Available online at www.sciencedirect.com
SCIENCE DIRECT®

Spectrochimica Acta Part A 61 (2005) 2915–2918

SPECTROCHIMICA ACTA PART A

www.elsevier.com/locate/saa

Synthesis and spectral studies of [RuCl(CO)(L)(PPh$_3$)(B)] (HL = 2′-hydroxychalcones and B = PPh$_3$, pyridine or piperidine) and their catalytic and biological applications

M.V. Kaveri, R. Prabhakaran, R. Karvembu, K. Natarajan*

Department of Chemistry, Bharathiar University, Coimbatore 641046, Tamil Nadu, India

Received 27 April 2004; accepted 1 November 2004

Abstract

The reactions of [RuHCl(CO)(PPh$_3$)$_2$(B)] (B = PPh$_3$, pyridine or piperidine) and 2′-hydroxychalcones led to the formation of [RuCl(CO)(PPh$_3$)(L)(B)] (L = chalconate). The new complexes have been characterized by analytical and spectral (IR, electronic, ^{1}H NMR and ^{31}P NMR) data. They have been assigned an octahedral structure. The complexes have been used as catalysts for the aerial oxidation of cinnamyl alcohol. Some of the complexes have been tested in vitro for growth inhibitory activity against the bacteria *E. coli*, *S. typhi* and *Pseudomonas* sp. and the fungi *A. fumigatus*.

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

1. Introduction

The selective oxidation of alcohols to carbonyl compounds is a pivotal reaction in organic synthesis and many stoichiometric oxidants notably chromium and manganese reagents, producing enormous amounts of heavy metal wastes, have been utilized to accomplish the reaction [1]. The search for catalytic oxidations with inexpensive green oxidants, such as molecular oxygen or air, still play a key role in the development of industrial processes [2]. In this line, triphenylphosphine complexes of ruthenium have been found to be efficient catalysts for the aerobic oxidation of alcohols [3]. Besides, ruthenium triphenylphosphine complexes also exhibited biological activity against pathogenic microbes [4]. Hence, synthesis and spectral characterization of new ruthenium complexes containing triphenylphosphine are 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 [5]. We here disclose the simple procedure for the synthesis of ruthenium(II) complexes containing triphenylphosphine and chalcone and also 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 [6]. The ligands 2′-hydroxychalcones [7] and complexes of the type [RuHCl(CO)(B)(EPh$_3$)$_2$] (where B = PPh$_3$, pyridine or piperidine) [8] were prepared by the literature methods.

2.2. Physical measurements

IR spectra of the complexes were recorded in KBr pellets with a Nicolet FT-IR spectrophotometer in the 400–4000 cm^{-1} range. Electronic spectra of the complexes have been recorded in methanol using a Systronics 119 spec-

---

* Corresponding author. Tel.: +91 422 2424655; fax: +91 422 2422387.
E-mail address: k_natraj6@yahoo.com (K. Natarajan).

1386-1425/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2004.11.001

trophotometer in the 200–800 nm range. ^{1}H NMR and ^{31}P NMR spectra were recorded in Varian AMX-400 instrument using TMS and orthophosphoric acid as the standards, respectively. Microanalysis of the complexes was performed by VarioEL III elemental analyzer.

2.3. Recommended procedures

2.3.1. Synthesis of ruthenium(II) complexes

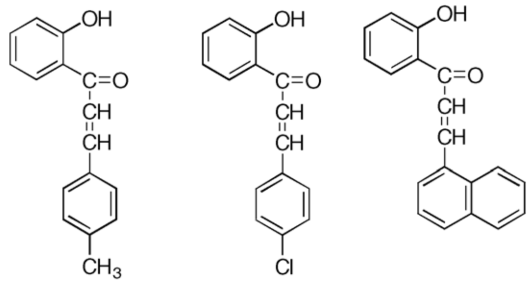
To a solution of [RuHCl(CO)(B)(EPh$_3$)$_2$] (where B = PPh$_3$ or pyridine or piperidine) (0.077–0.11 g; 0.1 mmol) in benzene (20 cm^3), the appropriate chalcone ligands (0.24–0.284 g; 0.1 mmol) were added in 1:1 molar ratio. The mixture was heated under reflux for 5 h. The resulting solution was concentrated 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$_2$Cl$_2$/petroleum ether mixture and dried under vacuum.

2.3.2. Catalytic studies

The catalytic activity of ruthenium(II) complexes in aerial oxidation of cinnamaldehyde was followed spectrophotometrically by monitoring the increase in the cinnamic acid absorbance as a function of time. A CH$_2$Cl$_2$ solution of the ruthenium(II) complexes (2 cm^3, 1×10^{-4} M) and freshly distilled cinnamaldehyde in CH$_2$Cl$_2$ (2 cm^3, 1×10^{-4} M) were mixed in a 1 cm quartz cell at room temperature (26 °C) and the absorbance change at 279 nm was recorded.

