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Synthesis, spectral characterization and catalytic studies of new ruthenium(II) chalcone thiosemicarbazone complexes

Research Article

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Abstract: A series of new hexa-coordinated ruthenium(II) complexes of the type [Ru(CO)(EPh_3)(B)(L)] (E = P or As; B = PPh_3, $AsPh_3$ or Py; L = chalcone thiosemicarbazone) have been prepared by reacting [RuHCl(CO)(EPh_3)$_2$(B)] (E = P or As; B = PPh_3, $AsPh_3$ or Py) with chalcone thiosemicarbazones in benzene under reflux. The new complexes have been characterized by analytical and spectroscopic (IR, UV-vis, ^{1}H, ^{31}P and ^{13}C NMR) methods. On the basis of data obtained, an octahedral structure was assigned for all of the complexes. The chalcone thiosemicarbazones behave as dianionic tridentate O, N, S donors and coordinate to ruthenium *via* the phenolic oxygen of chalcone, the imine nitrogen of thiosemicarbazone and thienol sulfur. The new complexes exhibit catalytic activity for the oxidation of primary and secondary alcohols to their corresponding aldehydes and ketones and they were also found to be efficient catalysts for the transfer hydrogenation of carbonyl compounds.

Keywords: *Spectroscopic characterization • Catalytic oxidation • Catalytic transfer hydrogenation • Chalcone thiosemicarbazone complexes*

1. Introduction

Thiosemicarbazones have received considerable attention due to their antibacterial [1,2] and cytotoxic activity [3] against cancer cells. In recent years, various metal complexes of thiosemicarbazide derivatives have been the subject of interest due to their wide range of pharmacological properties, such as antimicrobial [4,5], antiameobic [6], antitumor [7] and antiviral activity [8]. Transition metal complexes of thiosemicarbazones possess some degree of cytotoxic activity [9]. The chemistry of complexes of ruthenium with thiosemicarbazones, which can coordinate to the metal either in neutral thione form or in the anionic thiolate form, has received attention in recent years primarily due to their varied coordination mode, novel electrochemical and electronic properties, as well as their biological importance [10-12].

Transition metal complexes containing triphenylphosphine have been extensively synthesized and investigated because phosphine ligands are reactive and versatile homogeneous catalysts in alkene polymerization [13], Heck [14] and Suzuki [15] reactions and oxidation of alcohols [16,17]. Oxidation of alcohols are of paramount importance in organic syntheses because of the importance of the product carbonyl compounds as intermediates for medicines, agricultural chemicals, and fragrances [18].

The reduction of ketones and aldehydes to the corresponding alcohols, which can be performed by a variety of methods, is another fundamental reaction in organic synthesis. Among the methods used, transfer hydrogenation [19] is an elegant strategy that can be accomplished with homogeneous [20], heterogeneous [21], perfluorinated [22], and water-soluble catalysts [23], using different hydrogen sources, such as

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isopropyl alcohol and formic acid derivatives. Transfer hydrogenation of carbonyl compounds using isopropyl alcohol as reducing agent as well as solvent has attracted a lot of attention over the last few years due to the comparatively benign nature of the reagents [24]. Although a number of transition metal catalysts have been used for this transformation, ruthenium(II) complexes [24,25] have attracted the most interest. In contrast to conventional hydrogenation using dihydrogen and metal catalysts, which frequently require a high hydrogen pressure [26], the transfer hydrogenation has some unique advantages in its simplicity and avoidance of cumbersome reducing agents. However, in most cases, the reactions are effective only with ketones. It has been shown, however, that ruthenium complexes containing phosphine or acetonitrile ligands are effective catalysts for reduction of aldehydes [27]. Encouraged by these reports, we wanted to explore the efficacy of the newly synthesized [ONS]-type chalcone thiosemicarbazone ruthenium(II) complexes containing triphenylphosphine/arsine.

Hence, in this paper we report the synthesis, characterization and catalytic activities of a series of hexacoordinated ruthenium(II) chalcone thiosemicarbazone complexes containing PPh_3/$AsPh_3$. The characterizations of the complexes were accomplished by analytical and spectroscopic (IR, UV-vis, ^1H, ^{31}P and ^{13}C NMR) methods.

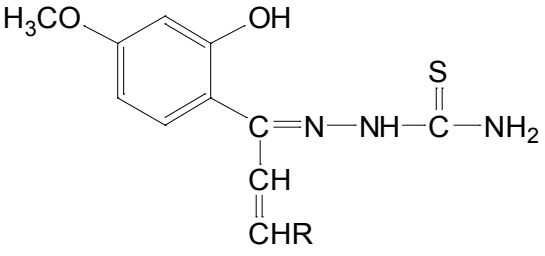
2. Experimental procedure

2.1. Reagents and materials

All the reagents used were chemically pure and AR grade. The solvents were purified and dried according to standard procedures [28]. $RuCl_3 \cdot 3H_2O$ was purchased from Loba Chemie Pvt. Ltd., and was used without further purification. The starting complexes [RuHCl(CO)$(PPh_3)_3$] [29], [RuHCl(CO)$(AsPh_3)_3$] [30] and [RuHCl(CO)(Py)$(PPh_3)_2$] [31] were prepared according to literature methods. The general structure of the chalcone thiosemicarbazone ligands used in this study is given below (Fig. 1).

