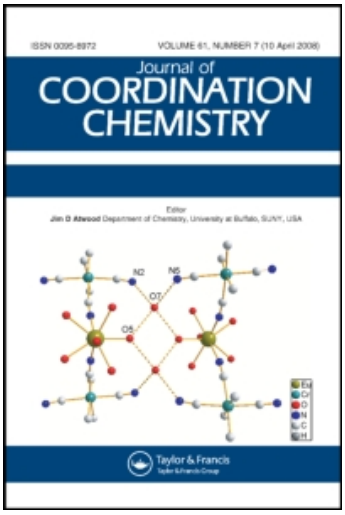


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Spectral, catalytic, and antifungal studies of ruthenium(II) chalcone complexes

M. Muthukumar[a]; P. Viswanathamurthi[a]
[a] Department of Chemistry, Periyar University, Salem 636011, Tamil Nadu, India

First published on: 25 March 2010

To cite this Article Muthukumar, M. and Viswanathamurthi, P.(2010) 'Spectral, catalytic, and antifungal studies of ruthenium(II) chalcone complexes', Journal of Coordination Chemistry, 63: 7, 1263 — 1272, First published on: 25 March 2010 (iFirst)
To link to this Article: DOI: 10.1080/00958971003728304
URL: http://dx.doi.org/10.1080/00958971003728304

Journal of Coordination Chemistry
Vol. 63, No. 7, 10 April 2010, 1263–1272

Taylor & Francis
Taylor & Francis Group

Spectral, catalytic, and antifungal studies of ruthenium(II) chalcone complexes

M. MUTHUKUMAR and P. VISWANATHAMURTHI*

Department of Chemistry, Periyar University, Salem 636011, Tamil Nadu, India

(*Received 4 August 2009; in final form 11 November 2009*)

Reactions of $[RuHCl(CO)(B)(EPh_3)_2]$ ($B = EPh_3$ or Py; $E = P$ or As) and chalcones in benzene with equal molar ratio led to the formation of new complexes of the type $[RuCl(CO)(EPh_3)(B)(L^{1-4})]$ ($B = PPh_3$, $AsPh_3$ or Py; $E = P$ or As; L = chalcone). The new complexes have been characterized by analytical and spectroscopic (IR-, electronic, ^{1}H-, ^{31}P-, and ^{13}C-NMR) data. Based on these data, an octahedral structure has been assigned for all the complexes. The chalcones are monobasic bidentate (O,O) donors and coordinate to ruthenium *via* phenolic and carbonyl oxygen. The new complexes exhibit efficient catalytic activity for the transfer hydrogenation of carbonyl compounds. Antifungal properties of the ligands and their complexes have been examined and compared with standard Bavistin.

Keywords: Ruthenium(II) chalcone complexes; Spectroscopic characterization; Catalytic transfer hydrogenation; Antifungal study

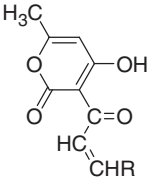
1. Introduction

Coordination complexes of ruthenium have versatile applications [1–5]. Among the different metal-catalyzed hydrogenation reactions, ruthenium-based catalytic systems are effective in the transfer hydrogenation of ketones [6–9]. In view of the low cost of reducing agent and its operational simplicity, the ruthenium-catalyzed 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 [10]. Hence, the synthesis of new ruthenium complexes with different types of ligands as catalysts for transfer hydrogenation is of particular interest.

The preparation of a new ligand is perhaps the most important step in the development of metal complexes with unique properties and novel reactivity. Chalcones, an important class of compounds that are widely distributed in nature, have displayed an impressive array of pharmacological activities including antimalarial and antileishmanial [11], as well as antimicrobial, anti-inflammatory, and antiviral effects [12]. Several chalcones are intensively studied, modified, and synthesized in order to develop more potential biological activities [13–16].

*Corresponding author. Email: viswanathamurthi@rediffmail.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958971003728304



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.

In this article, we describe the synthesis, catalytic, and antifungal studies of a series of ruthenium(II) chalcone complexes. The chalcone used in this study was derived from dehydroacetic acid (DHA, 3-acetyl-4-hydroxy-6-methyl-2-oxo-2H-pyran). The general structure of the chalcone ligands used in this study is given in figure 1.

