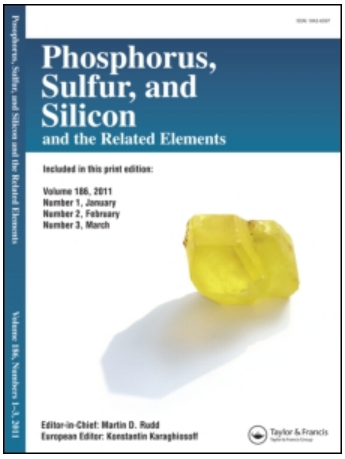

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Studies on Ruthenium(III) Chalconate Complexes Containing PPh_3/$AsPh_3$

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STUDIES ON RUTHENIUM(III) CHALCONATE COMPLEXES CONTAINING $PPh_3/AsPh_3$

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***The reactions of $[RuX_3(EPh_3)_3]$ ($X = Cl$ or Br; $E = P$ or As) with 2′-hydroxychalcones in benzene under reflux led to the formation of $[RuX_2(EPh_3)_2(L)]$ ($X = Cl$ or Br; $E = P$ or As; L = chalconates). The new complexes have been characterized by analytical and spectroscopic (IR, electronic, and EPR) data. The redox behavior of the complexes has also been studied. Based on the data, an octahedral structure has been assigned for all the complexes. The new complexes exhibit efficient 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 also found efficient catalytic activity for the transfer hydrogenation of ketones. The antifungal properties of the complexes have also been examined and compared with standard* Bavistin.**

Supplemental materials are available for this article. Go to the publisher's online edition of* Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.

Keywords Antifungal study; catalytic activity; cyclic voltammetry; ruthenium(III) complexes; spectroscopic characterization

INTRODUCTION

The chemistry of ruthenium has been attracting considerable current interest,[1] largely because of the fascinating photochemical, photophysical, and redox properties exhibited by complexes of this metal. As all these properties are primarily directed by the coordination environment around the metal center, complexation of ruthenium by ligands of selected types are of significant importance,[2] and the present study has originated from our interest in this area. Chalcones are precursors to the flavonoids, natural products that play a significant role in the disease and parasite resistance of plants. Indeed, there is interest in the use of chalcone derivatives for pharmaceutical purposes including as antibiotic, antitumor, and antimalarial agents.[3]

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Ruthenium complexes have been used as catalysts or catalyst precursors for a variety of purposes including hydrogenation, oxidation, isomerization, polymerization, nucleophilic addition to multiple bonds, and carbon–carbon bond formation.[4] The oxidation of alcohols into their corresponding aldehydes and ketones is of greater importance in synthetic organic chemistry.[5–7] Though several ruthenium catalytic systems have been reported with a wide range of oxidants viz., *tert*-butyl hydroperoxide,[8] chloramine-T,[9] benzoquinone,[10] hydrogen peroxide,[11] molecular oxygen,[12] iodosylbenzene,[13] and $NaIO_4$,[14] *N*-methylmorpholine-*N*-oxide (NMO) as an oxidant has received less coverage in the literature.

More recently, transition metal–catalyzed transfer hydrogenation reactions using isopropanol as the hydrogen source have become efficient methods in organic synthesis, as illustrated by several useful applications.[15] Among the different metal-catalyzed reactions, ruthenium-based catalytic systems are effective in the transfer hydrogenation of ketones.[16–23] Even though there are a number of reports available on catalytic oxidation and the transfer hydrogenation of ketones, to the best of our knowledge, there are no reports available for catalytic oxidation of alcohols by ruthenium(III) chalconate complexes incorporating O,O-donors in the presence of NMO and catalytic transfer hydrogenation of ketones in the presence of isopropanol and KOH.

In view of the growing interest in the catalytic and biological activities of ruthenium complexes, in this article we report the synthesis of a series of hexacoordinated ruthenium(III) chalconate complexes containing PPh_3/$AsPh_3$. A few of the synthesized complexes have been effectively used as catalysts in oxidation of alcohols in the presence of NMO and in transfer hydrogenation of ketones in the presence of isopropanol and KOH. Further, the new complexes have been screened for their antifungal studies.