2.2. Instruments

CHN analyses were performed by using Carlo-Erba 1108 model analyzer at Central Drug Research Institute (CDRI), Lucknow, India. FT-IR spectra were recorded in KBr pellets with a Nicolet FT-IR spectrophotometer over the 400-4000 cm^{-1} range. UV-vis spectra of the complexes were recorded in dichloromethane solution on a Shimadzu UV-visible 1650 PC spectrophotometer over the 200-800 nm range. NMR spectra (^1H, ^{31}P and ^{13}C) were recorded on a Jeol GSX-500 spectrometer in $CDCl_3$. ^1H NMR and ^{13}C NMR spectra were obtained at room temperature using TMS as the internal standard. ^{31}P NMR spectra of the complexes were obtained using orthophosphoric acid as a reference. The catalytic yields were determined using ACME 6000 series gas chromatography instrument equipped with a flame ionization detector (FID) using a DP-5 column of 30 m length, 0.53 mm diameter and 5.00 µm film thickness. Melting points were recorded on a Technico micro heating table and are uncorrected.



Ligand	R
L^1	4-$(CH_3)C_6H_4$
L^2	4-$(OCH_3)C_6H_4$
L^3	4-$(Cl)C_6H_4$
L^4	3,4-$(OCH_3)_2C_6H_3$

Figure 1. Structure of chalcone thiosemicarbazones

2.3. Preparation of ONS tridentate chalcone thiosemicarbazone ligands

Ligands were prepared by a two-step processes. In the first step, the 2-hydroxychalcone ligands were prepared by stirring 4-substituted benzaldehyde (0.6008-0.8309 g, 5 mmol) with 2-hydroxy-4-methoxyacetophenone (0.8309 g, 5 mmol) in the presence of 50 cm^3 alcoholic sodium hydroxide solutions (20%). After 24 h stirring, the product was precipitated by addition of concentrated hydrochloric acid, then filtered and recrystallized from ethanol. In the second step, 2-hydroxychalcones (0.2683-0.3143 g, 1 mmol) were reacted with thiosemicarbazide (0.4253 g, 4.7 mmol) in ethanol (100 cm^3) containing concentrated hydrochloric acid (0.5 cm^3). The reaction mixture was refluxed for 8 h and the solvent was evaporated under vacuum. The resulting residue (yield 60-65%) was recrystallized from ethanol. The ligands were characterized by analytical and spectroscopic methods (Tables 1-4).

2.4. Synthesis of new ruthenium(II) chalcone thiosemicarbazone 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) (0.1 g) in benzene (20 cm^3), the appropriate chalcone thiosemicarbazone (0.0315-0.0504 g) was added in 1:1 molar ratio. The mixture was heated under reflux for 6 h on a water bath. The reaction mixture gradually became intensely colored during heating. The contents were then concentrated to approximately 3 cm^3 by removing the solvent under reduced pressure. The contents were cooled and the product was separated by the addition of 10 cm^3 of petroleum ether (60-80°C). The product was recrystallized from a dichloromethane/petroleum ether mixture. The compounds were dried under vacuum over fused calcium chloride and the purity of the complexes was checked by TLC (Yield 76-89%).

2.5. Procedure for catalytic oxidation of alcohols

Catalytic oxidation of primary alcohols to the corresponding aldehydes and secondary alcohols to ketones by ruthenium(II) chalcone thiosemicarbazone complexes were studied in the presence of NMO as co-oxidant. A typical reaction using the complex as a catalyst and primary or secondary alcohols as substrates at 1:100 molar ratio was as follows: A solution of ruthenium complex (0.01 mmol) in dichloromethane (20 cm^3) was added to the mixture containing substrate (1 mmol), NMO (3 mmol) and molecular sieves. The solution mixture was reacted under reflux for 10 min, and the solvent was then evaporated from the mother liquor under reduced pressure. The solid residue was then extracted with diethyl ether (60-80°C) (20 cm^3) and concentrated to approximately 1 cm^3. The extract was dried over anhydrous sodium sulfate and analyzed