2. Experimental

2.1. *Materials and methods*

All reagents were chemically pure and of AR grade. The solvents were purified and dried according to the standard procedures [17]. $RuCl_3 \cdot 3H_2O$ was purchased from Loba Chemie Pvt. Ltd. and used without purification. Analyses of carbon, hydrogen, and oxygen were performed in a 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 ranging from 400 to 4000 cm^{-1}. Electronic spectra of the complexes were recorded on a Shimadzu UV-Vis 1650 PC spectrophotometer ranging 200–800 nm using CH_2Cl_2 as solvent. NMR spectra (^1H, ^{31}P, and ^{13}C) were recorded in Jeol GSX-500 instrument in $CDCl_3$. The ^1H- and ^{13}C-NMR spectra were obtained using TMS as an internal standard. ^{31}P-NMR spectra of the complexes were obtained using orthophosphoric acid as 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. The starting complexes $[RuHCl(CO)(PPh_3)_3]$ [18], $[RuHCl(CO)(AsPh_3)_3]$ [19], $[RuHCl(CO)(Py)(PPh_3)_2]$ [20], and chalcone ligands [21] were prepared according to the literature methods.

2.2. *Synthesis of new ruthenium(II) chalcone complexes*

All complexes were prepared by the following procedure. An appropriate chalcone (0.0249–0.0411 g; 0.1 mmol) was added in 1 : 1 molar ratio to a solution of

$[RuHCl(CO)(EPh_3)_2(B)]$ (E = P or As; B = PPh_3, $AsPh_3$ or Py) (0.1 g; 0.1 mmol) in benzene (20 cm^3). The mixture was heated under reflux for 6 h in a water bath. The reaction mixture gradually changed to a deep color during heating. 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 the CH_2Cl_2/petroleum ether mixture and dried under vacuum over fused calcium chloride. The purity of the complexes was checked by thin-layer chromatography (TLC; yield 76–89%).

2.3. *Procedure for catalytic transfer hydrogenation of carbonyl compounds*

Catalytic transfer hydrogenation was studied using $[RuCl(CO)(AsPh_3)_2(L^4)]$, $[RuCl(CO)(PPh_3)_2(L^4)]$, and $[RuCl(CO)(Py)(PPh_3)(L^4)]$ as catalysts, carbonyl compounds as substrate, and KOH as promoter at 1 : 300 : 2.5 molar ratios, respectively, by the following procedure. A mixture containing carbonyl compounds (3.75 mmol), ruthenium complex (0.0125 mmol), and KOH (0.03 mmol) in 10 cm^3 of isopropyl alcohol was reacted under reflux in a water bath for 2 h. After the 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 HCl. The ether layer was filtered through a short path of silica gel by column chromatography. The filtrate was concentrated to $\approx$1 cm^3 and subjected to GC analysis, and the hydrogenated product was identified and determined with the authentic samples.

2.4. *Procedure for antifungal activities*

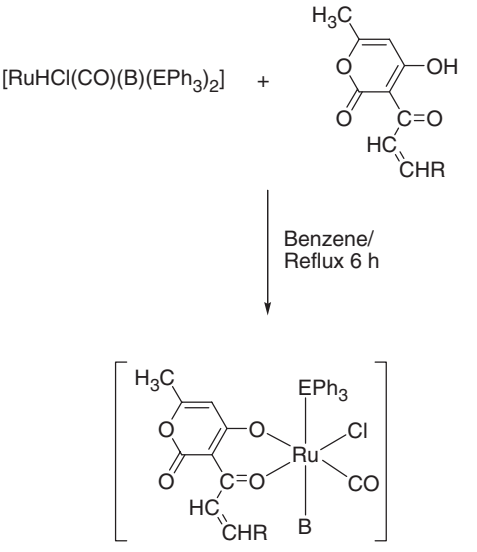
Some of the ligands and their ruthenium complexes were tested for *in vitro* growth inhibitory activity against pathogenic fungi, *Aspergillus niger* and *Mucor* sp. cultured on sabour dextrose agar medium and incubated at 30°C for 72 h. The solvent (DMSO) was used as a control in a similar manner to the prepared solutions of the compounds. Inhibition of fungal growth, expressed in percentage terms, was determined from the growth on test plates compared to the respective control plates, as given by the following equation:

$$\text{Inhibition}(\%) = \frac{100(C - T)}{C}$$

where C and T denote the diameter of fungal growth on the control plate and the test plate, respectively.

3. Results and discussion

Ruthenium(II) complexes $[RuCl(CO)(EPh_3)(B)(L^{1-4})]$ were synthesized in good yield from the reaction of $[RuHCl(CO)(EPh_3)_2(B)]$ with the chalcone ligands in dry benzene in equal molar ratio (scheme 1). In all these reactions, the chalcones are monobasic



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

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

bidentate chelating ligands, replacing a triphenylphosphine/arsine and a hydride from the starting complexes.

