Full Paper

Applied Organometallic Chemistry

Received: 7 July 2008 Revised: 25 October 2008 Accepted: 9 November 2008 Published online in Wiley Interscience: 18 December 2008

(www.interscience.com) DOI 10.1002/aoc.1475

Synthesis, characterization and catalytic studies of ruthenium(II) chalconate complexes

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Stable ruthenium(II) carbonyl complexes of the type [RuCl(CO)(EPh$_3$)(B)(L)] (E = P or As; B = PPh$_3$, AsPh$_3$ or Py; L = 2′-hydroxychalcones) were synthesized from the reaction of [RuHCl(CO)(EPh$_3$)$_2$(B)] (E = P or As; B = PPh$_3$, AsPh$_3$ or Py) with 2′-hydroxychalcones in benzene under reflux. The new complexes were characterized by analytical and spectroscopic (IR, electronic ^{1}H, ^{31}P and ^{13}C NMR) data. They were assigned an octahedral structure. The complexes exhibited 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. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: ruthenium(II) complexes; spectroscopic studies; catalytic oxidation; catalytic transfer hydrogenation

Introduction

Chalcones are open chain flavonoids whose basic structure includes two aromatic rings bound by an α,β-unsaturated carbonyl groups. They are usually obtained from natural products with extractive techniques[1,2] or by several homogeneous[3,4] and heterogeneous[5,6] synthetic methods. The importance of chalcones lies in the wide range of pharmacological activities such as antioxidant, antitumor,[7] antimalarial,[8] anticancer[9] anti-inflammatory,[10] anti-leishmanial[11] and antimicrobial.[12] The antioxidant activity of flavonoids is basically associated with the reduction or inhibition of lipid peroxidation, which is strongly related to aging and carcinogenesis, by their ability to act as free radical scavengers and also to chelate transition metal ions.[13–15]

Transition metal complexes of 2′-hydroxychalcones and related ligands have been extensively studied due to their interesting behaviour as weak or strong field ligands to bivalent metal ions.[16] 2′-Hydroxychalconate complexes of ruthenium(II)-containing triphenylphosphine were found to show significant catalytic oxidation and biological activities.[17] In addition, the catalytic activity of ruthenium complexes with tertiary phosphine or arsine ligands is well documented.[18] The oxidation of alcohols into their corresponding aldehydes and ketones is of greater importance in synthetic organic chemistry.[19] The use of transition metal complexes as catalysts for hydrogen transfer from a suitable donor has been the subject of ongoing research for some decades.[20] Among the different metal catalyzed hydrogenation reactions, ruthenium-based catalytic systems are found to be effective in the transfer hydrogenation of ketones.[20] Hence, synthesis of new ruthenium complexes containing triphenylphosphine with chalcone ligands is of greater importance among various transition metal complexes.

We here disclose a simple procedure for the synthesis of ruthenium(II) chalconate complexes containing triphenylphosphine/triphenylarsine and 2′-hydroxychalcone and two catalytic applications.

Experimental

Reagents and materials

All the reagents used were chemically pure and AR grade. The solvents were purified and dried according to standard procedures.[21] $RuCl_3.3H_2O$ was purchased from Loba Chemie Pvt Ltd, and was used without further purification. The 2′-hydroxychalcones were prepared in 80–90% yield by stirring 2-hydroxy-5-methyl acetophenone (0.25 mol) with corresponding aldehydes (0.25 mol) in the presence of 50 ml alcoholic sodium hydroxide solution (20%) in a 100 ml round-bottom flask at room temperature and pressure. After 24 h stirring, the product was precipitated by adding concentrated hydrochloric acid, filtered and recrystallized from ethanol.[22] The starting complexes [RuHCl(CO)(PPh$_3$)$_3$],[23] [RuHCl(CO)(AsPh$_3$)$_3$][24] and [RuHCl(CO)(Py)(PPh$_3$)$_2$][25] were prepared according to the literature methods. The general structures of the 2′-hydroxychalcone ligands used in this study are given below (Fig. 1).

Physical Measurements

Elemental analyses

Elemental analyses of carbon, hydrogen and nitrogen were performed in a Carlo-Erba 1160-model 240 Perkin- Elmer analyzer at the Central Drug Research Institute (CDRI), Lucknow, India.

IR spectra

FT-IR spectra were recorded in KBr pellets with a Nicolet FT-IR spectrophotometer in a 400–4000 cm^{-1} range with a resolution of 4 cm^{-1} in transmittance mode.

