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Synthesis and spectral characterization of 2′-hydroxy chalconate complexes of ruthenium(II) and their catalytic and biological applications

M. Muthukumar [a], P. Viswanathamurthi [a,*], K. Natarajan [b]

[a] *Department of Chemistry, Periyar University, Salem 636011, India*
[b] *Department of Chemistry, Bharathiar University, Coimbatore 641046, India*

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Abstract

The reactions of $[RuHCl(CO)(B)(EPh_3)_2]$ (B = EPh_3 or pyridine; E = P or As) and 2′-hydroxychalcones in 1:2 ratio led to the formation of $[Ru(CO)(B)(L)_2]$ (B = PPh_3, $AsPh_3$ or Py; L = 2′-hydroxychalcones). The new complexes have been characterized by analytical and spectral (IR, electronic and ^1H NMR) data. They have been assigned an octahedral structure. The new complexes were found to catalyze the oxidation of alcohols to aldehydes using *N*-methylmorpholine-*N*-oxide as co-oxidant. All the new complexes were found to be active against bacteria such as *E. coli*, *Salmonella typhi* and fungi *Aspergillus niger*. The activity was compared with standard *Streptomycin* or *Bavistin*.

Keywords: Ruthenium(II) complexes; Spectral studies; Catalytic oxidation; Antibacterial activity; Antifungal activity

1. Introduction

Chalcones and their analogues are well known for having variable bactericidal [1], fungicidal [2] and carcinogenic activity [3]. Moreover, 2′-hydroxychalcones have been employed as analytical reagents for some metal ions [4,5]. The most common and widespread compounds of the chalconoid group are the chalcones, which possess a 1,3-diaryl-2-propen-1-one carbon frame work [6–8]. Unsubstituted and substituted chalcones had higher activity in tissue culture. A wide range of pharmacological activities have been identified for various chalcones, these include antioxidant, antitumor [9], antimalarial [10] and anticancer activities [11]. 2′-Hydroxychalcone was the most effective in enzyme activities and gene expressions [12]. Studies on 2′-hydroxychalcone complexation with some transition metal ions (Co^{II}, Ni^{II}, Cu^{II}, Pt^{II} and Pd^{II}) led to stable complexes, with a square planar configuration, in a 1:2 metal:ligand stoichiometry [13,14]. 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 [15]. In this line, triphenylphosphine complexes of ruthenium have been found to be efficient catalyst for the aerobic oxidation of alcohols [16]. Besides, ruthenium triphenylphosphine complexes also exhibited biological activity against pathogenic microbes [17]. Hence, synthesis of new ruthenium complexes containing triphenylphoshine is of greater importance. Moreover, transition metal complexes of 2′-hydroxychalcones and related ligands have been studied extensively due to their interesting behaviour as weak field or strong field ligands to bivalent metal ions [18].

We here disclose the simple procedure for the synthesis of ruthenium(II) complexes containing triphenylphosphine, triphenylarsine and chalcones and examined their catalytic and biological applications.

2. Experimental

2.1. Reagents and materials

All the reagents used were of analar or chemically pure grade. The solvents used were freshly distilled by literature methods [19]. The ligands 2′-hydroxychalcones [20], and the starting complexes $[RuHCl(CO)(PPh_3)_3]$ [21], $[RuHCl(CO)(AsPh_3)_3]$ [22], $[RuHCl(CO)(Py)(PPh_3)_2]$ [23] were prepared according

* Corresponding author. Tel.: +91 427 2345766; fax: +91 427 2345124.
E-mail address: viswanathamurthi@yahoo.com (P. Viswanathamurthi).

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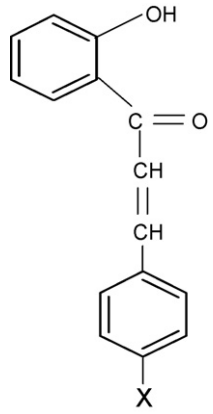


Fig. 1. Structure of 2′-hydroxychalcones

Ligand	X
L^1	H
L^2	OCH_3
L^3	Cl
L^4	CH_3

to the literature methods. The general structure of the chalcone ligands used in this study is given in Fig. 1.

2.2. Physical measurements

IR spectra of the complexes 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 using a Shimadzu UV-1650 PC spectrophotometer in 200–800 nm range. ^1H NMR spectra were recorded in Jeol GSX-400 instrument using $CDCl_3$ as solvent. Elemental analyses were performed at Central Drug Research Institute, Lucknow, India. Melting points were recorded on a Technico microheating table and are uncorrected.