The complexes are stable in air at room temperature, reddish brown in color, non-hygroscopic, and highly soluble in common organic solvents such as dichloromethane, acetonitrile, chloroform, benzene, and DMSO. The analytical data given in table 1 are in good agreement with the general molecular formulas proposed for these complexes.

3.1. *Infrared spectroscopic analysis*

Important IR absorption frequencies of the ligands and their metal complexes along with their assignments are provided in the "Supplementary material". The free chalcone ligands showed a strong $\nu_{C=O}$ band at 1628–1622 cm^{-1}, which shifts to higher wavenumber 1659–1634 cm^{-1} in the ruthenium complexes indicating coordination through carbonyl oxygen [22]. A strong phenolic ν_{C-O} band at 1323–1307 cm^{-1} in the free chalcone shifts to 1360–1339 cm^{-1} in the complexes [22]. This is further supported by the disappearance of the broad ν_{OH} band at 3450–3350 cm^{-1} in the complexes, indicating the deprotonation of the phenolic proton prior to coordination to ruthenium. Bands at 1708–1704 cm^{-1} for the ligands are due to the lactone carbonyl group and remain unchanged after complexation, indicating that they do not participate in bond formation with ruthenium. Absorption due to ν_{C-C} of the free ligands appeared as a separate band around 1600 cm^{-1}, but could not be identified in the spectra of the ruthenium complexes because of their merging with $\nu_{C=O}$ [23]. A strong band at 1958–1941 cm^{-1} and a medium intensity band at 1028–1024 cm^{-1} indicate the presence of carbon monoxide [24] and nitrogen base [25], respectively. The other bands due to

Table 1. Analytical data of free ligands and their ruthenium(II) chalcone complexes.

Compound	Formula	Yield (%)	Melting point (°C)	Calculated (found) (%) C	H	O
L^1	$C_{16}H_{14}O_4$	55	125	71.10 (71.08)	5.22 (5.18)	23.67 (23.37)
L^2	$C_{16}H_{14}O_5$	58	138	67.12 (67.14)	4.92 (4.85)	27.94 (27.78)
L^3	$C_{15}H_{11}O_4Cl$	61	140	61.97 (61.89)	3.81 (3.83)	22.01 (22.05)
L^4	$C_{17}H_{16}O_6$	64	162	64.55 (64.53)	5.09 (5.15)	30.34 (30.29)
$[RuCl(CO)(PPh_3)_2(L^1)]$	$C_{53}H_{43}O_5ClP_2Ru$	56	145	66.42 (66.32)	4.52 (4.53)	8.35 (8.27)
$[RuCl(CO)(PPh_3)_2(L^2)]$	$C_{53}H_{43}O_6ClP_2Ru$	64	158	65.33 (65.38)	4.45 (4.50)	9.85 (9.80)
$[RuCl(CO)(PPh_3)_2(L^3)]$	$C_{52}H_{40}O_5Cl_2P_2Ru$	67	141	63.80 (63.72)	4.12 (4.15)	8.17 (8.10)
$[RuCl(CO)(PPh_3)_2(L^4)]$	$C_{54}H_{45}O_7ClP_2Ru$	71	135	64.57 (64.62)	4.52 (4.52)	11.15 (11.10)
$[RuCl(CO)(AsPh_3)_2(L^1)]$	$C_{53}H_{43}O_5ClAs_2Ru$	73	123	60.84 (60.86)	4.14 (4.13)	7.64 (7.60)
$[RuCl(CO)(AsPh_3)_2(L^2)]$	$C_{53}H_{43}O_6ClAs_2Ru$	69	180	59.92 (60.02)	4.08 (4.08)	9.04 (9.12)
$[RuCl(CO)(AsPh_3)_2(L^3)]$	$C_{52}H_{40}O_5Cl_2As_2Ru$	63	192	58.55 (58.49)	3.78 (3.68)	7.49 (7.52)
$[RuCl(CO)(AsPh_3)_2(L^4)]$	$C_{54}H_{45}O_7ClAs_2Ru$	79	184	59.38 (59.40)	4.15 (4.19)	10.25 (10.21)
$[RuCl(CO)(Py)(PPh_3)(L^1)]$	$C_{40}H_{33}O_5ClNPRu$	56	138	61.98 (61.94)	4.29 (4.18)	10.31 (10.29)
$[RuCl(CO)(Py)(PPh_3)(L^2)]$	$C_{40}H_{33}O_6ClNPRu$	65	120	60.72 (60.63)	4.20 (4.16)	12.13 (12.12)
$[RuCl(CO)(Py)(PPh_3)(L^3)]$	$C_{39}H_{30}O_5NCl_2PRu$	68	152	58.87 (58.86)	3.80 (3.75)	10.05 (10.00)
$[RuCl(CO)(Py)(PPh_3)(L^4)]$	$C_{41}H_{35}O_7NClPRu$	70	128	59.96 (60.01)	4.29 (4.30)	13.63 (13.60)