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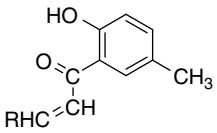


Ligand	R
L^1	4-H_3C-C_6H_4
L^2	4-H_3CO-C_6H_4
L^3	4-Cl-C_6H_4
L^4	3,4-$(H_3CO)_2C_6H_3$

Figure 1. Structure of 2′-hydroxychalconate.

UV–vis spectra

Electronic spectra of the complexes were taken in CH_2Cl_2 solution in 1 cm quartz cells. The spectra were then recorded on a Shimadzu UV–visible 1650 PC spectrophotometer over a 200–900 nm range at room temperature and pressure.

NMR spectra

All the NMR spectra (^{1}H, ^{31}P and ^{13}C) were recorded using a Jeol GSX- 400 instrument in $CDCl_3$ at room temperature. ^{1}H NMR chemical shifts were referenced to tetramethylsilane (TMS) as an internal standard and ^{13}C NMR chemical shifts were referenced to the internal solvent resonance. ^{31}P NMR spectra of the complexes were obtained at room temperature using *o*-phosphoric acid as a reference. Signals are quoted in parts per million (ppm) as δ downfield from TMS as an internal reference.

GC analyses

Gas chromatographic (GC) analyses were conducted on an ACME 6000 series 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

Melting points were recorded on a Technico micro heating table and are uncorrected.

Synthesis of new Ruthenium(II) Chalconate Complexes

All complexes were prepared by the following common procedure. To a solution of $[RuHCl(CO)(EPh_3)_2(B)]$ (E = P or As; B = PPh_3, $AsPh_3$ or Py) (100 mg; 0.1 mmol) in benzene (20 cm^3), the appropriate 2′-hydroxychalcone (23–40 mg; 0.1 mmol) was added in 1 : 1 molar ratio in a 100 ml round-bottom flask. The mixture was heated under reflux for 6 h in a water bath. The reaction mixture gradually changed to a deep colour during heating. After the reaction time, the contents were concentrated to around 3 cm^3 by removing the solvent under reduced pressure. The contents were 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 CH_2Cl_2–petroleum ether mixture. The compounds were dried under vacuum and the purity of the complexes was checked by TLC.

Catalytic Oxidation

Catalytic oxidation of primary alcohols to corresponding aldehydes and secondary alcohols to ketones by ruthenium(II) chalconate complexes was 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 performed 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 in a 100 ml round-bottom flask containing air. The solution mixture was reacted under stirring for 20 h at room temperature and pressure, and the solvent was then evaporated from the mother liquor under reduced pressure. The solid residue was then extracted with petroleum ether (60–80 °C; 20 cm^3), concentrated to ~1 cm^3 and was analyzed by GC. The oxidation products were identified by GC co-injection with authentic commercial samples.

Catalytic Transfer Hydrogenation

The catalytic transfer hydrogenation reactions were also studied using ruthenium(II) chalconate complexes as a catalyst, ketone as substrate and KOH as base at 1 : 300:2.5 molar ratios. The procedure was described as follows. A mixture containing ketone (3.75 mmol), the ruthenium complex (0.0125 mmol) and KOH (0.03 mmol) in 10 ml of *i*-prOH was taken in a 100 ml round-bottom flask containing air. The solution mixture was reacted under reflux in water bath for 2 h at 95 °C and normal pressure. After completion of reaction the catalyst was removed from the reaction mixture by the addition of petroleum 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 cm^3 and subjected to GC analysis, and the hydrogenated product was identified and determined with authentic samples.

Results and Discussion

Diamagnetic, hexa-coordinated low-spin ruthenium(II) complexes of general formula $[RuCl(CO)(EPh_3)(B)(L)]$ (E = P or As; B = PPh_3, $AsPh_3$ or Py; L = 2′-hydroxychalcone) were synthesized in good yields from the reaction of $[RuHCl(CO)(EPh_3)_2(B)]$ (E = P or As; B = PPh_3, $AsPh_3$ or Py) with 2′-hydroxychalcone ligands in dry benzene in equal molar ratio (Scheme 1). In all these reactions, it was observed that the 2′-hydroxychalcones behave as uninegative bidentate chelating ligands by replacing a triphenylphosphine/arsine and a halide ion from the starting complexes.

All the complexes were stable in air at room temperature, brown in colour, non-hygroscopic in nature and highly soluble in common organic solvents such as dichloromethane, acetonitrile, chloroform and DMSO. The greater solubility of the complexes may be due to the presence of chlorides. The analytical data are listed in Table 1 and are in good agreement with the general molecular formula proposed for all the complexes.