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

Compound	Formula	Yield (%)	M.Pt (˚C)	Calculated (found) (%)		
				C	H	N
L^1	$C_{18}H_{19}O_2N_3S$	60	094	63.32(63.38)	5.61(5.58)	12.31(12.37)
L^2	$C_{18}H_{19}O_3N_3S$	63	163	60.48(60.54)	5.35(5.31)	11.75(11.70)
L^3	$C_{17}H_{16}O_2ClN_3S$	61	185	56.43(56.39)	4.45(4.43)	11.61(11.58)
L^4	$C_{19}H_{21}O_4N_3S$	65	180	58.89(58.93)	5.46(5.45)	10.84(10.79)
$[Ru(CO)(PPh_3)_2(L^1)]$	$C_{55}H_{47}O_3N_3SP_2Ru$	86	156	66.52(66.61)	4.77(4.73)	4.23(4.21)
$[Ru(CO)(PPh_3)_2(L^2)]$	$C_{55}H_{47}O_4N_3SP_2Ru$	85	227	65.45(65.48)	4.69(4.70)	4.16(4.20)
$[Ru(CO)(PPh_3)_2(L^3)]$	$C_{54}H_{44}O_3N_3SClP_2Ru$	82	224	63.99(64.10)	4.37(4.35)	4.14(4.10)
$[Ru(CO)(PPh_3)_2(L^4)]$	$C_{56}H_{49}O_5N_3SP_2Ru$	78	232	64.73(64.72)	4.75(4.72)	4.04(4.00)
$[Ru(CO)(AsPh_3)_2(L^1)]$	$C_{55}H_{47}O_3N_3SAs_2Ru$	87	138	61.11(61.16)	4.38(4.43)	3.88(3.90)
$[Ru(CO)(AsPh_3)_2(L^2)]$	$C_{55}H_{47}O_4N_3SAs_2Ru$	79	165	60.22(60.18)	4.32(4.28)	3.83(3.85)
$[Ru(CO)(AsPh_3)_2(L^3)]$	$C_{54}H_{44}O_3N_3SClAs_2Ru$	81	154	58.88(58.79)	4.02(3.98)	3.81(3.79)
$[Ru(CO)(AsPh_3)_2(L^4)]$	$C_{56}H_{49}O_5N_3SAs_2Ru$	89	134	59.68(59.60)	4.38(4.39)	3.73(3.71)
$[Ru(CO)(Py)(PPh_3)(L^1)]$	$C_{42}H_{37}O_3N_4SPRu$	76	224	62.28(62.24)	4.60(4.58)	6.91(6.89)
$[Ru(CO)(Py)(PPh_3)(L^2)]$	$C_{42}H_{37}O_4N_4SPRu$	86	222	61.08(61.13)	4.51(4.56)	6.78(6.72)
$[Ru(CO)(Py)(PPh_3)(L^3)]$	$C_{41}H_{34}O_3N_4SClPRu$	78	173	59.30(59.26)	4.12(4.11)	6.74(6.69)
$[Ru(CO)(Py)(PPh_3)(L^4)]$	$C_{43}H_{39}O_5N_4SPRu$	89	170	60.34(60.36)	4.59(4.61)	6.54(6.50)

Table 2. IR absorption frequencies (cm^{-1}) of free ligands and their ruthenium(II) chalcone thiosemicarbazone complexes

Compound	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{C=N} + \nu_{C=C}$	ν_{C-O}	ν_{C-S}	$PPh_3/AsPh_3$
L^1	-	1610	-	1330	816	-
L^2	-	1609	-	1343	835	-
L^3	-	1605	-	1332	830	-
L^4	-	1606	-	1328	822	-
$[Ru(CO)(PPh_3)_2(L^1)]$	1930	1590	1556	1368	745	1433, 1092, 696
$[Ru(CO)(PPh_3)_2(L^2)]$	1929	1582	1559	1365	746	1433, 1092, 697
$[Ru(CO)(PPh_3)_2(L^3)]$	1929	1585	1563	1344	746	1432, 1091, 697
$[Ru(CO)(PPh_3)_2(L^4)]$	1917	1585	1561	1371	746	1432, 1092, 697
$[Ru(CO)(AsPh_3)_2(L^1)]$	1929	1590	1554	1343	739	1434, 1082, 694
$[Ru(CO)(AsPh_3)_2(L^2)]$	1943	1596	1559	1362	739	1435, 1086, 694
$[Ru(CO)(AsPh_3)_2(L^3)]$	1935	1585	1560	1342	740	1435, 1086, 694
$[Ru(CO)(AsPh_3)_2(L^4)]$	1935	1584	1562	1361	740	1436, 1079, 694
$[Ru(CO)(Py)(PPh_3)(L^1)]$	1930	1582	1559	1343	746	1432, 1092, 697
$[Ru(CO)(Py)(PPh_3)(L^2)]$	1926	1583	1554	1358	746	1432, 1092, 697
$[Ru(CO)(Py)(PPh_3)(L^3)]$	1930	1581	1553	1368	746	1432, 1091, 696
$[Ru(CO)(Py)(PPh_3)(L^4)]$	1930	1583	1559	1367	746	1432, 1092, 697

Table 3. UV-vis spectroscopic data of free ligands and their ruthenium(II) chalcone thiosemicarbazone complexes.