3. Results and discussion

All the complexes are in brown colour. Air and light stable complexes of general formula [RuCl(CO)(L)(PPh$_3$)(B)] (where L = 2′-hydroxychalcones and B = PPh$_3$, pyridine (py) or piperidine (pip)) have been obtained from the reaction of equimolar amounts of [RuHCl(CO)(PPh$_3$)$_2$(B)] (B = PPh$_3$, py or pip) and 2′-hydroxychalcones (HL) 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 one of the triphenylphosphine groups and the hydride ion from the starting complexes. The analytical data (Table 1) of all the complexes are in good agreement with the proposed formula (Fig. 1).



(HL^1) (HL^2) (HL^3)

Fig. 1. Structure of 2′-hydroxychalcones.

3.1. Spectroscopic studies

In the IR spectra of the free ligands (Table 2), a strong band is observed around 1640 cm^{-1} due to ν(C–O). This 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 [5a]. The phenolic C–O stretching absorptions of the free ligands occur as a doublet in the region 1330–1360 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 and appeared as a singlet or a doublet. Further, the absorption due to ν(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 ν(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 ν(C–O) [9]. In the complexes, the absorption due to the phenylalkene vibration appeared in the region 1530–1560 cm^{-1}, which is slightly lower than that observed in the spectra of the free

Table 1
Analytical data of new ruthenium(II) complexes

Complex	Yield (%)	mp (°C)	Calculated (found) (%)		
			C	H	N
[RuCl(CO)(PPh$_3$)$_2$(L^1)]	64	158	68.94 (69.54)	4.68 (5.61)	–
[RuCl(CO)(PPh$_3$)$_2$(L^2)]	61	138	65.96 (64.32)	4.25 (4.10)	–
[RuCl(CO)(PPh$_3$)$_2$(L^3)]	60	129	67.90 (66.80)	4.80 (4.26)	–
[RuCl(CO)(PPh$_3$)(py)(L^1)]	59	136	64.64 (64.38)	4.47 (4.86)	1.88 (2.08)
[RuCl(CO)(PPh$_3$)(py)(L^2)]	63	118	61.34 (62.06)	3.96 (4.28)	1.83 (1.98)
[RuCl(CO)(PPh$_3$)$_2$(py)(L^3)]	56	123	63.16 (62.06)	4.92 (4.84)	1.81 (2.21)
[RuCl(CO)(PPh$_3$)(pip)(L^1)]	60	147	65.73 (64.72)	5.24 (5.47)	1.86 (2.16)
[RuCl(CO)(PPh$_3$)$_2$(pip)(L^2)]	58	150	60.86 (61.50)	4.70 (4.92)	1.82 (2.10)
[RuCl(CO)(PPh$_3$)$_2$(pip)(L^3)]	52	111	62.77 (61.05)	4.15 (4.08)	1.80 (1.92)

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

Compound	$\nu_{(C\equiv O)}$	$\nu_{(C=O)}$	$\nu_{(Ph-C-O)}$	$\nu_{(C=C)}$	$\lambda_{max\ (nm)}$
HL^1	–	1640 s	1339 m	1582 s	–
HL^2	–	1635 s	1341 m	1577 s	–
HL^3	–	1638 s	1340 m	1580 s	–
$[RuCl(CO)(PPh_3)_2(L^1)]$	1946 vs	1619 s	1346 m	1580 s	340
$[RuCl(CO)(PPh_3)_2(L^2)]$	1945 vs	1905 s	1358 m	1548 s	345, 265
$[RuCl(CO)(PPh_3)_2(L^3)]$	1960 vs	1918 s	1355 m	1589 s	330, 270
$[RuCl(CO)(PPh_3)(py)(L^1)]$	1945 vs	1905 s	1357 m	1586 s	340, 270
$[RuCl(CO)(PPh_3)(py)(L^2)]$	1948 vs	1605 s	1357 m	1546 s	335, 225
$[RuCl(CO)(PPh_3)(py)(L^3)]$	1952 vs	1618 s	1377 m	–	340, 265
$[RuCl(CO)(PPh_3)(pip)(L^1)]$	1944 vs	1610 s	1378 m	–	330, 270
$[RuCl(CO)(PPh_3)(pip)(L^2)]$ $[RuCl(CO)(PPh_3)(pip)(L^3)]$	1943 vs	1618 s	1376 m	1545 s	344, 230
HL^1	1949 vs	1610 s	1380 m	1556 s	360, 270

vs: very strong; s: strong; m: medium intensity.

ligands [7b]. A strong band around 1940 cm^{-1} indicates the presence of terminally coordinated carbon monoxide [4b]. The other characteristic absorptions due to triphenylphosphine were also found to be present in the expected region [10]. In the case of the complexes containing coordinated heterocyclic nitrogen bases, a medium intensity band was observed in the region 1000–1025 cm^{-1} [8b].