Infrared Spectroscopic Analysis

The IR spectra of the complexes in comparison with those of the free ligands, display certain changes, which give an idea

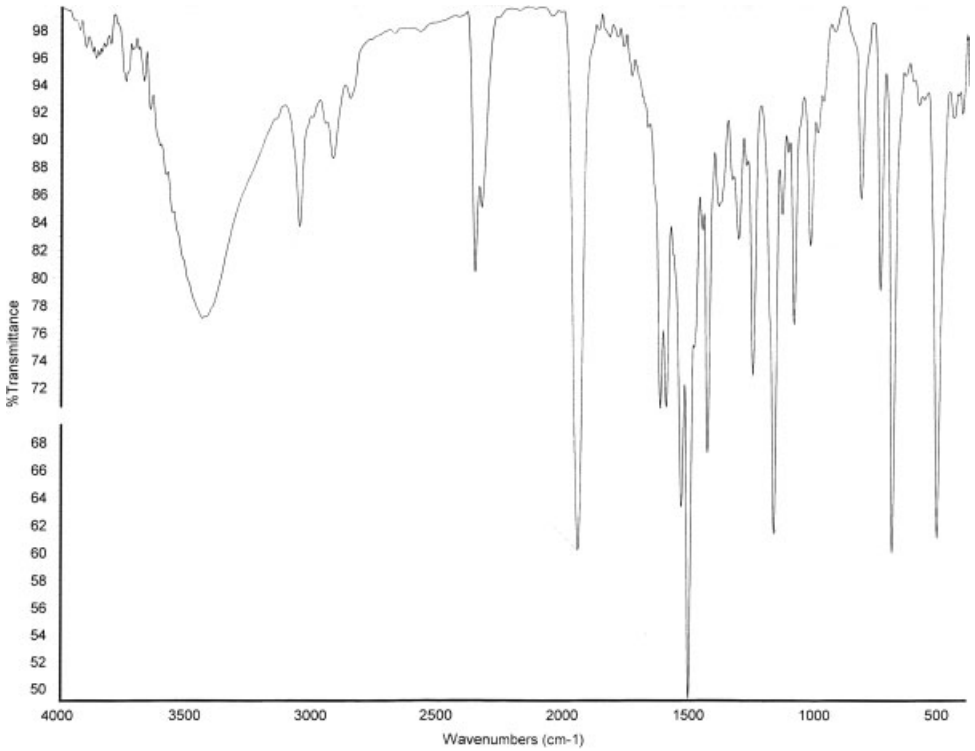


Figure 2. IR spectrum of [RuCl(CO)$(PPh_3)_2(L^2)$].

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

Complexes	Formula	Yield (%)	Melting point (°C)	Calculated (found) (%)		
				C	H	N
[RuCl(CO)$(PPh_3)_2(L^1)$]	$C_{54}H_{45}O_3P_2ClRu$	56	147	68.97(68.72)	4.82(4.68)	–
[RuCl(CO)$(PPh_3)_2(L^2)$]	$C_{54}H_{45}O_4P_2ClRu$	65	135	67.82(67.80)	4.74(4.70)	–
[RuCl(CO)$(PPh_3)_2(L^3)$]	$C_{53}H_{42}O_3P_2Cl_2Ru$	72	125	66.25(65.96)	4.41(4.35)	–
[RuCl(CO)$(PPh_3)_2(L^4)$]	$C_{55}H_{47}O_5P_2ClRu$	58	148	66.97(66.92)	4.80(4.72)	–
[RuCl(CO)$(AsPh_3)_2(L^1)$]	$C_{54}H_{45}O_3As_2ClRu$	67	137	63.07(63.12)	4.41(4.43)	–
[RuCl(CO)$(AsPh_3)_2(L^2)$]	$C_{54}H_{45}O_4As_2ClRu$	74	152	62.11(62.08)	4.34(4.28)	–
[RuCl(CO)$(AsPh_3)_2(L^3)$]	$C_{53}H_{42}O_3As_2Cl_2Ru$	61	150	60.70(60.68)	4.07(3.97)	–
[RuCl(CO)$(AsPh_3)_2(L^4)$]	$C_{55}H_{47}O_5As_2ClRu$	59	131	61.49(61.50)	4.41(4.39)	–
[RuCl(CO)(Py)$(PPh_3)(L^1)$]	$C_{41}H_{35}O_3PNClRu$	62	138	65.03(65.24)	4.66(4.46)	1.85(1.79)
[RuCl(CO)(Py)$(PPh_3)(L^2)$]	$C_{41}H_{35}O_4PNClRu$	56	140	63.69(63.58)	4.56(4.58)	1.81(1.92)
[RuCl(CO)(Py)$(PPh_3)(L^3)$]	$C_{40}H_{32}O_3PNCl_2Ru$	68	151	61.78(61.86)	4.15(4.11)	1.80(1.84)
[RuCl(CO)(Py)$(PPh_3)(L^4)$]	$C_{42}H_{37}O_5PNClRu$	71	115	62.80(61.92)	4.64(4.71)	1.74(1.78)