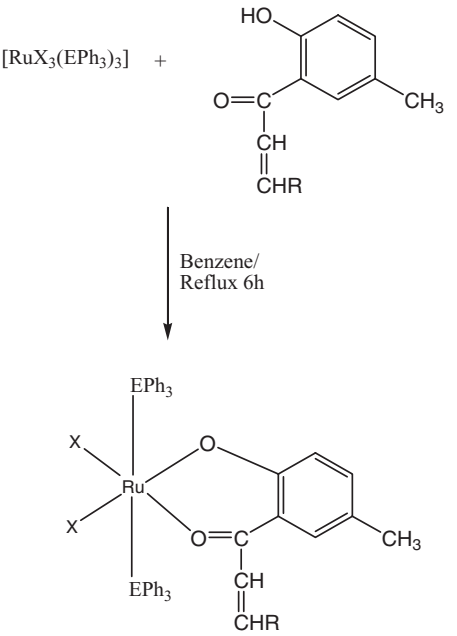
RESULTS AND DISCUSSION

Paramagnetic, hexa-coordinated, low-spin ruthenium(III) complexes of the general formula $[RuX_2(EPh_3)_2(L)]$ (X = Cl or Br; E = P or As; L = chalconates) were synthesized in good yields from the reaction of $[RuX_3(EPh_3)_3]$ (X = Cl or Br; E = P or As) with 2′-hydroxychalcone ligands in dry benzene in equal molar ratio (Scheme 1). In all these reactions, it has been observed that the 2′-hydroxychalcones behave as monobasic bidentate chelating ligands by replacing a triphenylphosphine/arsine and a chloride/bromide ion from the starting complexes.

All the complexes are stable in air at room temperature, brown in color, non-hygroscopic, and highly soluble in common organic solvents such as dichloromethane, acetonitrile, chloroform, and DMSO. The analytical data are in good agreement with the general molecular formula proposed for all the complexes.

Infrared Spectroscopic Analysis

The free chalcone ligands showed a strong band in the region 1632–1647 cm^{-1} due to $\upsilon_{C=O}$. This band has been shifted to a lower wave number 1612–1629 cm^{-1} in the ruthenium complexes, indicating the coordination of the ligands to ruthenium through the carbonyl oxygen atom.[24] A strong band observed at 1300–1305 cm^{-1} in the free chalcone ligands has been assigned to phenolic υ_{C-O} stretching. This band has been shifted to higher wave number 1306–1317 cm^{-1} in the spectra of the complexes due to its coordination to the ruthenium ion through the oxygen atom of the phenolic group.[25] This has been



(X = Cl or Br; E = P or As; 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(III) chalconate complexes.

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 the ruthenium metal. Hence, from the infrared spectroscopic data, it is inferred that both the carbonyl and phenolic oxygen atoms are involved in the coordination of the 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 $\upsilon_{C=O}$.[26] In the complexes, the absorption due to the phenyl alkene vibration appeared in the region 1536–1551 cm^{-1}, which is slightly lower than that observed in the spectra of the free ligands.[27] In addition, the other characteristic bands due to triphenylphosphine or triphenylarsine (around 1440, 1090, and 700 cm^{-1}) were also present in the spectra of all the complexes.[28] The observed bands in the regions 460–475 cm^{-1} in the mononuclear complexes are tentatively assigned to the υ_{Ru-Cl} vibrations.[29]

Electronic Spectroscopic Analysis

The electronic spectra of the ruthenium(III) complexes were recorded in dichloromethane in the region 900–200 nm. Most of the complexes showed two to three bands in the region 830–207 nm. The ground state of ruthenium(III) in an octahedral environment is $^2T_{2g}$, arising from the t_{2g}^5 configuration, and the first excited doublet levels in the order of increasing energy are $^2A_{2g}$ and $^2T_{1g}$, arising from the t_{2g}^4 e_g^1 configuration. Hence, two bands corresponding to $^2T_{2g} \rightarrow {}^2A_{2g}$ and $^2T_{2g} \rightarrow {}^2T_{1g}$ are possible. The absorption bands around 830–802 nm and 442–401 nm are assigned to d–d and charge

transfer (LMCT) transitions respectively. In most ruthenium(III) complexes, charge transfer bands of the type $L_{\pi y} \rightarrow T_{2g}$ are prominent in the low-energy region, which obscures the weaker bands due to d–d transitions.[30] It is therefore difficult to assign conclusively the bands of the ruthenium(III) complexes that appear in the visible region.