2.3. Recommended procedures

2.3.1. Synthesis of new ruthenium(II) chalconato complexes

To a solution of $[RuHCl(CO)(B)(EPh_3)_2]$ where B = EPh_3 or pyridine; E = P or As (0.1 mmol) in benzene (20 cm^3), the appropriate chalcone (0.2 mmol) were added in a 1:2 molar ratio. The mixture was heated under reflux for 5 h. The resulting solution was concentrated to about 3 cm^3. The product was separated by the addition of small amount of petroleum ether (60–80 °C) and recrystallized from CH_2Cl_2/petroleum ether mixture and dried under vacuum.

2.4. Catalytic studies

Catalytic oxidation of primary alcohols to corresponding aldehyde and secondary alcohol to ketone by ruthenium(II) chalconato complexes were studied in the presence of NMO as co-oxidant. A typical reaction using the complex as a catalyst and benzyl alcohol, cyclohexanol as substrates at 1:100 molar ratios is described as follows. A solution of ruthenium complex (0.01 mmol) in 20 cm^3 CH_2Cl_2 was added to the solution of substrate (1 mmol) and NMO (3 mmol) and molecular sieves. The solution mixture was stirred for 3 h at room temperature and the solvent was then evaporated to dryness. The solid residue was then extracted with petroleum ether (60–80 °C) (3×10 cm^3) and the combined extracts were filtered and evaporated to give corresponding aldehyde, which was then quantified as 2,4-dinitrophenylhydrazone derivative [19].

3. Results and discussion

All the complexes are in brown colour. Air and light stable complexes of general formula $[Ru(CO)(B)(L)_2]$ (where L = 2′-hydroxychalcones and B = PPh_3, $AsPh_3$ or Py) have been obtained from the reaction of $[RuHCl(CO)(B)(EPh_3)_2]$ (B = EPh_3 or pyridine; E = P or As) and 2′-hydroxychalcones in boiling benzene for 5 h. In all these reactions, it has been observed that the 2′-hydroxychalcones behave as uninegative bidentate chelating ligands by replacing two of the triphenylphosphine groups, a hydride and a chloride ion from the starting complexes. The analytical data (Table 1) of all the complexes are in good agreement with the proposed molecular formula.

3.1. Infrared spectral analysis

In the IR spectra of the free ligands (Table 2), a strong band is observed around 1640 cm^{-1} due to $\upsilon_{C=O}$. This band has been shifted to a lower wave number by 20–30 cm^{-1} in the ruthenium complexes indicating the coordination of the ligands to ruthenium through the carbonyl oxygen atom [20]. The phenolic υ_{C-O} stretching absorptions of the free ligands occur in the region 1339–1343 cm^{-1}. This band has been shifted to higher wave number in the spectra of the complexes due to its coordination to ruthenium ion through the oxygen atom of the phenolic group [24]. Further, the absorption due to υ_{O-H} was not observed in the infrared spectra of the complexes in the region 3400–3600 cm^{-1} suggesting the deprotonation of the ligands 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 absorption due to 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} [25]. In the complexes, the absorption due to the phenylalkene vibration appeared in the region 1542–1551 cm^{-1}, which is slightly lower than that observed in the spectra of the free ligands [20]. A strong band around 1945–1959 cm^{-1} indicates the presence of terminally coordinated carbon monoxide [26]. In the complexes containing coordinated pyridine, a weak band is observed at 1027–1029 cm^{-1} [27]. In addition, the other characteristic absorption due to triphenylphosphine were also found to be present in the expected region [28].

Table 1
Analytical data of ruthenium(II) chalconato complexes

Complexes	Yield (%)	m.p. (°C)	Calculated (found)(%)		
			C	H	N
$[Ru(CO)(PPh_3)(L^1)_2]$	61	100	70.24 (70.34)	4.45 (4.35)	–
$[Ru(CO)(PPh_3)(L^2)_2]$	68	146	68.22 (68.12)	4.60 (4.70)	–
$[Ru(CO)(PPh_3)(L^3)_2]$	72	112	64.91 (64.51)	3.89 (3.79)	–
$[Ru(CO)(PPh_3)(L^4)_2]$	58	164	70.74 (70.54)	4.77 (4.87)	–
$[Ru(CO)(Py)(L^1)_2]$	56	085	66.05 (66.35)	4.16 (4.36)	2.14 (2.24)
$[Ru(CO)(Py)(L^2)_2]$	60	100	63.86 (63.56)	4.37 (4.27)	1.96 (1.98)
$[Ru(CO)(Py)(L^3)_2]$	69	110	59.76 (59.86)	3.48 (4.68)	1.94 (1.90)
$[Ru(CO)(Py)(L^4)_2]$	63	105	66.85 (66.75)	4.58 (4.48)	2.05 (2.10)
$[Ru(CO)(AsPh_3)(L^1)_2]$	74	125	66.74 (66.94)	4.23 (4.13)	–
$[Ru(CO)(AsPh_3)(L^2)_2]$	69	133	65.05 (65.25)	4.39 (4.59)	–
$[Ru(CO)(AsPh_3)(L^3)_2]$	56	128	61.90 (61.80)	3.70 (3.66)	–
$[Ru(CO)(AsPh_3)(L^4)_2]$	65	130	67.32 (67.42)	4.54 (4.64)	–