about the type of co-ordination and their structure. The free chalconate ligands showed a strong $\upsilon_{C=O}$ band in the region 1632–1647 cm^{-1} (Table 2, Fig. 2). This band shifts to lower wave number 1617–1628 cm^{-1} in the ruthenium complexes on coordination through the carbonyl oxygen atom.[26] A strong phenolic υ_{C-O} band observed at 1300–1305 cm^{-1} in the free chalconate shifts to higher wave number, 1311–1340 cm^{-1}, in the spectra of the complexes on coordination to ruthenium.[27] This is 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 it is inferred that both the carbonyl and phenolic oxygen atoms coordinate to ruthenium ion in all the complexes. In addition, appearance of a strong band at 1944–1963 cm^{-1} and a medium intensity band at 1024–1028 cm^{-1} regions indicate the presence of carbon monoxide[28] and nitrogen base[29] respectively.

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 $t^6{}_{2g}$ configuration, and the excited states corresponding to the $t^5{}_{2g}\,e^1{}_g$ configuration are $^3T_{1g}$, $^3T_{2g}$ and $^1T_{1g}$. Hence, three bands corresponding to the transitions $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^3T_{2g}$ and $^1A_{1g} \rightarrow {}^1T_{1g}$ are possible in order of increasing energy.

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

Compound	$\nu_{C\equiv O}$	$\nu_{C=O}$	ν_{c-o}	$\nu_{C=C}$	$PPh_3/AsPh_3$	λ_{max} (ε) ($dm^3\ mol^{-1}\ cm^{-1}$)
L^1	–	1637	1302	1569	–	–
L^2	–	1635	1300	1555	–	–
L^3	–	1647	1304	1571	–	–
L^4	–	1632	1305	1547	–	–
$[RuCl(CO)(PPh_3)_2(L^1)]$	1949	1628	1317	1542	1435, 1078, 692	834 (521), 338(25580), 233(31160)
$[RuCl(CO)(PPh_3)_2(L^2)]$	1947	1625	1311	1539	1434, 1093, 696	828(564), 358(22360), 234(31370)
$[RuCl(CO)(PPh_3)_2(L^3)]$	1958	1625	1340	1540	1435, 1093, 696	830(542), 330(28190), 233(31160)
$[RuCl(CO)(PPh_3)_2(L^4)]$	1948	1622	1317	1541	1437, 1094, 696	831(537), 376(19247), 232(31040)
$[RuCl(CO)(AsPh_3)_2(L^1)]$	1963	1627	1317	1549	1436, 1077, 693	831(537), 237(33172)
$[RuCl(CO)(AsPh_3)_2(L^2)]$	1961	1625	1312	1544	1435, 1076, 692	833(532), 234(31370)
$[RuCl(CO)(AsPh_3)_2(L^3)]$	1960	1625	1312	1542	1435, 1076, 694	832(528), 234(31370)
$[RuCl(CO)(AsPh_3)_2(L^4)]$	1961	1628	1312	1548	1435, 1076, 693	836(512), 235(32326)
$[RuCl(CO)(Py)(PPh_3)(L^1)]$	1946	1624	1336	1541	1438, 1093, 696	824(592), 333(26970), 234(31370)
$[RuCl(CO)(Py)(PPh_3)(L^2)]$	1944	1623	1319	1540	1440, 1093, 696	355(23750), 234(35890), 221(29563)
$[RuCl(CO)(Py)(PPh_3)(L^3)]$	1945	1623	1332	1541	1441, 1093, 695	632(598), 329(28920), 234(31370)
$[RuCl(CO)(Py)(PPh_3)(L^4)]$	1946	1617	1316	1542	1435, 1091, 694	370(21580), 234(31370), 221(29563)

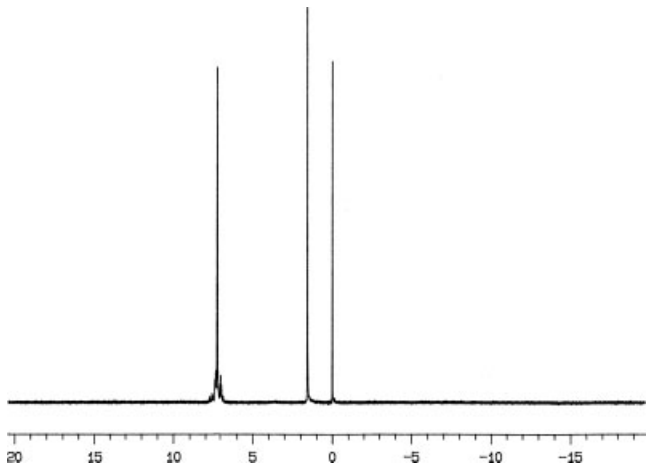


Figure 3. ^1H NMR spectrum of $[RuCl(CO)(AsPh_3)_2(L^3)]$.