However, the extinction coefficients for the bands 830–802 nm are found to be low compared to that of the charge transfer bands. Hence the bands around 830–802 nm have been assigned to $^2T_{2g} \rightarrow {}^2A_{2g}$, which is in conformity with the assignment made for similar octahedral ruthenium(III) complexes.[31,32] The absorptions in the ultraviolet region below 400 nm are very similar and are attributable to the transitions within the ligand orbital (π–π^*, n–π^*) that are taking place in the chalcone ligands. The pattern of the electronic spectra of all the complexes indicated the presence of an octahedral environment around the ruthenium(III) ion.

Cyclic Voltammetry

The electrochemical properties of some of the complexes have been examined cyclic voltammetrically under N_2 atmosphere at glassy carbon working electrode in acetonitrile solution (0.05 M: NBu_4ClO_4), and the redox potentials are expressed with reference to Ag/AgCl. All the complexes (1×10^{-3} M) are electroactive with respect to the metal centers and exhibited two redox processes in the potential range +1.5 V to −1.5 V. The complexes display a reversible oxidative (RuIV/RuIII) and reversible reductive response (RuIII/RuII) at the scan rate of 100 mVs^{-1}. (See Table S1 in the Supplemental Materials, available online.)

EPR Spectroscopic Analysis

The solid state EPR spectra of all the ruthenium(III) chalconate complexes (a representative spectrum is given in Figure 1) were recorded in X-band frequencies at room temperature. All the new complexes showed a single isotropic line with "g" values in the range 2.30–2.52, indicating a high symmetry around the ruthenium ion. Such isotropic lines are due either to the results of intermolecular spin exchange, which can broaden the lines, or to occupancy of the unpaired electron in a degenerate orbital.

The nature and pattern of the EPR spectra suggest an almost perfect octahedral environment around the ruthenium ion in the complexes,[33,34] and there are no hyperfine interactions with any other nuclei present in the complexes.

Based on the above analytical and spectroscopic data, an octahedral structure (Scheme 1) has been suppositionally proposed for all the ruthenium(III) chalconate complexes.

Catalytic Oxidation

Catalytic oxidation of primary alcohols and secondary alcohols by the synthesized ruthenium(III) chalconate complexes was carried out in CH_2Cl_2 in the presence of NMO, and the byproduct water was removed by using molecular sieves. All the complexes oxidize primary alcohols to the corresponding aldehydes and secondary alcohols to ketones with high yields. The aldehydes or ketones formed after 3 h of refluxing were determined by GC, and there was no detectable oxidation in the absence of ruthenium complex.

The oxidation of benzylalcohol to benzaldehyde resulted in 93–99% yield, and cyclohexanol to cyclohexanone resulted in 53–82% yield. The relatively higher product yield