triphenylphosphine or triphenylarsine (around 1440, 1090, and 695 cm^{-1}) were also present in the spectra of all these complexes [26]. The observed bands in the region 474–456 cm^{-1} in the mononuclear complexes are tentatively assigned to ν_{Ru-Cl} [27]. From the IR spectral data, the chalcones are monobasic bidentate ligands coordinating through the deprotonated phenolic and the carbonyl oxygens.

3.2. *Electronic spectroscopic analysis*

All the chalcone ruthenium complexes are diamagnetic, indicating ruthenium in the 2+ oxidation state. The electronic spectra of all the complexes in dichloromethane showed two to four bands in the region 254–433 nm (table 2). The bands around 339–433 nm have been assigned to charge transfer (CT) transitions based on their extinction coefficient values (table 2) [28]. The other high-intensity bands around 296–299 and 254–256 nm are designated as n–π^* and π–π^* transitions, respectively, for electrons localized on the phenolic and carbonyl groups of the chalcones. The nature of the observed electronic spectra and the position of absorption bands are consistent with those of other similar ruthenium(II) octahedral complexes [29].

3.3. *^{1}H-NMR spectroscopic analysis*

^{1}H-NMR spectra of the ruthenium(II) chalcone complexes and ligands were recorded to confirm the binding mode of chalcone to ruthenium ion. All the complexes exhibit overlapping multiplets in the region 6.5–8.0 ppm (Supplementary material), assigned to phenyl groups present in PPh_3, $AsPh_3$, pyridine, and chalcone [30]. The signal due to two alkene protons at 6.6–7.1 ppm merged with the multiplets of aromatic protons [30]. Methine proton, which appeared as a singlet around 5.3 ppm in the complexes [31],

Table 2. Electronic spectroscopic data (nm) of ruthenium(II) chalcone complexes.

Complex	λ_{max} (ε, $dm^3\,mol^{-1}\,cm^{-1}$)	Assignments
$[RuCl(CO)(PPh_3)_2(L^1)]$	406 (6574), 368 (7986), 297 (19,130), 254 (23,215)	n–π^*, π–π^*, CT
$[RuCl(CO)(PPh_3)_2(L^2)]$	406 (6574), 369 (8543), 299 (20,430), 254 (23,215)	n–π^*, π–π^*, CT
$[RuCl(CO)(PPh_3)_2(L^3)]$	392 (6285), 369 (8543), 297 (19,130), 256 (24,532)	n–π^*, π–π^*, CT
$[RuCl(CO)(PPh_3)_2(L^4)]$	433 (6963), 406 (7543), 369 (8543), 297 (19,130)	n–π^*, π–π^*, CT
$[RuCl(CO)(AsPh_3)_2(L^1)]$	353 (7196), 296 (18,128), 256 (24,532)	n–π^*, π–π^*, CT
$[RuCl(CO)(AsPh_3)_2(L^2)]$	395 (6318), 371 (9108), 297 (19,130), 254 (23,215)	n–π^*, π–π^*, CT
$[RuCl(CO)(AsPh_3)_2(L^3)]$	339 (6596), 296 (18,128), 256 (24,532)	n–π^*, π–π^*, CT
$[RuCl(CO)(AsPh_3)_2(L^4)]$	368 (7986), 256 (24,532)	n–π^*, π–π^*, CT
$[RuCl(CO)(Py)(PPh_3)(L^1)]$	364 (7254), 297 (19,130), 256 (24,532)	n–π^*, π–π^*, CT
$[RuCl(CO)(Py)(PPh_3)(L^2)]$	395 (6318), 369 (8543), 254 (23,215)	n–π^*, π–π^*, CT
$[RuCl(CO)(Py)(PPh_3)(L^3)]$	364 (7254), 297 (19,130), 256 (24,532)	n–π^*, π–π^*, CT
$[RuCl(CO)(Py)(PPh_3)(L^4)]$	400 (6293), 369 (8543), 297 (19,130), 256 (24,532)	n–π^*, π–π^*, CT

shifted upfield from the spectra of the free ligands. The absence of resonance for OH in the complexes indicates the deprotonation of the phenol on complexation. All the complexes showed a sharp peak at 2.14–2.17 ppm due to the methyl group attached to the pyrone ring. The peak at 1.42–1.43 ppm is assigned to aldehyde methyl and methoxy proton that appeared as a singlet at 3.62–3.83 ppm.