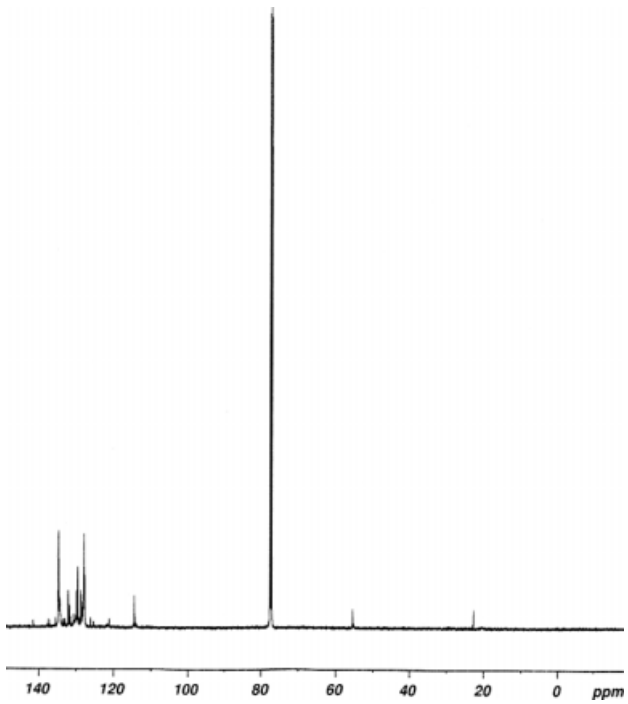


Figure 4. ^{13}C NMR spectrum of $[RuCl(CO)(PPh_3)_2(L^2)]$.

The electronic spectra of all the complexes in dichloromethane showed two to three bands in the region 836–221 nm (Table 2). The bands around 836–632 nm are assigned to d–d transition.[30] The other high intensity bands around 376–329 nm are assigned to charge transfer transitions arising from the excitation of an electron from the metal t_{2g} level to the unfilled molecular orbital derived from the π^* level of the ligands.[31] The bands that appeared below 300 nm are characterized by intra-ligand charge transfer. The nature of the observed electronic spectra and the position of absorption bands are consistent with those of other similar ruthenium(II) octahedral complexes.[29]

^1H NMR Spectroscopic Analysis

All the ruthenium complexes exhibit a multiplet in the region 6.81–7.69 ppm (Table 3, Fig. 3), due to triphenylphosphine/arsine phenyl group protons and 2′-hydroxychalcone ligands.[32] The signal due to two alkene protons also appears in the region 6.9–7.1 ppm and hence is merged with the multiplet of aromatic protons.[33] The peak for methyl protons appears as a singlet at 1.53–1.56 ppm.[34] In addition, a peak corresponding to -OCH_3 was observed in the expected region.

^{31}P NMR Spectroscopic Analysis

^{31}P NMR spectra of some of the complexes confirm the presence of triphenylphosphine groups (Table 4). In the case of the complexes containing two triphenylphosphine ligands, a sharp singlet was observed around 25.63–25.85 ppm for magnetically equivalent phosphorus atoms *trans* to each other.[34] The spectrum of all other complexes exhibited a singlet around 24.46–24.52 ppm corresponding to the presence of triphenylphosphine group trans to heterocyclic nitrogen base.[16]

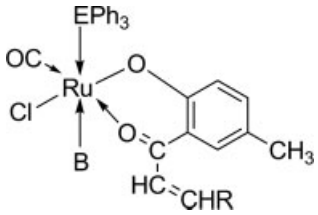


Figure 5. Proposed structure of new ruthenium(II) chalconate complexes.