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 methanol and they showed two to three bands in the region 380–225 nm (Table 3). The bands around 380–315 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 [3b]. The bands that appeared below 300 nm are characterized by intra-ligand charge transfer.

All the ruthenium complexes exhibit a multiplet at 6.95–7.96 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 ligand. 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 [11]. In addition, the signal corresponding to CH_3 and piperidine were also observed in the expected region.

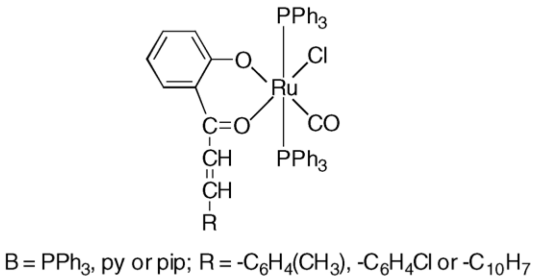


Fig. 2. Proposed structure of new ruthenium(II) complexes.

^{31}P NMR spectra were recorded in order to confirm the presence of triphenylphosphine groups and to determine the geometry of the complexes. In the case of the complexes containing two triphenylphosphine ligands, a sharp singlet was observed at 24.49 ppm for the presence of magnetically equivalent phosphorus atoms suggesting the presence of two triphenylphosphine groups in a position *trans* to each other. The spectrum of all other complexes exhibited a singlet at 24.46 ppm corresponding to the presence of triphenylphosphine group in a position *trans* to heterocyclic nitrogen base.

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

3.2. Catalytic oxidation

The catalytic activity of ruthenium(II) complexes in aerial oxidation of cinnamaldehyde was followed spectrophotomet-

Table 3
^1H NMR and ^{31}P NMR data (δ in ppm) of ruthenium(II) complexes

Complex	^1H NMR	^{31}P NMR
$[RuCl(CO)(PPh_3)_2(L^2)]$	6.95–7.96 (m, —CH=CH— and aromatic)	[a]
$[RuCl(CO)(PPh_3)_2(L^3)]$	7.06–7.96 (m, —CH=CH— and aromatic)	24.49
$[RuCl(CO)(PPh_3)(py)(L^1)]$	7.15–7.7 (m, —CH=CH— and aromatic), 1.28 (s, CH_3)	24.46
$[RuCl(CO)(PPh_3)(py)(L^2)]$	6.6–6.9 (m, —CH=CH—), 7.0–7.9 (m, aromatic)	[a]
$[RuCl(CO)(PPh_3)(pip)(L^1)]$	7.2–7.9 (m, —CH=CH— and aromatic), 3.1–3.4 (m, piperidine)	24.66
$[RuCl(CO)(PPh_3)_2(pip)(L^3)]$	7.0–7.9 (m, —CH=CH— and aromatic), 3.1–3.4 (m, piperidine)	24.66

[a] Not recorded.

Table 4
Catalytic activity data of ruthenium(II) complexes

Complex	Rate constant, k (M^{-1} S^{-1})
$[RuCl(CO)(PPh_3)_2(L^1)]$	1.8×10^{-2}
$[RuCl(CO)(PPh_3)_2(L^2)]$	2.1×10^{-2}
$[RuCl(CO)(PPh_3)_2(L^3)]$	3.0×10^{-2}

Table 5
Antibacterial activity data of ruthenium(II) complexes

Compound	Diameter of inhibition zone (mm)			
	E. coli		*S. typhi*	
	0.25%	0.5%	0.25%	0.5%
HL^2	4	6	5	8
$[RuCl(CO)(PPh_3)_2(L^2)]$	6	8	6	17
$[RuCl(CO)(py)(PPh_3)(L^2)]$	10	1	9	11
$[RuCl(CO)(pip)(PPh_3)(L^2)]$	18	20	8	9