3.4. *^{31}P-NMR spectroscopic analysis*

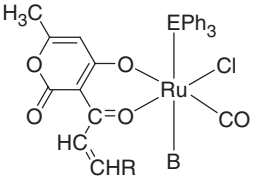
^{31}P-NMR spectra confirm the presence of triphenylphosphine in the new complexes (Supplementary material). For complexes containing two triphenylphosphines, a sharp singlet at 21.65–27.99 ppm indicates magnetically equivalent *trans* phosphorus [22]. The spectrum of all other complexes exhibited a singlet at 20.82–20.86 ppm corresponding to the presence of triphenylphosphine *trans* to heterocyclic nitrogen [30].

3.5. *^{13}C-NMR spectroscopic analysis*

The ^{13}C-NMR spectra (Supplementary material) exhibit a resonance at 185.39–192.86 ppm assigned to the metal coordinated –C=O. The signal for the metal coordinated –C–O appeared at 179.98–181.58 ppm [32]. A signal for carbon monoxide carbon was at 206.68–209.53 ppm in all the complexes. Carbons attached with the methyl group and the lactone carbonyl in the pyrone ring are singlets at 159.98–162.93 and 153.88–158.89 ppm, respectively [33]. Multiplets around 110.66–138.32 ppm have been assigned to the aromatic carbons. Alkene carbons at 115.45–130.58 ppm merged with the aromatic carbons. Sharp singlets at 19.84–19.97 ppm are assigned to methyl carbon attached to the pyrone ring and 16.25 ppm region is assigned to the aldehyde methyl group. Sharp singlet at 55.32–55.99 ppm is assigned to methoxy carbon. Based on the analytical and spectroscopic (IR-, electronic, ^{1}H-, ^{31}P-, and ^{13}C-NMR) data, an octahedral structure (figure 2) is proposed for the ruthenium(II) chalcone complexes.

3.6. *Catalytic transfer hydrogenation of carbonyl compounds*

Three ruthenium(II) chalcone complexes were studied for the catalytic transfer hydrogenation of various types of aldehydes and ketones in the presence of isopropyl



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

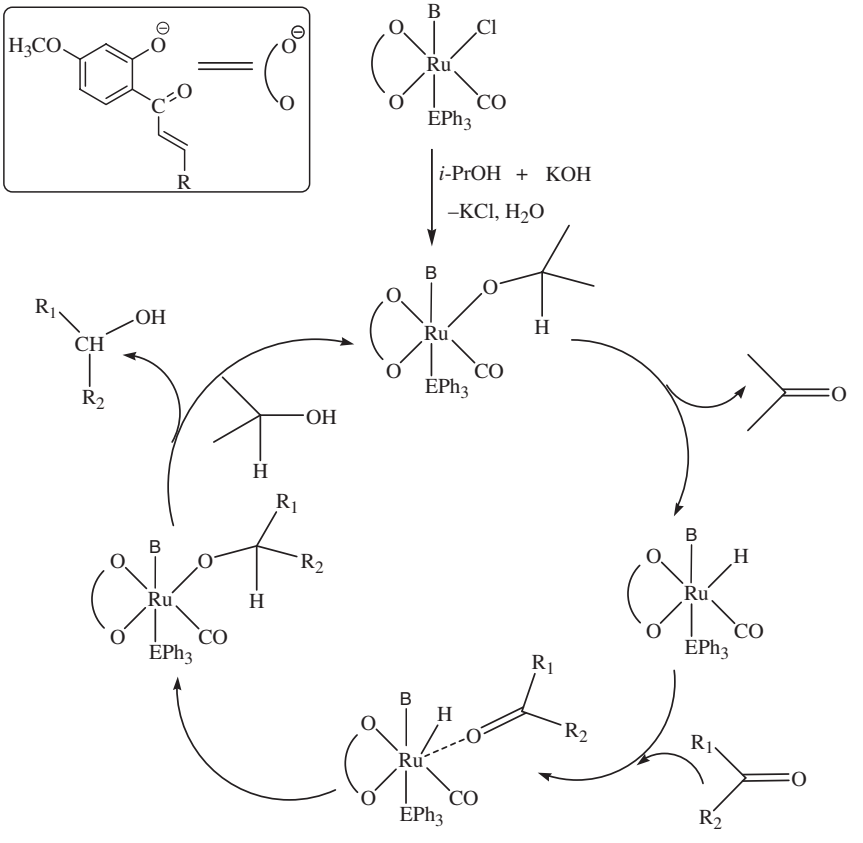
Figure 2. Proposed structure of new ruthenium(II) chalcone complexes.