Compound	$\lambda_{max,\ nm}$ (ε) ($dm^3\ mol^{-1}\ cm^{-1}$)
L^1	337(10562), 302(11630), 237(21956)
L^2	341(10358), 302(11630), 236(22182)
L^3	337(10562), 303(10849), 233(23956)
L^4	337(10562), 302(11630), 290(13425), 238(21242)
$[Ru(CO)(PPh_3)_2(L^1)]$	432(6574), 361(7986), 272(17130), 235(22890)
$[Ru(CO)(PPh_3)_2(L^2)]$	432(6574), 362(7543), 272(17130), 234(23215)
$[Ru(CO)(PPh_3)_2(L^3)]$	436(6285), 362(7543), 270(18213), 238(21242)
$[Ru(CO)(PPh_3)_2(L^4)]$	430(6763), 362(7543), 275(16025), 237(21956)
$[Ru(CO)(AsPh_3)_2(L^1)]$	351(9596), 267(19128), 235(22890)
$[Ru(CO)(AsPh_3)_2(L^2)]$	353(8318), 265(19956), 234(23215)
$[Ru(CO)(AsPh_3)_2(L^3)]$	351(9596), 267(19128), 234(23215)
$[Ru(CO)(AsPh_3)_2(L^4)]$	352(8952), 267(19128), 236(22182)
$[Ru(CO)(Py)(PPh_3)(L^1)]$	431(6692), 363(7121), 272(17130), 235(22890)
$[Ru(CO)(Py)(PPh_3)(L^2)]$	431(6695), 362(7543), 272(17130), 235(22890)
$[Ru(CO)(Py)(PPh_3)(L^3)]$	431(6698), 362(7543), 270(18213), 234(23215)
$[Ru(CO)(Py)(PPh_3)(L^4)]$	428(6993), 362(7543), 271(17986), 235(22890)

Table 4. ^{1}H NMR data of free ligands and their ruthenium(II) chalcone thiosemicarbazone complexes.

Compound	δ (ppm)
L^1	8.67 (NH), 6.96-7.88 (m, aromatic and -CH=CH-), 6.32 (OH), 5.10 (NH_2), 3.81 (OCH_3), 2.39 (CH_3)
L^2	8.59 (NH), 6.62-7.88 (m, aromatic and -CH=CH-), 6.30 (OH), 5.12 (NH_2), 3.85, 3.81 (OCH_3)
L^3	8.63 (NH), 6.85-7.76 (m, aromatic and -CH=CH-), 6.31 (OH), 5.10 (NH_2), 3.81 (OCH_3)
$[Ru(CO)(PPh_3)_2(L^1)]$	7.27-7.36 (m, aromatic and -CH=CH-), 4.38 (NH_2), 3.50 (OCH_3), 2.38 (CH_3)
$[Ru(CO)(PPh_3)_2(L^2)]$	6.95-7.36 (m, aromatic and -CH=CH-), 4.42 (NH_2), 3.84, 3.50 (OCH_3)
$[Ru(CO)(PPh_3)_2(L^3)]$	7.27-7.38 (m, aromatic and -CH=CH-), 4.39 (NH_2), 3.51 (OCH_3)
$[Ru(CO)(AsPh_3)_2(L^1)]$	7.15-7.35 (m, aromatic and -CH=CH-), 4.38 (NH_2), 3.50 (OCH_3), 2.39 (CH_3)
$[Ru(CO)(AsPh_3)_2(L^2)]$	6.85-7.32 (m, aromatic and -CH=CH-), 4.42 (NH_2), 3.84, 3.51 (OCH_3)
$[Ru(CO)(Py)(PPh_3)(L^2)]$	6.91-7.30 (m, aromatic and -CH=CH-), 4.40 (NH_2), 3.85, 3.50 (OCH_3)
$[Ru(CO)(Py)(PPh_3)(L^3)]$	7.18-7.36 (m, aromatic and -CH=CH-), 4.39 (NH_2), 3.51 (OCH_3)

by GC. The oxidation products were identified by GC co-injection with authentic samples of the appropriate aldehyde or ketone.

2.6. Procedure for catalytic transfer hydrogenation of carbonyl compounds

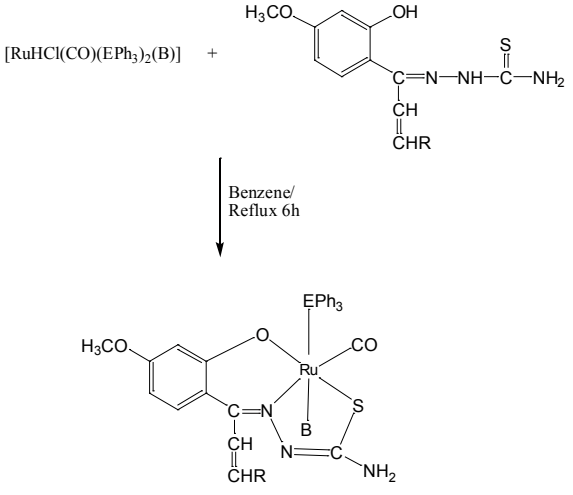
The catalytic transfer hydrogenation reactions were also studied using ruthenium(II) chalcone thiosemicarbazone complex as a catalyst, carbonyl compounds as substrate and KOH as promoter at 1:300:2.5 molar ratios. The procedure was as follows: A mixture containing carbonyl compounds (3.75 mmol), the ruthenium complex (0.0125 mmol) and KOH (0.03 mmol) in isopropyl alcohol (10 cm^3) was reacted under reflux in a water bath for different time periods. 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 1M HCl. The ether layer was filtered through a short path of silica gel by column chromatography. The filtrate was concentrated to approximately 1 cm^3 and subjected to GC analysis. The hydrogenated product was identified and determined by comparison with authentic samples of the appropriate alcohol.