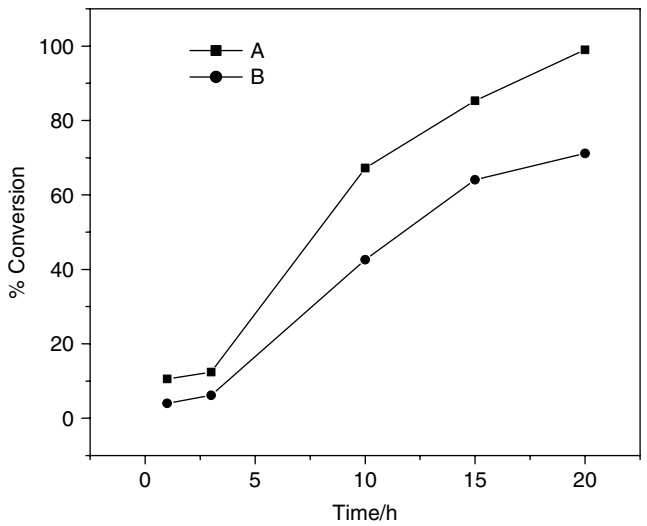
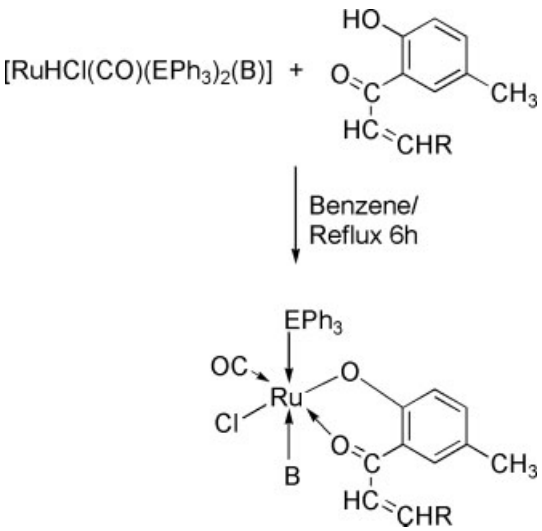


Figure 6. Catalytic oxidation of benzaldehyde (A) and cyclohexanone (B) in different time intervals.



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

^{13}C NMR Spectroscopic Analysis

The ^{13}C NMR spectra of some of the complexes (Table 4, Fig. 4) show that the peaks at 120.05–122.34 and 143.84–144.91 ppm regions are due to α, β alkene carbon, respectively. A peak around 80 ppm may be the solvent peak ($CDCl_3$). The presence of a peak at 186.66–195.42 ppm region is due to C≡O. Multiplets appear around 128.09–137.48 ppm region are assigned to aromatic carbons. In addition, sharp singlets at 55.57–57.96 and 21.68–22.73 ppm are assigned to methoxy and methyl carbons, respectively. This confirms the formation of new ruthenium(II) chalconate complexes.

Table 3. ^{1}H NMR data (δ in ppm) of ruthenium(II) chalconate complexes

Complexes	^{1}H NMR (ppm)
$[RuCl(CO)(PPh_3)_2(L^1)]$	7.21–7.33 (m,-CH=CH- and aromatic), 1.56 (s,CH_3)
$[RuCl(CO)(PPh_3)_2(L^3)]$	7.13–7.43 (m,-CH=CH- and aromatic), 1.55 (s,CH_3)
$[RuCl(CO)(AsPh_3)_2(L^2)]$	7.32–7.69 (m,-CH=CH- and aromatic), 1.56 (s,CH_3), 3.97 (s, OCH3)
$[RuCl(CO)(AsPh_3)_2(L^3)]$	6.97–7.39 (m,-CH=CH- and aromatic), 1.56 (s,CH_3)
$[RuCl(CO)(Py)(PPh_3)(L^1)]$	6.81–7.23 (m,-CH=CH- and aromatic), 1.53 (s,CH_3)
$[RuCl(CO)(Py)(PPh_3)(L^4)]$	7.22–7.67 (m,-CH=CH- and aromatic), 1.56 (s,CH_3), 3.95 (s, OCH3)

Based on the analytical and spectroscopic (IR, electronic, ^{1}H, ^{31}P and ^{13}C NMR) data, an octahedral structure (Fig. 5) has been tentatively proposed for all the ruthenium(II) chalconate complexes.

Catalytic Oxidation

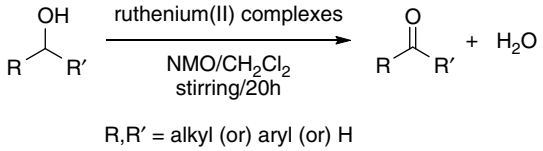
Catalytic oxidations of primary alcohols and secondary alcohols by the synthesized ruthenium(II) carbonyl chalconate complexes were carried out in CH_2Cl_2 in the presence of NMO. By-product water was removed using molecular sieves. All the complexes oxidize primary alcohols to the corresponding aldehydes and secondary alcohols to ketones (Scheme 2) with high yields, and the results are listed in Table 5. The aldehydes or ketones formed after 20 h of stirring were determined by GC and there was no detectable oxidation in the absence of ruthenium complex.