Table 3. Catalytic transfer hydrogenation of carbonyl compounds by ruthenium(II) chalcone complexes[a] with isopropyl alcohol.[b]

Substrate	Product	Conversion for **1** (%)[c]	Conversion for **2** (%)[c]	Conversion for **3** (%)[c]
C_6H_5CHO	$C_6H_5CH_2OH$	94	92	87
p-MeC_6H_4CHO	*p*-$MeC_6H_4CH_2OH$	91	86	88
$C_{10}H_7CHO$	$C_{10}H_7CH_2OH$	82	80	77
p-$MeOC_6H_4CHO$	*p*-$MeOC_6H_4CH_2OH$	87	83	85
p-$NO_2C_6H_4CHO$	*p*-$NO_2C_6H_4CH_2OH$	76	72	74
p-ClC_6H_4CHO	*p*-$ClC_9H_4CH_2OH$	79	78	74
$C_6H_{10}O$	$C_6H_{11}OH$	99	99	96
$C_6H_5C(O)Me$	$C_6H_5CH(OH)Me$	72	70	69
$Ph_2C(O)$	Ph_2CHOH	78	75	78
$Me_2CHCH_2C(O)Me$	$Me_2CHCH_2CH(OH)Me$	58	55	57

[a]**1** – [RuCl(CO)$(AsPh_3)_2(L^4)$]; **2** – [RuCl(CO)$(PPh_3)_2(L^4)$]; and **3** – [RuCl(CO)(Py)$(PPh_3)(L^4)$].
[b]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.
[c]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 comparing with the authentic samples.

alcohol and KOH. The catalysts performed efficiently for the conversion of aldehydes and ketones to alcohols (table 3). Benzaldehyde was converted into benzyl alcohol in 87–94% yield; for 4-methyl benzaldehyde and 4-methoxy benzaldehyde, the conversions were 86–91% and 83–87%, respectively. Reduction of 4-chlorobenzaldehyde and 4-nitrobenzaldehyde to the corresponding alcohol occurred in 74–79% and 69–76% yields, respectively. The catalyst performed moderately for the reduction of naphthaldehyde. These catalysts show good activity for the transfer hydrogenation of aliphatic and aromatic ketones to the corresponding alcohols; cyclohexanone, acetophenone, and benzophenone were converted to the corresponding alcohols in 96–99%, 69–72%, and 75–78% yields, respectively, after 2 h reactions. For iso-butyl methyl ketone, the efficiency of the catalyst was moderate (55–58%). No transfer hydrogenation takes place in the absence of base. Although no studies have been carried out to determine the mechanism for these particular catalytic processes, it is generally assumed that the base facilitates the formation of ruthenium alkoxide by abstracting the proton from the alcohol and subsequently alkoxide undergoes β-elimination to give ruthenium hydride, which is an active species in the transfer hydrogenation reaction (scheme 2) [7, 34–36]. The workup process is very simple for this



(E = P or As; B = PPh_3, $AsPh_3$ or Py)

Scheme 2. Mechanism of catalytic transfer hydrogenation reactions.

catalytic system as the catalyst is stable in all organic solvents and can be easily recovered.

3.7. *Antifungal activity*

The *in vitro* antifungal screening against *A. niger* and *Mucor* species for the ligands and ruthenium(II) chalcone complexes have been carried out by disc diffusion method [37]. The ruthenium complexes (table 4) are more toxic than their parent ligands against the same microorganisms under the identical experimental conditions. The increase in the antifungal activity of the metal chelates may be due to Tweedy's chelation theory [38, 39]. Toxicity of the compounds increases with an increase in concentration. Though the complexes possess activity, they do not reach the effectiveness of the standard drug Bavistin. The 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.

Table 4. Fungicidal activity data for selected ligands and their ruthenium(II) chalcone complexes.

	Diameter of inhibition zone (mm)			
	A. niger		*Mucor* sp.	
Compound	50 ppm	100 ppm	50 ppm	100 ppm
L^1	7	11	8	13
$[RuCl(CO)(PPh_3)_2(L^1)]$	18	34	16	32
$[RuCl(CO)(AsPh_3)_2(L^1)]$	16	32	15	30
$[RuCl(CO)(Py)(PPh_3)(L^1)]$	15	33	17	35
L^2	10	13	7	11
$[RuCl(CO)(PPh_3)_2(L^2)]$	15	28	18	34
$[RuCl(CO)(AsPh_3)_2(L^2)]$	20	37	26	31
$[RuCl(CO)(Py)(PPh_3)(L^2)]$	22	38	24	35
Bavistin	38	56	42	53