3. Results and discussion

Diamagnetic, hexa-coordinated low spin ruthenium (II) complexes of general formula $[Ru(CO)(EPh_3)(B)(L)]$ (E = P or As; B = PPh_3, $AsPh_3$ or Py; L = chalcone thiosemicarbazone) 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 chalcone thiosemicarbazone ligands in dry benzene in an equal molar ratio (Scheme 1).

In all of these reactions, it was observed that the chalcone thiosemicarbazones behave as dibasic tridentate chelating ligands by replacing a triphenylphosphine/arsine, chloride and hydride ion from the starting complexes.

All of the complexes are stable in air at room temperature, yellowish-green in color, non-hygroscopic and highly soluble in common organic solvents such as dichloromethane, acetonitrile, chloroform, benzene and DMSO. The analytical data are listed in Table 1 and are in good agreement



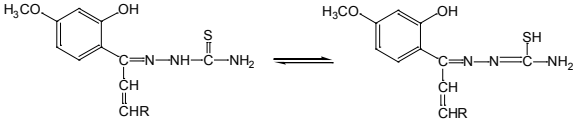
(E = P or As; B = PPh_3, $AsPh_3$ or Py; R = 4-$(CH_3)C_6H_4$, 4-$(OCH_3)C_6H_4$, 4-(Cl) C_6H_4 or 3,4-$(OCH_3)_2C_6H_3$)

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

with the general molecular formula proposed for the complexes.

3.1. Infrared Spectroscopic analysis

The important IR absorption frequencies of the ligands and their metal complexes, along with their assignments, are listed in Table 2. The ligands used in the present study can exhibit thione-thienol tautomerism (Scheme 2).



Scheme 2. Tautomerism in chalcone thiosemicarbazones

The free chalcone thiosemicarbazone ligands showed a strong band in the region 1605-1610 cm^{-1} due to $\nu_{C=N}$. This band was shifted to a lower wave number (1581-1596 cm^{-1}) in the ruthenium complexes indicating the coordination of the ligands to ruthenium through the azomethine nitrogen atom [32] and this lowering of the wave number may be attributed to the decrease in electron density on the nitrogen atom of the azomethine group. In all of the complexes, the bands that appeared in the region 1536-1551 cm^{-1} were assigned to the mixed mode of vibration arising from $\nu_{C=N}$ and $\nu_{C=C}$ vibrations [33]. This also indicates that the coordination is through the nitrogen atom. A strong band observed at 1328-1343 cm^{-1} in the free chalcone thiosemicarbazone ligands was assigned to phenolic ν_{C-O} stretching. This band was shifted to higher wave number (1342-1371 cm^{-1}) in the spectra of the complexes due to its coordination to ruthenium ion through the oxygen atom of the phenolic group [34]. This was further supported by the disappearance of the broad ν_{OH} band around 3400-3600 cm^{-1} in the complexes, indicating deprotonation of the phenolic proton prior to coordination to the ruthenium metal. The band due to ν_{C-S} appeared around 816-835 cm^{-1} in the free ligands but disappeared upon complexation and a new band appeared around 739-746 cm^{-1}. These observations may be attributed to thienolisation of the –NH-C=S group and subsequent coordination through the deprotonated sulfur [35]. Hence, from the infrared spectroscopic data, it is inferred that the azomethine nitrogen, phenolic oxygen and thienol sulfur atoms are involved in the coordination of the chalcone thiosemicarbazone to ruthenium ion in all complexes. In addition, the appearance of a strong band at 1917-1943 cm^{-1} and a medium intensity band at 1000-1030 cm^{-1} indicate the presence of carbon monoxide and nitrogen base [34], respectively. All the other characteristic bands due to triphenylphosphine or triphenylarsine (around 1440, 1090 and 700 cm^{-1}) were also present in the spectra of all complexes [17].

3.2. Electronic spectroscopic analysis

All the chalcone thiosemicarbazone 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 $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$. Hence, four bands corresponding to the transitions $^1A_{1g}\rightarrow{}^3T_{1g}$, $^1A_{1g}\rightarrow{}^3T_{2g}$, $^1A_{1g}\rightarrow{}^1T_{1g}$ and $^1A_{1g}\rightarrow{}^1T_{2g}$ are possible in order of increasing energy.