The oxidation of benzyl alcohol to benzaldehyde resulted in 88–99% yield and cyclohexanol to cyclohexanone resulted in 66–77% yield. The relatively higher product yield obtained for the oxidation of benzyl alcohol as compared with cyclohexanol is due to its benzylic and the α-CH unit of benzyl alcohol.[35] We observed that the triphenylarsine ruthenium(II) chalconate complexes possess greater catalytic activity than triphenylphosphine complexes. The conversion of primary and secondary alcohols to corresponding aldehydes and ketones increases with increased reaction time (Fig. 6). The ruthenium(II) chalconate complexes have better catalytic efficiency (>70%) in the case of oxidation of primary and secondary alcohols when compared with an earlier report[26] on similar ruthenium complexes as catalysts in the presence of NMO. In addition, the yield of conversion is higher than with the conventional catalyst $K_2Cr_2O_7$.

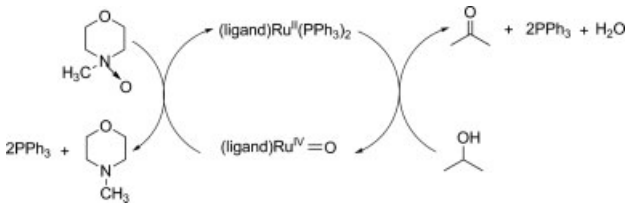
The present investigations suggest that the complexes react efficiently with NMO to yield a high-valency ruthenium-oxo species[36] capable of oxygen atom transfer to alcohols. This was further supported by spectroscopic changes that occur on addition of NMO to a dichloromethane solution of the ruthenium(II) complexes. The appearance of a peak at 390 nm is attributed to the formation of high-valency Ru^{IV}=O species, which is coformed with other oxo ruthenium(IV) complexes.[37,38] Further support comes from FT-IR of the solid (obtained by evaporation of the

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

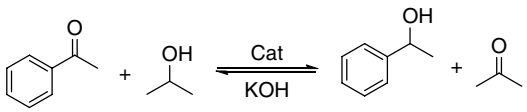
Complexes	^{13}C NMR (ppm)	^{31}P NMR (ppm)
$[RuCl(CO)(PPh_3)_2(L^1)]$	128.52–136.52(aromatic),120.18,144.84(α, β-CH=CH-), 190.82(C=O), 55.62(OCH_3), 21.76(CH_3)	25.63
$[RuCl(CO)(PPh_3)_2(L^2)]$	128.09–137.48(aromatic),120.05,143.84(α, β-CH=CH-), 186.66(C=O), 55.57(OCH_3), 21.68(CH_3)	25.85
$[RuCl(CO)(Py)(PPh_3)(L^1)]$	129.26–136.84(aromatic), 122.34,143.96(α, β-CH=CH-), 195.42(C=O), 56.87(OCH_3), 22.43(CH_3)	24.46
$[RuCl(CO)(Py)(PPh_3)(L^4)]$	128.13–135.52(aromatic), 121.45,144.91(α, β-CH=CH-), 192.69(C=O), 57.96(OCH_3), 22.73(CH_3)	24.52



Scheme 2. Reaction of catalytic oxidation.



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



Scheme 4. Reaction of catalytic transfer hydrogenation.

resultant solution to dryness), which shows a band at 860 cm^{-1}, characteristic of Ru^{IV}=O species (Scheme 3),[27] which is absent in the ruthenium catalyst. Except for the difference noted above, the IR spectra of the catalyst and solid appear quite similar, which suggests that the coordinated ligands remain intact in the oxidation process and that the catalytic oxidation proceeds through metal-oxo intermediate.

Catalytic Transfer Hydrogenation

As the starting point, the performance of the ruthenium(II) chalconate catalysts in transfer hydrogenation was screened using acetophenone as a model substrate (Scheme 4). As the Ru(II) chalconate complexes are the most active catalyst for transfer hydrogenation, the reduction of ketones other than acetophenone was attempted in the presence of these complexes. A variety of ketones (S/C/base molar ratio 300 : 1:2.5) were transformed to the corresponding secondary alcohols. Typical results, shown in Table 6, show that the catalysts performed efficiently for both aliphatic and aromatic ketones with high conversions (>98%). The yield of conversion was higher than with the conventional catalyst, $NaBH_4$. In addition, in the absence of base, no transfer hydrogenation was observed. The role of KOH is to generate the catalyst from the chloro precursor and the reaction mediates through the hydride species.[39] The base facilitates the formation