4. Conclusions

Several new ruthenium(II) chalcone complexes were synthesized from the derivatives of dehydroacetic acid and 4-substituted benzaldehyde. An octahedral structure has been proposed for the complexes which showed efficient catalytic activity for the transfer hydrogenation of aldehydes and ketones with high conversions. Though some ruthenium complexes have been found in recent literature [40–45], the ruthenium(II) chalcone complexes have been rarely seen as catalysts for this kind of transfer hydrogenation reaction. In our system, labile triphenylphosphine makes these complexes catalytically active and the activity may be tuned by altering the substituents in the chalcone. The complexes exhibited a considerable antibacterial activity.

Acknowledgments

The authors express their sincere thanks to the Council of Scientific and Industrial Research (CSIR), New Delhi, (grant no. 01(2065)/06/EMR-II) for providing financial support. M. Muthukumar thanks CSIR for awarding Senior Research Fellowship.

References

[1] R. Prabhakaran, A. Geetha, M. Thilagavathi, R. Karvembu, V. Krishnan, H. Bertagnolli, K. Natarajan. *J. Inorg. Biochem.*, **98**, 2131 (2004).
[2] K. Karidi, A. Garoufis, A. Tsipis, N. Hadjiliadis, H. Dulk, J. Reedijk. *J. Chem. Soc., Dalton Trans.*, 1176 (2005).
[3] S. Nag, P. Gupta, R.J. Butcher, S. Bhattacharya. *Inorg. Chem.*, **43**, 4814 (2004).
[4] D. Chatterjee. *Coord. Chem. Rev.*, **252**, 176 (2008).
[5] M.D. Ward. *Coord. Chem. Rev.*, **250**, 3128 (2006).
[6] (a) R. Noyori, M. Yamakawa, S. Hashiguchi. *J. Org. Chem.*, **66**, 7931 (2001); (b) M. Bernard, V. Guiral, F. Delbecq, F. Fache, P. Sautet, M. Lemaire. *J. Am. Chem. Soc.*, **120**, 1441 (1998).
[7] R. Noyori, S. Hashiguchi. *Acc. Chem. Res.*, **30**, 97 (1997).