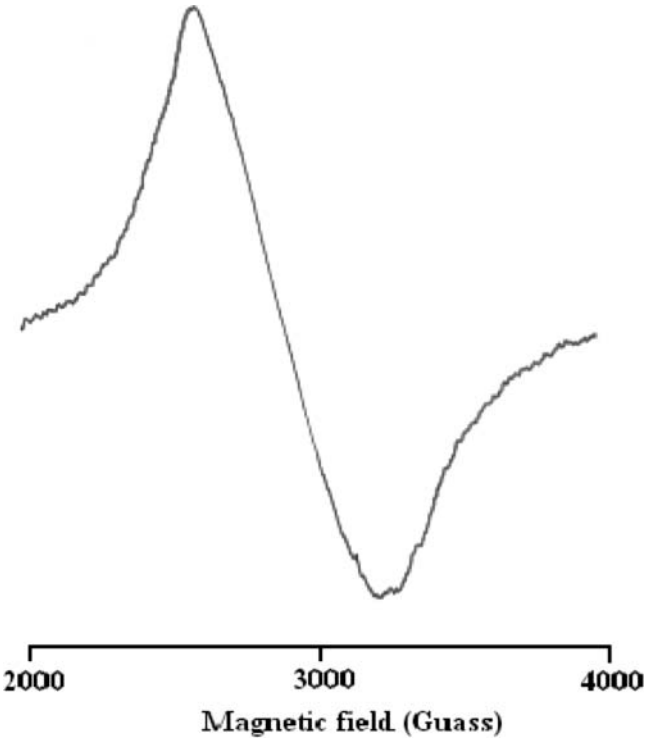


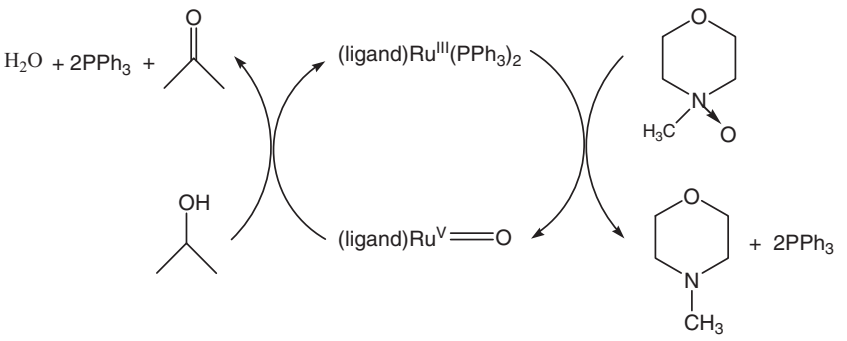
Figure 1 EPR spectrum of $[RuCl_2(AsPh_3)_2(L^1)]$.

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.[35] It has been observed that the triphenylarsine ruthenium(III) chalconate complexes possess slight changes in catalytic activity compared to triphenylphosphine complexes. The conversion of primary and secondary alcohols to corresponding aldehydes and ketones increases with increase in reaction time up to 3 h (Table S2, Supplemental Materials).

The results of the present investigations suggest that the complexes are able to react efficiently with NMO to yield a high-valent ruthenium-oxo species[36] capable of oxygen atom transfer to alcohols. This was further supported by spectroscopic changes that occur by addition of NMO to dichloromethane solution of the ruthenium(III) complexes. The appearance of a peak at 390 nm is attributed to the formation of $Ru^V = O$ species, which is in conformity with other oxo ruthenium(V) complexes.[37,38] Further support in favor of the formation of such species was identified from the IR spectrum of the solid mass (obtained by evaporation of the resultant solution to dryness), which showed a band at 860 cm^{-1}, characteristic of $Ru^V = O$ species[36,38] (Scheme 2).

Catalytic Transfer Hydrogenation

The catalytic transfer hydrogenation of acetophenone in the presence of ruthenium chalconate complexes has been studied in isopropanol–KOH medium using a molar ratio of 1:2.5:300 for the catalyst, KOH, and the ketone in 10 mL of isopropanol.



Scheme 2 Proposed catalytic cycle for the oxidation of alcohols by the ruthenium(III) chalconate complexes.

The catalyst performed efficiently for both aliphatic and aromatic ketones with high conversion. Cyclohexanone was converted into cyclohexanol in 78–99% yield (Table S3, Supplemental Materials). Acetophenone was converted into corresponding alcohol in 28–95% yield. Similarly, benzophenone underwent transfer hydrogenation to afford the corresponding alcohol in 84–99% yield. The product formation in the absence of base was very low. The role of KOH is to generate the catalyst from the chloro precursor, and the reaction mediates through the hydride species. The base facilitated the formation of the ruthenium alkoxide by abstracting the proton of the alcohol and, subsequently, the alkoxide underwent β-elimination to give ruthenium hydride, which is the active species in this reaction.[39]

Antifungal Activity

The *in vitro* antifungal screening against *Aspergillus niger* and *Mucor Sp.* for the ligands and some of their ruthenium(III) chalconate complexes has been carried out by the disc diffusion method[40] (see the Supplemental Materials for complete details). The results showed that the ruthenium complexes are more toxic than their parent ligands against the same microorganisms under identical experimental conditions (Table S4, Supplemental Materials).