Table 5. Catalytic oxidation data of ruthenium(II) chalconate complexes

Complex	Substrate	Product	Yield (%)[a]
$[RuCl(CO)(PPh_3)_2(L^3)]$	Benzyl alcohol	A	92
	Cyclohexanol	B	68
$[RuCl(CO)(PPh_3)_2(L^4)]$	Benzyl alcohol	A	88
	Cyclohexanol	B	66
$[RuCl(CO)(AsPh_3)_2(L^1)]$	Benzyl alcohol	A	98
	Cyclohexanol	B	77
$[RuCl(CO)(AsPh_3)_2(L^2)]$	Benzyl alcohol	A	99
	Cyclohexanol	B	74
$[RuCl(CO)(Py)(PPh_3)(L^2)]$	Benzyl alcohol	A	96
	Cyclohexanol	B	71
$[RuCl(CO)(Py)(PPh_3)(L^4)]$	Benzyl alcohol	A	93
	Cyclohexanol	B	68
$K_2Cr_2O_7/H_2SO_4$	Benzyl alcohol	A	07
	Cyclohexanol	B	04

A: benzaldehyde; B: cyclohexanone,
[a] Yield determined by GC compared with the analyses of authentic samples.

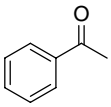
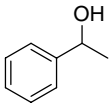
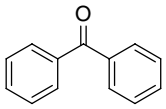
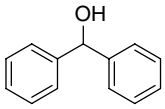
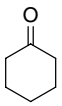
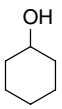
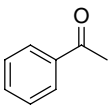
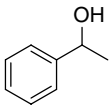
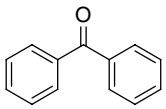
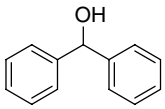
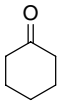
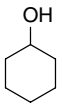
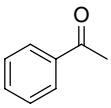
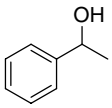
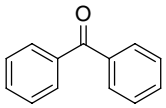
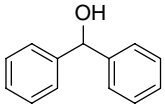
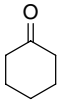
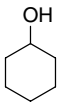
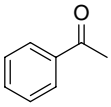
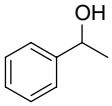
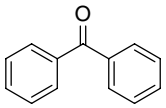
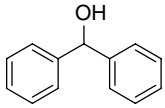
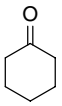
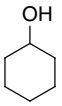
of the ruthenium alkoxide by abstracting the proton of the alcohol and subsequently the alkoxide undergoes β-elimination to give a ruthenium hydride which is the active species in this reaction.[40]

Addition of bases like KOH, NaOH or Na-(*i*OPr) leads to similar final conversion, but the highest rates are observed when KOH is employed.[41] Pamies and Backvall[42] studied the mechanism for a number of bisphosphineruthenium(II) complexes by monitoring the racemization of monodeuterated *S*-phenylethyl alcohol with acetophenone and found that the catalysts under study in most of the cases followed the monohydride pathway. Since our catalysts are similar to those studied by Pamies and Backvall, we assumed that the reactions followed the monohydride pathway.

Conclusions

Several ruthenium(II) chalconate complexes were synthesized using chalconate formed from derivatives of benzaldehyde and 2-hydroxy-5-methylacetophenone. The new complexes have been characterized by analytical and spectroscopic data. An octahedral structure has been tentatively proposed for all the complexes. The complexes showed efficient catalysts for the oxidation of both primary and secondary alcohols to the corresponding carbonyl compounds with excellent yields in the presence of *N*-methylmorpholine-*N*-oxide, and also for transfer

Table 6. Catalytic transfer hydrogenation of ketones by ruthenium(II) chalconate complexes[a]

Complex	Substrate	Product	Yield(%)	Conversion(%)[b]
$[RuCl(CO)(PPh_3)_2(L^2)]$				96
				95
				96
$[RuCl(CO)(AsPh_3)_2(L^1)]$				88
				97
				93
$[RuCl(CO)(Py)(PPh_3)(L^1)]$				98
				99
				98
$NaBH_4$				20
				32
				34

[a] Conditions: reactions were carried out heated to reflux using 3.75 mmol of ketone (5 ml isopropanol); catalyst–ketone–KOH ratio 1 : 300:2.5.
[b] Yield of product was determined using a ACME 6000 series GC-FID with a DP-5 column of 30 m length, 0.53 mm diameter and 5.00 μm film thickness and by comparison with authentic samples.

hydrogenation of aliphatic and aromatic ketones with high conversions (>98%).

Acknowledgment

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 financial support. One of the authors (M.M.) thanks CSIR for the award of Senior Research Fellowship.

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