[8] H. Doucet, T. Okumara, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, F.A. England, T. Ikariya, R. Noyori. *Angew. Chem. Int. Ed.*, **37**, 1703 (1998).
[9] E.P. Kelson, P.P. Phengsy. *J. Chem. Soc., Dalton Trans.*, 4023 (2000).
[10] S. Hashiguchi, A. Fujii, J. Takehara, T. Ikariya, R. Noyori. *J. Am. Chem. Soc.*, **117**, 7562 (1995).
[11] M. Liu, P. Wilairat, S.L. Croft, A.L. Tan, M. Go. *Bioorg. Med. Chem.*, **11**, 2729 (2003).
[12] Z. Nowakowska. *Eur. J. Med. Chem.*, **42**, 125 (2007).
[13] A. Valla, B. Valla, D. Cartier, R. Guillou, R. Labia, L. Florent, S. Charneau, J. Schrevel, P. Potier. *Eur. J. Med. Chem.*, **41**, 142 (2006).
[14] P. Boeck, C.A.B. Falcao, P.C. Leal, R.A. Yunes, V.C. Filho, E.C. Torres-Santos, B. Rossi-Bergmann. *Bioorg. Med. Chem.*, **14**, 1538 (2006).
[15] A. Modzelewska, C. Pettit, G. Achanta, N.E. Davidson, P. Huang, S.R. Khan. *Bioorg. Med. Chem.*, **14**, 3491 (2006).
[16] Y. Xia, Z. Yang, P. Xia, K.F. Bastow, Y. Nakanishi, K. Lee. *Bioorg. Med. Chem. Lett.*, **10**, 699 (2000).
[17] A.I. Vogel. *Textbook of Practical Organic Chemistry*, 5th Edn, ELBS, London (1989).
[18] N. Ahmed, J.J. Lewison, S.D. Robinson, M.F. Uttley. *Inorg. Synth.*, **15**, 48 (1974).
[19] R.A. Sanchez-Delgado, W.Y. Lee, S.R. Choi, Y. Cho, M.J. Jun. *Transition Met. Chem.*, **16**, 241 (1991).
[20] S. Gopinathan, I.R. Unny, S.S. Deshpande, C. Gopinathan. *Indian J. Chem. A*, **25**, 1015 (1986).
[21] V.K. Mahesh, R.S. Gupta. *Indian J. Chem.*, **12**, 956 (1974).
[22] N. Chitrapriya, V. Mahalingam, M. Zeller, R. Jayabalan, K. Swaminathan, K. Natarajan. *Polyhedron*, **27**, 939 (2008).
[23] N. Fuson, M.L. Josien, E.M. Shelton. *J. Am. Chem. Soc.*, **76**, 2526 (1954).
[24] (a) A.M. El-Hendawy, A.H. Alkubaisi, A.G. El-Ghany, A. El-Kourashy, M.M. Shanab. *Polyhedron*, **12**, 2343 (1993); (b) G. Venkatachalam, N. Raja, D. Pandiarajan, R. Ramesh. *Spectrochim. Acta, Part A*, **71**, 884 (2008).
[25] K. Nareshkumar, R. Ramesh. *Spectrochim. Acta, Part A*, **60**, 2913 (2004).
[26] J.R. Dyer. *Application of Absorption Spectroscopy of Organic Compounds*, Prentice-Hall, New Jersey (1978).
[27] M.S. El-Shahawi, A.F. Shoair. *Spectrochim. Acta, Part A*, **60**, 121 (2004).
[28] R. Karvembu, K. Natarajan. *Polyhedron*, **21**, 1721 (2002).
[29] R. Ramesh, M. Sivagamasundari. *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 899 (2003).
[30] M.V. Kaveri, R. Prabhakaran, R. Karvembu, K. Natarajan. *Spectrochim. Acta, Part A*, **61**, 2915 (2005).
[31] S. Kannan, M. Sivagamasundari, R. Ramesh, Y. Liu. *J. Organomet. Chem.*, **693**, 2251 (2008).
[32] M. Cindric, V. Vrdoljak, T. Kajfez, P. Novak, A. Brbot-Saranovic, N. Strukan, B. Kamenar. *Inorg. Chim. Acta*, **328**, 23 (2002).
[33] M. Cindric, V. Vrdoljak, N. Strukan, P. Tepes, P. Novak, A. Brbot-Saranovic, G. Giester, B. Kamenar. *Eur. J. Inorg. Chem.*, 2128 (2002).
[34] (a) H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, F.A. England, T. Ikariya, R. Noyori. *Angew. Chem. Int. Ed.*, **37**, 1703 (1998); (b) M.J. Palmer, M. Will. *Tetrahedron: Asymmetry*, **10**, 2045 (1999); (c) J.E. Backvall. *J. Organomet. Chem.*, **652**, 105 (2002).
[35] (a) E.P. Kelson, P.P. Phengsy. *J. Chem. Soc., Dalton Trans.*, 4023 (2000); (b) H. Zhang, B.C. Yang, Y.Y. Li, Z.R. Donga, J.X. Gao, H. Nakamura, K. Murata, T. Ikariya. *Chem. Commun.*, 142 (2003); (c) J.S. Chen, Y. Li, Z. Dong, B. Li, J. Gao. *Tetrahedron Lett.*, **45**, 8415 (2004); (d) J. Hannedouche, G.J. Clarkson, M. Wills. *J. Am. Chem. Soc.*, **126**, 986 (2004).
[36] R. Noyori, T. Ohkuma. *Angew. Chem. Int. Ed.*, **40**, 40 (2001).
[37] C.H. Colins, P.M. Lyne. *Microbial Methods*, University Park Press, Baltimore (1970).
[38] B.G. Tweedy. *Phytopathology*, **25**, 910 (1964).
[39] S.C. Singh, N. Gupta, R.V. Singh. *Indian J. Chem. A*, **34**, 733 (1995).
[40] N. Sathya, P. Muthusamy, N. Padmapriya, G. Raja, K. Deivasigamani, C. Jayabalakrishnan. *J. Coord. Chem.*, **62**, 3532 (2009).
[41] M.K. Singh, N.K. Kar, R.A. Lal. *J. Coord. Chem.*, **62**, 1677 (2009).
[42] S.N. Shukla, P. Gaur, R. Mehrotra, M. Prasad, H. Kaur, M. Prasad, R.S. Srivastava. *J. Coord. Chem.*, **62**, 2556 (2009).
[43] M.K. Singh, N.K. Kar, R.A. Lal, M. Asthana. *J. Coord. Chem.*, **62**, 2893 (2009).
[44] J.Y. Wang, P.P. Yang, W. Gu, W.Z. Wang, X. Liu, D.Z. Liao. *J. Coord. Chem.*, **62**, 923 (2009).
[45] Y.J. Liu, J.F. He, J.H. Yao, W.J. Mei, F.H. Wu, L.X. He. *J. Coord. Chem.*, **62**, 665 (2009).