MATERIALS AND METHODS

All the reagents used were chemically pure and AR grade. The solvents were purified and dried according to standard procedures.[41] $RuCl_3 \cdot 3H_2O$ was purchased from Loba Chemie Pvt. Ltd., and was used without further purification. The microanalyses of carbon, hydrogen, and nitrogen were recorded by a Carlo-Erba 1108 model analyzer at Central Drug Research Institute (CDRI), Lucknow, India. Infrared spectra of the ligands and 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 CH_2Cl_2 using a Shimadzu UV-visible 1650 PC spectrophotometer in the 200–900 nm range. Electron paramagnetic resonance spectra (EPR) of the powdered samples were recorded with a JEOL JES-FA200 instrument at X-band frequencies in room temperature using 2,2-diphenyl-1-picrylhydrazyl radical (DPPH) as internal standard at Pondicherry University, Pondicherry, India. Cyclic voltammetric measurements were carried out with a BAS CV-27 electrochemical analyzer

in acetonitrile using $[NBu_4]ClO_4$ (TBAP) as the supporting electrolyte under nitrogen atmosphere. A three-electrode cell was employed with a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. Melting points were recorded on a Technico micro heating table and are uncorrected. The catalytic yields were determined using ACME 6000 series GC-FID with a DP-5 column of 30 m length, 0.53 mm diameter, and 5.00 μm film thickness. The starting complexes $[RuCl_3(PPh_3)_3]$,[42] $[RuCl_3(AsPh_3)_3]$,[43] and $[RuBr_3(AsPh_3)_3]$[44] were prepared according to the methods in the literature.

Synthesis of 2′-Hydroxychalcone Ligands

2′-Hydroxychalcone ligands were prepared by condensing 4-substituted benzaldehyde (0.6007–0.8309 g, 5 mmol) with 2-hydroxy-5-methylacetophenone (0.7509 g, 5 mmol) in the presence of alcoholic sodium hydroxide solution (50 mL, 20%). After 24 h of stirring, the product was precipitated by the addition of concentrated hydrochloric acid, followed by filtration, and then the product was recrystallized from ethanol.

L^1: FT-IR (KBr, cm^{-1}): ν(C=O) 1637, ν(C−O) 1302, ν(C=C) 1569. **L^2**: FT-IR (KBr, cm^{-1}): ν(C=O) 1635, ν(C−O) 1300, ν(C=C) 1555. **L^3**: FT-IR (KBr, cm^{-1}): ν(C=O) 1647, ν(C−O) 1302, ν(C=C) 1571. **L^4**: FT-IR (KBr, cm^{-1}): ν(C=O) 1632, ν(C−O) 1305, ν(C=C) 1547.

Synthesis of New Ruthenium(III) Chalconate Complexes

All reactions were carried out under anhydrous conditions and were prepared by the following common procedure. To a solution of $[RuX_3(EPh_3)_3]$ (X = Cl or Br; E = P or As) (0.1 g) in benzene (20 mL), the appropriate 2′-hydroxychalcone (0.02–0.03 g) was added in 1:1 molar ratio. The mixture was heated under reflux for 6 h. The reaction mixture gradually changed to deep color, and the solvent was removed under reduced pressure. The product was separated by the addition of a small amount of petroleum ether (60–80°C) and recrystallized from a CH_2Cl_2/petroleum ether mixture. The compounds were dried under vacuum, and the purity of the complexes was checked by TLC.

$[RuCl_2(PPh_3)_2(L^1)]$. Brown, dp 202°C, yield 61%, Anal. Calcd. for $C_{53}H_{45}O_2P_2Cl_2Ru$: C, 67.16; H, 4.78. Found: C, 67.21; H, 4.72%. FT-IR (KBr, cm^{-1}): ν(C=O) 1619; ν(C−O) 1315; ν(C=C) 1536; (PPh_3/$AsPh_3$) 1435, 1091, 694. UV (CH_2Cl_2, nm (ε, $dm^3mol^{-1}cm^{-1}$)): 830(1321), 402(15280), 358(24160).