The electronic spectral data of the free ligands and their complexes in dichloromethane are listed in Table 3. The spectra of all the free ligands showed two types of transitions. The absorbance that appears in the 233–238 nm range was assigned to π- π* transitions involving molecular orbitals located on the phenolic chromophore. These peaks have been shifted in the spectra of the complexes; this may be due to the donation of a lone pair of electrons by the oxygen of the phenoxy group to the central metal atom [36]. The second type of transitions appeared at the 290–341 nm range and were assigned to n-π* transitions involving molecular orbitals of the -C=N chromophore and the benzene ring. These bands were also shifted upon complexation, indicating that the imine group nitrogen atom appears to be coordinated to the metal ion [37].

The spectra of all the complexes show another type of transition (Fig. 2) different from the free ligands. The broad bands appeared at the 351–436 nm range, which can be assigned to charge transfer (C.T) transitions [38]. The nature of the observed electronic spectra and the position of absorption bands are consistent with those of other similar ruthenium(II) octahedral complexes [38].

3.3. ^{1}H NMR Spectroscopic analysis

The ^{1}H NMR spectra of the ruthenium(II) chalcone thiosemicarbazone complexes and ligands were recorded in $CDCl_3$ to confirm the binding of chalcone thiosemicarbazone to the ruthenium ion. All of the complexes exhibit a series of overlapping multiplets in the region 7.38-6.85 ppm in their spectra (Table 4), which were assigned to the protons of the phenyl groups present in the PPh_3 or $AsPh_3$ or Py ligands and chalcone thiosemicarbazone [39]. The signal due to two alkene protons also appeared in the region 7.3-6.9 ppm and hence merged with the multiplets of aromatic protons. This clearly revealed the absence of alkene coordination

to the metal, as alkene carbon coordination would result in shifts of the olefinic protons to lower δ value at least by 2 ppm [39]. The signal for OH protons appeared as a broad singlet in the region 6.32-6.30 ppm in free chalcone thiosemicarbazone ligands, but in complexes no peak was observed for the OH protons, supporting the assumption that the phenolic group is deprotonated. This suggests coordination occurs through the phenolic oxygen of chalcone thiosemicarbazones to the ruthenium ion. The signal for the terminal NH_2 protons appeared as a singlet at 4.40-4.37 ppm in complexes, which corresponds to an up-field shift in comparison with that of the NH_2 resonance free ligands. Where present on the chalcone thiosemicarbazones, the methoxy protons on the benzaldehyde-derived aromatic ring were observed in 3.85-3.84 ppm region in both complexes and the free ligands. The acetophenone-derived methoxy protons appeared as a singlet in 3.51-3.50 ppm region in the metal complexes, corresponding to an up-field shift in comparison with that of the corresponding free ligands, which indicates a shielding effect of an aromatic ring. Further, the signal for methyl proton appeared as a singlet at 2.39 ppm in both complexes and the free ligand.

3.4. ^{31}P NMR Spectroscopic analysis

^{31}P NMR spectra of some of the complexes were recorded to confirm the presence of triphenylphosphine groups in the new complexes (Table 5, Fig. 3). In the case of complexes containing two triphenylphosphine ligands, a sharp singlet was observed around 36.15-36.21 ppm for magnetically equivalent phosphorus atoms *trans* to each other [35]. The spectra of all other complexes exhibited a singlet around 34.82-34.86 ppm, corresponding to the presence of a triphenylphosphine group *trans* to a heterocyclic nitrogen base [39].