3.2. Electronic spectral analysis

All the new complexes have been found to be diamagnetic indicating the presence of ruthenium in +2 oxidation state arising from t_{2g}^6 configuration. The electronic spectra of all the complexes were taken in CH_2Cl_2 and they showed two bands in the region 359–225 nm (Table 2). The bands around 359–312 nm have been assigned to charge transfer transition arising from the excitation of an electron from the metal t_{2g} level to the unfilled molecular orbitals derived from the π* level of the ligands [29]. The bands that appeared below 300 nm are characterized by intra-ligand charge transfer.

3.3. ^1H NMR spectral analysis

All the ruthenium complexes exhibit a multiplet in the region 7.05–8.20 ppm in their ^1H NMR spectra (Table 3), which has been assigned to the protons of phenyl groups present in the triphenylphosphine and 2′-hydroxychalcone ligands [24]. 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 δ value at least by 2 ppm [30]. In addition, the signal corresponding to CH_3 was also observed in the expected region.

Based on the analytical and spectral data, an octahedral structure (Fig. 2) has been tentatively proposed for all the ruthenium(II) chalconato complexes.

Table 3
^1H NMR data (δ in ppm) of ruthenium(II) chalconato complexes

Complexes	^1H NMR (ppm)
$[Ru(CO)(PPh_3)(L^1)_2]$	7.05–7.67 (m, –CH=CH– and aromatic)
$[Ru(CO)(PPh_3)(L^3)_2]$	7.21–7.25 (m, –CH=CH– and aromatic)
$[Ru(CO)(Py)(L^3)_2]$	7.74–8.20 (m, –CH=CH– and aromatic)
$[Ru(CO)(AsPh_3)(L^1)_2]$	7.01–7.69 (m, –CH=CH– and aromatic)
$[Ru(CO)(AsPh_3)(L^4)_2]$	7.25–7.78 (m, –CH=CH– and aromatic), 1.28 (s, CH_3)
$[Ru(CO)(AsPh_3)(L^3)_2]$	7.20–7.90 (m, –CH=CH– and aromatic)

Table 2
IR absorption frequencies (cm^{-1}) and electronic spectral data (nm) of free ligands and their ruthenium(II) chalconato complexes

Compound	$\nu_{C\equiv O}$	$\nu_{C=O}$	ν_{C-O}	$\nu_{C=C}$	λ_{max} (ε)($dm^3\ mol^{-1}\ cm^{-1}$)
L^1	–	1639	1340	1572	–
L^2	–	1639	1343	1564	–
L^3	–	1640	1339	1585	–
L^4	–	1634	1341	1562	–
$[Ru(CO)(PPh_3)(L^1)_2]$	1949	1625	1384	1548	323(26,580), 232(31,040)
$[Ru(CO)(PPh_3)(L^2)_2]$	1946	1623	1363	1544	359(22,360), 232(31,040)
$[Ru(CO)(PPh_3)(L^3)_2]$	1951	1606	1350	1545	312(28,190), 233(31,160)
$[Ru(CO)(PPh_3)(L^4)_2]$	1957	1622	1400	1542	339(24,270), 232(31,040)
$[Ru(CO)(Py)(L^1)_2]$	1946	1606	1359	1549	321(27,890), 235(32,320)
$[Ru(CO)(Py)(L^2)_2]$	1945	1604	1359	1544	355(21,840), 234(31,370)
$[Ru(CO)(Py)(L^3)_2]$	1945	1605	1357	1551	316(30,120), 242(35,480)
$[Ru(CO)(Py)(L^4)_2]$	1945	1605	1400	1543	340(23,960), 245(36,530)
$[Ru(CO)(AsPh_3)(L^1)_2]$	1958	1617	1401	1548	329(25,370), 243(35,640)
$[Ru(CO)(AsPh_3)(L^2)_2]$	1959	1619	1400	1544	341(23,750), 244(35,890)
$[Ru(CO)(AsPh_3)(L^3)_2]$	1959	1623	1401	1545	329(25,370), 237(33,170)
$[Ru(CO)(AsPh_3)(L^4)_2]$	1959	1618	1400	1543	330(25,580), 225(30,460)

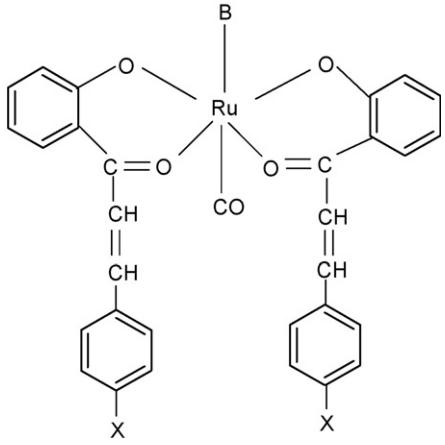
Table 4
Catalytic activity data of ruthenium(II) chalconato complexes