$[RuCl_2(PPh_3)_2(L^2)]$. Brown, dp 175°C, yield 58%, Anal. Calcd. for $C_{53}H_{45}O_3P_2Cl_2Ru$: C, 66.04; H, 4.70. Found: C, 66.10; H, 4.70%. FT-IR (KBr, cm^{-1}): ν(C=O) 1623; ν(C−O) 1310; ν(C=C) 1536; (PPh_3/$AsPh_3$) 1434, 1091, 694. UV (CH_2Cl_2, nm (ε, $dm^3mol^{-1}cm^{-1}$)): 380(22360), 231(31143).

$[RuCl_2(PPh_3)_2(L^3)]$. Brown, dp 172°C, yield 64%, Anal. Calcd. for $C_{52}H_{42}O_2P_2Cl_3Ru$: C, 64.50; H, 4.37. Found: C, 64.46; H, 4.35%. FT-IR (KBr, cm^{-1}): ν(C=O) 1620; ν(C−O) 1312; ν(C=C) 1536; (PPh_3/$AsPh_3$) 1435, 1091, 694. UV (CH_2Cl_2, nm (ε, $dm^3mol^{-1}cm^{-1}$)): 802(1442), 350(25190), 232(31160).

$[RuCl_2(PPh_3)_2(L^4)]$. Brown, dp 178°C, yield 71%, Anal. Calcd. for $C_{54}H_{47}O_4P_2Cl_2Ru$: C, 65.26; H, 4.76. Found: C, 65.32; H, 4.72%. FT-IR (KBr, cm^{-1}): ν(C=O) 1623; ν(C−O) 1311; ν(C=C) 1541; (PPh_3/$AsPh_3$) 1438, 1093, 695. UV (CH_2Cl_2, nm (ε, $dm^3mol^{-1}cm^{-1}$)): 401(15137), 232(31160), 209(27694).

[$RuCl_2(AsPh_3)_2(L^1)$]. Brown, dp 160°C, yield 59%, Anal. Calcd. for $C_{53}H_{45}O_2As_2Cl_2Ru$: C, 61.46; H, 4.38. Found: C, 61.42; H, 4.41%. FT-IR (KBr, cm^{-1}): ν(C=O) 1627; ν(C−O) 1317; ν(C=C) 1542; (PPh_3/$AsPh_3$) 1436, 1077, 693. UV (CH_2Cl_2, nm (ε, $dm^3mol^{-1}cm^{-1}$)): 817(1367), 236(32175).

[$RuCl_2(AsPh_3)_2(L^2)$]. Brown, dp 149°C, yield 65%, Anal. Calcd. for $C_{53}H_{45}O_3As_2Cl_2Ru$: C, 60.52; H, 4.30. Found: C, 60.48; H, 4.28%. FT-IR (KBr, cm^{-1}): ν(C=O) 1624; ν(C−O) 1315; ν(C=C) 1551; (PPh_3/$AsPh_3$) 1435, 1078, 692. UV (CH_2Cl_2, nm (ε, $dm^3mol^{-1}cm^{-1}$)): 364(23532), 233(31530), 223(28478).

[$RuCl_2(AsPh_3)_2(L^3)$]. Brown, dp 135°C, yield 72%, Anal. Calcd. for $C_{52}H_{42}O_2As_2Cl_3Ru$: C, 59.13; H, 4.00. Found: C, 59.09; H, 3.97%. FT-IR (KBr, cm^{-1}): ν(C=O) 1625; ν(C−O) 1312; ν(C=C) 1542; (PPh_3/$AsPh_3$) 1435, 1076, 694. UV (CH_2Cl_2, nm (ε, $dm^3mol^{-1}cm^{-1}$)): 383(22128), 223(28354).

[$RuCl_2(AsPh_3)_2(L^4)$]. Brown, dp 153°C, yield 64%, Anal. Calcd. for $C_{54}H_{47}O_4As_2Cl_2Ru$: C, 59.95; H, 4.38. Found: C, 60.01; H, 4.39%. FT-IR (KBr, cm^{-1}): ν(C=O) 1622; ν(C−O) 1313; ν(C=C) 1548; (PPh_3/$AsPh_3$) 1435, 1076, 693. UV (CH_2Cl_2, nm (ε, $dm^3mol^{-1}cm^{-1}$)): 393(25495), 233(31530).