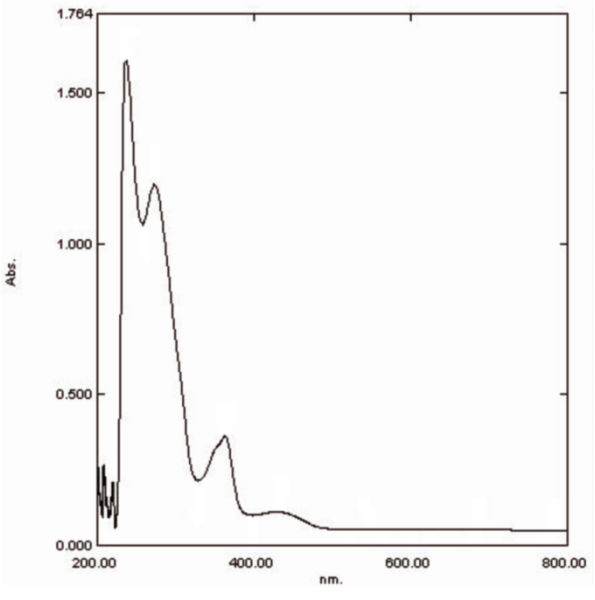


Figure 2. Electronic spectrum of $[Ru(CO)(PPh_3)_2(L^4)]$

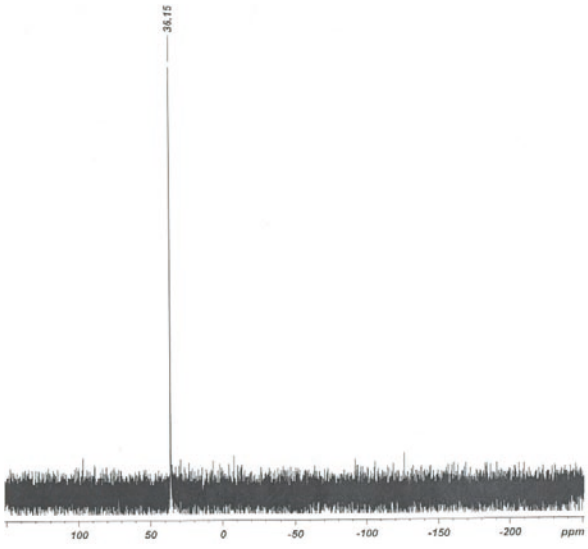


Figure 3. ^{31}P NMR spectrum of $[Ru(CO)(PPh_3)_2(L^2)]$

3.5. ^{13}C NMR Spectroscopic analysis

The ^{13}C spectra of ruthenium(II) chalcone thiosemicarbazone complexes (Table 5) exhibit a strong signal at 205.36-204.64 ppm and were assigned to CO carbon. A sharp singlet appeared at 177.98-176.35 ppm that was assigned to phenolic –C-O carbon. The appearance of a peak at 159.68-159.46 and 157.69-157.58 ppm were assigned to -C-S and –C=N carbons, respectively. Multiplets appeared around 138.22-114.27 ppm region have been assigned to aromatic carbons. The alkene carbons appeared in the region 130.58-115.45 ppm, and hence merged with the aromatic carbons. The presence of peak at 96.03-96.02 ppm was assigned to α =CH- carbon. Sharp singlets at 55.38 and 54.98-54.86 ppm were assigned to the methoxy carbon of benzaldehyde-derived and acetophenone-derived groups, respectively. In addition, a sharp singlet at 21.19-21.15 ppm was assigned to methyl carbons.

Based on the analytical and spectroscopic (IR, UV-vis, ^{1}H, ^{31}P and ^{13}C NMR) data, an octahedral structure (Fig. 4) has been tentatively proposed for all the ruthenium(II) chalcone thiosemicarbazone complexes.

Table 5. ^{13}C NMR and ^{31}P NMR data (δ in ppm) of ruthenium(II) chalcone thiosemicarbazone complexes.

Complex	^{13}C NMR	^{31}P NMR
$[Ru(CO)(PPh_3)_2(L^1)]$	204.89 (s), 176.54 (s), 159.53 (s), 157.63 (s), 138.22-120.50 (m), 96.03 (s), 54.93 (s), 21.19 (s)	36.21
$[Ru(CO)(PPh_3)_2(L^2)]$	205.36 (s), 176.24 (s), 159.68 (s), 157.69 (s), 133.91-114.27 (m), 96.02 (s), 55.38 (s), 54.92 (s)	36.15
$[Ru(CO)(Py)(PPh_3)(L^1)]$	204.64 (s), 176.35 (s), 159.46 (s), 157.58 (s), 134.54-116.36 (m), 96.03 (s), 54.98 (s), 21.15 (s)	34.86
$[Ru(CO)(Py)(PPh_3)(L^3)]$	205.12 (s), 177.98 (s), 159.62 (s), 157.67 (s), 136.52-117.13 (m), 96.02 (s), 54.86 (s)	34.82

3.6. Catalytic oxidation

Catalytic oxidation of primary and secondary alcohols by the synthesized ruthenium (II) chalcone thiosemicarbazone complexes were carried out in dichloromethane in the presence of NMO, and the by-product of water was removed by using molecular sieves. All of the complexes oxidize primary alcohols to the corresponding aldehydes, and secondary alcohols are oxidized to ketones in high yields and the results are listed in Table 6. The oxidation of benzyl alcohol to benzaldehyde and cinnamyl alcohol to cinnamaldehyde resulted in 94-99% and 96-99% yields, respectively.

The present investigations suggest that the complexes react efficiently with NMO to yield a high valent ruthenium-oxo species [40] 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 band at 390 nm in UV-vis spectra is attributed to the formation of high-valent Ru^{IV}=O species, which was also found for other oxo ruthenium(IV) complexes [41,42]. Further support comes from FT-IR of the solid (obtained by evaporation of the resultant solution to dryness), which shows a band at 860 cm^{-1}, characteristic of Ru^{IV}=O species (Scheme 3) [38], which is absent in the ruthenium catalyst. Except for the above difference noted, the IR spectra of the catalyst and solid appear quite similar, which suggest that the coordinated chalcone thiosemicarbazone ligand remains intact in the oxidation process. It follows that the catalytic oxidation proceeds through metal-oxo intermediate.

