	B	51
15	Benzyl alcohol	A	93
	Cyclohexanol	B	54
1	Benzyl alcohol	A	81
	Cyclohexanol	B	37
2	Benzyl alcohol	A	87
	Cyclohexanol	B	52
3	Benzyl alcohol	A	81
	Cyclohexanol	B	46

A: Benzaldehyde; B: Cyclohexanone
[a]Yields were determined by GC and comparing with the analyses of authentic samples[38] (Benzaldehyde, Cyclohexanone).

evaporation of the resultant solution to dryness), which showed a band at 860 cm^{-1}, characteristic of $Ru^{IV} = O$ species.[39,41]

3.7 *Catalytic transfer hydrogenation*

Ruthenium mediated transfer hydrogenation reactions are found to be effective catalytic systems in which hydrogen is transferred from one organic molecule to another and this made us interested to carry out this type of reactions.

The complexes $[RuCl(CO)(PPh_3)_2(L^4)]$ (7), $[RuCl(CO)(AsPh_3)_2(L^1)]$ (8) and $[RuCl(CO)(Py)(PPh_3)(L^3)]$ (14) are taken as model catalyst and the catalytic activity in the transfer hydrogenation of various aliphatic and aromatic ketones in the presence of isopropyl alcohol and KOH as promoter has been explored. The complexes catalyse the reduction of ketones to corresponding alcohols in excellent yields and in relatively short reaction times and the results of these organic transformations are presented in table 7.

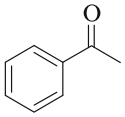
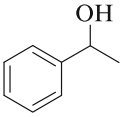
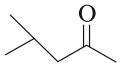
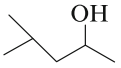
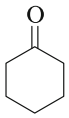
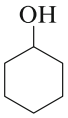
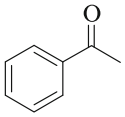
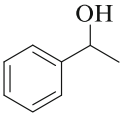
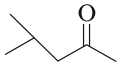
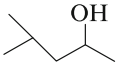
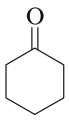
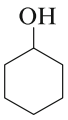
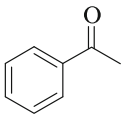
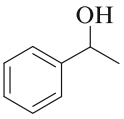
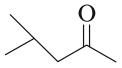
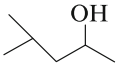
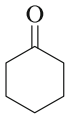
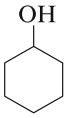
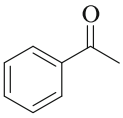
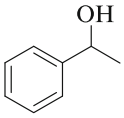
Cyclohexanone was converted into cyclohexanol in excellent yield (99%) for all the catalyst. Acetophenone was converted into corresponding alcohol in moderate yield (62–77%). Similarly, isobutyl methyl ketone underwent transfer hydrogenation to afford the corresponding alcohol in moderate yield (65–79%). It has been found that complexes containing triphenylphosphine or pyridine as ligands possess higher catalytic activity than triphenylarsine as ligands for the substances acetophenone and isobutyl methyl ketone. 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.

We were also interested in mechanism of the above transfer hydrogenation processes. Although no studies have been carried out to determine the mechanism for these particular catalytic processes, it is generally assumed that transition-metal-catalysed hydrogen transfer involves metal hydrides as key intermediates. An essential component for this reaction is potassium hydroxide, which facilitates 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 intermediate and release of acetone. Formation of Ru–H complexes from Ru–Cl precursors has been well-documented,[10] and such *in situ* formed Ru–H species can act as the active catalysts for transfer hydrogenation of ketones.[42,43] Coordination of a ketone substrate to Ru–H intermediate produces a new compound and is followed by insertion of the coordinated ketone carbonyl into the Ru–H bond to form new Ru-alkoxide which is then reacted with isopropyl alcohol to afford the alcohol product.

3.8 *Antifungal activity*

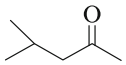
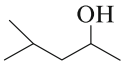
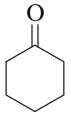
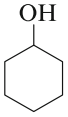
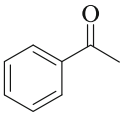
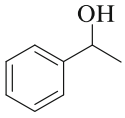
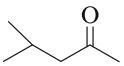
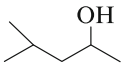
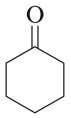
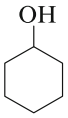
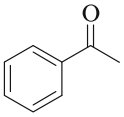
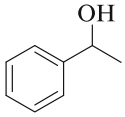
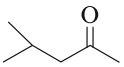
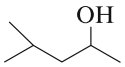
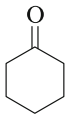
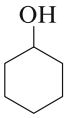
One of the chalcone ligands and their ruthenium chelates were screened *in vitro* in order to evaluate their antifungal activity against *Aspergillus niger* and *Mucor* Species at two different concentrations by disc diffusion method.[44] The results (table 8) showed that the ruthenium chelates are more toxic as compared with their parent ligand against the same microorganisms under identical experimental conditions. The increase in the antifungal activity of 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

Table 7. Catalytic transfer hydrogenation of ketones by ruthenium(II) chalconate complexes.[a]

Complex	Substrate	Product	Time (mts)	Conversion [b] (%)
7			120	72
			120	79
			60	99
8			120	62
			120	65
			15	99
14			120	77
			120	77
			60	99
1			120	28

considered in the light of Tweedy's chelation theory.[45] 'Chelation considerably reduces the polarity of the metal ion because of partial sharing of its positive charge with the donor groups and possible π-electron delocalization over the whole chelate ring. Such chelation could enhance the lipophilic character of the central metal atom, which subsequently favours its permeation through the lipid layers of 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*.

Table 7. (*continued*).

Complex	Substrate	Product	Time (mts)	Conversion [b] (%)
			120	26
			60	88
2			120	38
			120	26
			60	87
3			120	28
			120	26
			60	89

[a]Conditions: reactions were carried out under heated to reflux. 3.75 mmol of ketone (10 mL isopropyl alcohol); catalyst/ketone/KOH ratio 1:300:2.5
[b]Yields were determined by GC and comparison with authentic samples

Table 8. Fungicidal activity data for some ruthenium(II) chalconate complexes.

Compound	Diameter of inhibition zone (mm)			
	Aspergillus niger		*Mucor* Species	
	50 ppm	100 ppm	50 ppm	100 ppm
L^4	6	10	8	13
7	18	42	21	36
11	23	45	24	47
15	21	41	20	43
Bavistin	38	56	42	53

4. Conclusions

Several new ruthenium(II) chalconate complexes were synthesized using chalcone ligands synthesized from the reaction between benzaldehyde and 2-hydroxy-4-methoxyacetophenone. The new complexes have been characterized by analytical and spectroscopic 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 short reaction time and also for transfer hydrogenation of ketones

with high conversions. The complexes also exhibit considerable amount of antifungal activity at the time of screening.

Supplementary material

Representative Uv-Vis, ^{1}H NMR, ^{31}P{^{1}H} NMR and ^{13}C NMR spectrum of ruthenium(II) chalconate complexes have been provided as figures S1–S4 in supplementary materials (see www.ias.ac.in/chemsci).

Acknowledgements

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