Table 6
Antifungal activity data of ruthenium(II) complexes

Compound	Diameter inhibition zone (mm) (*A. fumigatus*)	
	0.25%	0.5%
HL^1	1.8	2.9
$[RuCl(CO)(PPh_3)_2(L^1)]$	3.3	5.7
$[RuCl(CO)(PPh_3)(py)(L^1)]$	3.9	6.8
$[RuCl(CO)(PPh_3)(pip)(L^1)]$	3.4	7
$[RuCl(CO)(AsPh_3)_2(L^1)]$	3.8	7.9

rically by monitoring the increase in the cinnamic acid absorbance as a function of time. A CH_2Cl_2 solution of the ruthenium(II) complex (2 cm^3, 1×10^{-4} M) and freshly distilled cinnamaldehyde in CH_2Cl_2 (2 cm^{-3}, 1×10^{-4} M) were mixed in a 1 cm quartz cell at room temperature (26 °C) and the absorbance change at 279 nm was recorded as a function of time. The catalytic activity is found to increase with decrease in electron donating ability of the substituent present in the coordinated ligands of the complexes [12]. Interestingly, only alcoholic group of cinnamyl alcohol gets oxidized selectively without affecting the double bonds. Plots of absorbance versus time are linear. The slope of the line is equal the rate constant (k) and the observed k values are given in Table 4. There is no change in the absorbance at 279 nm in the absence of the complex indicating the activity of the new complexes.

3.3. Antibacterial activity

The in vitro antibacterial screening against *E. coli*, *S. typhi* and *Pseudomonas* sp. and antifungal screening against *A. fumigatus* of the ligands and some of their ruthenium(II) complexes have been carried out by disc diffusion method [13]. The results (Tables 5 and 6) show that the ruthenium complexes are more toxic than their parent ligands against the same microorganisms and under identical experimental conditions. 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. Chelation reduces the polarity of the metal ion because of partial sharing of its positive charge with the donor groups and the 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. It has been observed that complexes containing heterocyclic nitrogen base possess more activity than other complexes.

4. Conclusion

In conclusion, we have synthesized nine ruthenium(II) complexes containing triphenylphosphine and 2′-hydroxychalcones. All the complexes have been characterized on the basis of analytical and spectral data. The complexes showed significant catalytic oxidation activity and biological activity.

References

[1] (a) K. Yasuda, S.V. Ley, J. Chem. Soc., Perkin Trans. 1 (2002) 1024;
(b) J.D. Lou, Z.N. Xu, Tetrahedron Lett. 43 (2002) 8843;
(c) S.V. Ley, A. Madin, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, vol. 7, Pergamon Press, Oxford, 1991, pp. 251–289.

[2] I.E. Marko, P.R. Giles, M. Tsukazaki, S.M. Brown, C.J. Urch, Science 274 (1996) 2044.

[3] (a) A. Wolfson, S. Wuyts, D.E. De Vos, I.F.J. Vankelecom, P.A. Jacobs, Tetrahedron Lett. 43 (2002) 8107;
(b) R. Karvembu, K. Natarajan, Polyhedron 21 (2002) 219;
(c) A. Dijksman, A. Marino-Gonzalez, A.M.I. Payeras, I.W.C.E. Arends, R.A. Sheldon, J. Am. Chem. Soc. 123 (2001) 6826.

[4] (a) R. Ramesh, S. Maheswaran, J. Inorg. Biochem. 96 (2003) 457;
(b) R. Karvembu, K. Natarajan, Polyhedron 21 (2002) 1721.

[5] (a) M. Palaniandavar, C. Natarajan, Aust. J. Chem. 33 (1980) 737;
(b) M. Palaniandavar, C. Natarajan, Aust. J. Chem. 8 (1983) 229;
(c) P. Shanthi, R. Murugesan, P.R. Athappan, C. Natarajan, Trans. Metall. Chem. 17 (1992) 39.

[6] A.I. Vogel, Textbook of Practical Organic Chemistry, 5th ed., ELBS, London, 1989.

[7] (a) C.H. Lin, C.T. Lin, C.L. Yeh, J. Chin. Chem. Soc. 14 (1969) 9;
(b) N. Dharmaraj, K. Natarajan, Synth. React. Inorg. Met.: Org. Chem. 27 (1997) 361.

[8] (a) N. Ahmed, J.J. Levision, S.D. Robinson, M.F. Uttley, Inorg. Synth. 15 (1974) 48;
(b) S. Gopinathan, I.R. Unny, S.S. Deshpande, C. Gopinathan, Indian J. Chem. A 25 (1986) 1015.

[9] N. Fuson, M.-L. Josien, E.M. Shelton, J. Am. Chem. Soc. 76 (1954) 2526.

[10] M.S. El-Shahawi, A.F. Shoair, Spectrochim. Acta A 60 (2004) 121.

[11] M.A. Bennett, M.J. Byrnes, A.C. Willis, Organometallics 22 (2003) 1018.

[12] R. Karvembu, S. Hemalatha, R. Prabhakaran, K. Natarajan, Inorg. Chem. Commun. 6 (2003) 486.

[13] C.H. Collins, P.M. Lyne, Microbial Methods, University Park Press, Baltimore, 1970.