[$RuBr_2(AsPh_3)_2(L^1)$]. Brown, dp 125°C, yield 59%, Anal. Calcd. for $C_{53}H_{45}O_2As_2Br_2Ru$: C, 56.60; H, 4.00. Found: C, 56.54; H, 4.06%. FT-IR (KBr, cm^{-1}): ν(C=O) 1625; ν(C−O) 1306; ν(C=C) 1543; (PPh_3/$AsPh_3$) 1435, 1080, 691. UV (CH_2Cl_2, nm (ε, $dm^3mol^{-1}cm^{-1}$)): 401(15137), 235(26970), 207(25682).

[$RuBr_2(AsPh_3)_2(L^2)$]. Brown, dp 145°C, yield 55%, Anal. Calcd. for $C_{53}H_{45}O_3As_2Br_2Ru$: C, 55.80; H, 3.97. Found: C, 55.78; H, 3.98%. FT-IR (KBr, cm^{-1}): ν(C=O) 1628; ν(C−O) 1311; ν(C=C) 1539; (PPh_3/$AsPh_3$) 1435, 1079, 691. UV (CH_2Cl_2, nm (ε, $dm^3mol^{-1}cm^{-1}$)): 440(16342), 234(35890), 221(27963).

[$RuBr_2(AsPh_3)_2(L^3)$]. Brown, dp 135°C, yield 63%, Anal. Calcd. for $C_{52}H_{42}O_2Cl$ As_2Br_2Ru: C, 54.54; H, 3.69. Found: C, 54.56; H, 3.71%. FT-IR (KBr, cm^{-1}): ν(C=O) 1629; ν(C−O) 1306; ν(C=C) 1545; (PPh_3/$AsPh_3$) 1435, 1079, 691. UV (CH_2Cl_2, nm (ε, $dm^3mol^{-1}cm^{-1}$)): 439(15598), 237(32398).

[$RuBr_2(AsPh_3)_2(L^4)$]. Brown, dp 138°C, yield 70%, Anal. Calcd. for $C_{54}H_{47}O_4$ As_2Br_2Ru: C, 55.40; H, 4.05. Found: C, 55.36; H, 4.07%. FT-IR (KBr, cm^{-1}): ν(C=O) 1612; ν(C−O) 1312; ν(C=C) 1537; (PPh_3/$AsPh_3$) 1435, 1080, 691. UV (CH_2Cl_2, nm (ε, $dm^3mol^{-1}cm^{-1}$)): 442(17580), 232(31160).

Catalytic Oxidation

Catalytic oxidation of primary alcohols to corresponding aldehydes and secondary alcohols to ketones by ruthenium(III) 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 substrates at 1:100 molar ratio was described as follows. A solution of ruthenium complex (0.01 mmol) in CH_2Cl_2 (20 mL) was added to the mixture containing substrate (1 mmol), NMO (3 mmol), and molecular sieves. The reaction mixture was refluxed for 3 h, 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 mL) and was analyzed by GC. The oxidation products were identified by GC co-injection with authentic samples.

Catalytic Transfer Hydrogenation of Ketones

The catalytic transfer hydrogenation reactions were also studied using ruthenium(III) chalconate complexes as a catalyst, ketone as substrate, and KOH as promoter in 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 *i*-prOH (10 mL) was reacted under reflux in a water bath for 2 h. After completion of the reaction, the catalyst was removed from the reaction mixture by the addition of diethyl ether followed by filtration and subsequent neutralization with 1 M HCl. The ether layer was filtered through a short path of silica gel by column chromatography. The filtrate was subjected to GC analysis, and the hydrogenated product was identified and determined with authentic samples.

CONCLUSIONS

Several new ruthenium(III) chalconate complexes were synthesized using chalcone formed from derivatives of benzaldehyde and 2-hydroxy-5-methylacetophenone. The new complexes have been characterized by analytical and spectroscopic (IR, electronic, and EPR) data. An octahedral structure has been tentatively proposed for all the complexes. The complexes showed efficient catalytic activity for the oxidation of both primary and secondary alcohols with excellent yields in the presence of *N*-methylmorpholine-*N*-oxide, and also for transfer hydrogenation of aliphatic and aromatic ketones with high conversions in the presence of isopropanol and KOH as promoter. The complexes exhibited considerable amounts of antifungal activity at the time of screening.

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