Complex	Substrate	Product	Yield (%)
$[Ru(CO)(PPh_3)(L^1)_2]$	Benzyl alcohol	A	38.5
	Cyclohexanol	B	07.0
$[Ru(CO)(PPh_3)(L^2)_2]$	Benzyl alcohol	A	26.5
	Cyclohexanol	B	05.9
$[Ru(CO)(PPh_3)(L^3)_2]$	Benzyl alcohol	A	39.0
	Cyclohexanol	B	08.9
$[Ru(CO)(PPh_3)(L^4)_2]$	Benzyl alcohol	A	28.2
	Cyclohexanol	B	06.7
$[Ru(CO)(Py)(L^1)_2]$	Benzyl alcohol	A	32.0
	Cyclohexanol	B	06.8
$[Ru(CO)(Py)(L^2)_2]$	Benzyl alcohol	A	18.3
	Cyclohexanol	B	05.6
$[Ru(CO)(Py)(L^3)_2]$	Benzyl alcohol	A	22.4
	Cyclohexanol	B	05.4
$[Ru(CO)(Py)(L^4)_2]$	Benzyl alcohol	A	22.4
	Cyclohexanol	B	06.8
$[Ru(CO)(AsPh_3)(L^1)_2]$	Benzyl alcohol	A	23.6
	Cyclohexanol	B	07.3
$[Ru(CO)(AsPh_3)(L^2)_2]$	Benzyl alcohol	A	26.1
	Cyclohexanol	B	07.9
$[Ru(CO)(AsPh_3)(L^3)_2]$	Benzyl alcohol	A	45.5
	Cyclohexanol	B	09.8
$[Ru(CO)(AsPh_3)(L^4)_2]$	Benzyl alcohol	A	29.2
	Cyclohexanol	B	06.6

A, benzaldehyde; B, cyclohexanone.

3.4. Catalytic activity

The oxidation of benzylalcohol and cyclohexanol was carried out with the new ruthenium(II) chalconato complexes as catalysts in the presence of *N*-methylmorpholine-*N*-oxide as co-oxidant and CH_2Cl_2 as solvent. All the complexes oxidize primary alcohols to corresponding aldehydes and secondary alcohols to corresponding ketones with low to moderate yield (Table 4). This reaction provides an efficient route to the conversion of alcoholic functions to carbonyl groups and water is the only by product during the course of the reaction which was removed by using molecular sieves. The aldehydes and ketones formed after stirring for about 3 h, which was then quantified as their 2,4-dinitrophenylhydrazone derivatives [19]. The results obtained are given in Table 4. The relatively higher product yield obtained for the oxidation of benzylalcohol as compared to cyclohexanol is due to the fact that the α-CH unit of benzylalcohol is more acidic than cyclohexanol [31].



(B= PPh_3, $AsPh_3$ or Py ; X= H, CH_3, OCH_3 or Cl)

Fig. 2. Proposed structure of new ruthenium(II) chalconato complexes.

3.5. Biocidal study

The results (Tables 5 and 6) showed that the ruthenium complexes are more toxic than their parent ligands against the same microorganisms and under identical experimental conditions [32]. The increase in biological 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 [33]. Chelation 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 the cell membrane [34]. 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 *Streptomycin* or *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 [35,36].

Table 5
Antibacterial activity data of ruthenium(II) chalconato complexes

Compound	Diameter of inhibition zone (mm)			
	E. coli		*Salmonella typhi*	
	0.25%	0.5%	0.25%	0.5%
L^2	3	5	4	7
$[Ru(CO)(PPh_3)(L^2)_2]$	6	7	5	9
$[Ru(CO)(Py)(L^2)_2]$	11	13	9	13
$[Ru(CO)(AsPh_3)(L^2)_2]$	14	18	11	14
Streptomycin	19	24	17	21

Table 6
Antifungal activity data of ruthenium(II) chalconato complexes

Compound	Diameter of inhibition zone (mm)	
	Aspergillus niger	
	0.25%	0.5%
L^1	2	3
$[Ru(CO)(PPh_3)(L^1)_2]$	3	5
$[Ru(CO)(Py)(L^1)_2]$	3.5	6
$[Ru(CO)(AsPh_3)(L^1)_2]$	3.8	8
Bavistin	11	16

4. Conclusions

Some new ruthenium(II) chalconato complexes have been synthesized using chalcones formed from derivatives of benzaldehyde and 2-hydroxyacetophenone. 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 significant catalytic and biological activity.

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