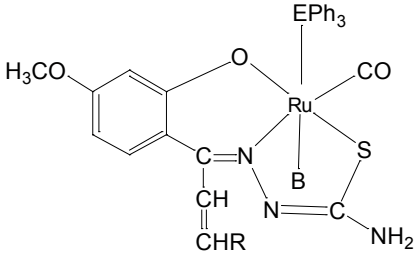
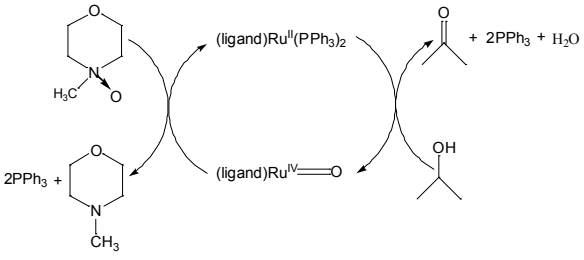


Figure 4. Proposed structure of the new ruthenium(II) chalcone thiosemicarbazone complexes (E = P or As; B = PPh_3, $AsPh_3$ or Py; R = 4-$(CH_3)C_6H_4$, 4-$(OCH_3)C_6H_4$, 4-$(Cl)C_6H_4$ or 3,4-$(OCH_3)_2C_6H_3$)



Scheme 3. Proposed catalytic cycle for the oxidation of alcohols by the ruthenium(II) chalcone thiosemicarbazone complexes

3.7. Catalytic transfer hydrogenation of carbonyl compounds

One of the newly synthesized complexes, $[Ru(CO)(AsPh_3)_2(L^1)]$, was employed as a "model" catalyst and the catalytic activity in transfer hydrogenation of various types of aldehydes and ketones in the presence of isopropyl alcohol and KOH was explored. In all of the reactions, this complex catalyzes the reduction of aldehydes and ketones to the corresponding alcohols

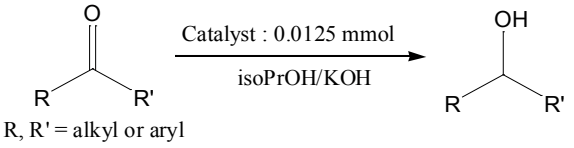
Table 6. Catalytic oxidation data of ruthenium(II) chalcone thiosemicarbazone complexes.

Complex	Substrate	Product	Yield (%)[a]
[Ru(CO)(PPh$_3$)$_2$(L^1)]	Benzyl alcohol	A	98
	Cinnamyl alcohol	B	99
[Ru(CO)(PPh$_3$)$_2$(L^2)]	Benzyl alcohol	A	97
	Cinnamyl alcohol	B	99
[Ru(CO)(PPh$_3$)$_2$(L^3)]	Benzyl alcohol	A	99
	Cinnamyl alcohol	B	99
[Ru(CO)(PPh$_3$)$_2$(L^4)]	Benzyl alcohol	A	95
	Cinnamyl alcohol	B	97
[Ru(CO)(AsPh$_3$)$_2$(L^1)]	Benzyl alcohol	A	99
	Cinnamyl alcohol	B	99
[Ru(CO)(AsPh$_3$)$_2$(L^2)]	Benzyl alcohol	A	96
	Cinnamyl alcohol	B	98
[Ru(CO)(AsPh$_3$)$_2$(L^3)]	Benzyl alcohol	A	98
	Cinnamyl alcohol	B	99
[Ru(CO)(AsPh$_3$)$_2$(L^4)]	Benzyl alcohol	A	99
	Cinnamyl alcohol	B	99
[Ru(CO)(Py)(PPh$_3$)(L^1)]	Benzyl alcohol	A	95
	Cinnamyl alcohol	B	97
[Ru(CO)(Py)(PPh$_3$)(L^2)]	Benzyl alcohol	A	94
	Cinnamyl alcohol	B	96
[Ru(CO)(Py)(PPh$_3$)(L^3)]	Benzyl alcohol	A	98
	Cinnamyl alcohol	B	99
[Ru(CO)(Py)(PPh$_3$)(L^4)]	Benzyl alcohol	A	99
	Cinnamyl alcohol	B	99

A: benzaldehyde; B: Cinnamaldehyde
[a] Yield determined by GC and comparing with the analyses of authentic samples.

via hydrogen transfer from isopropyl alcohol with KOH as a promoter (Scheme 4, Table 7).

Mechanistically, the base facilitates the formation of ruthenium alkoxide by abstracting proton from isopropyl alcohol and subsequently the alkoxide undergoes β-elimination to give ruthenium hydride, which is an active species. No transfer hydrogenation was observed in the absence of base. In addition, the work-up process is very simple for this catalytic system and as the catalyst is stable in all organic solvents, it can be recovered.

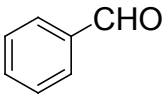
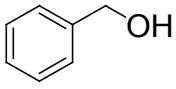
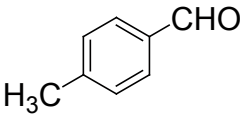
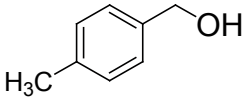
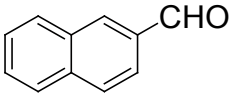
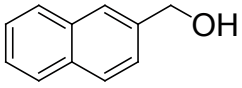
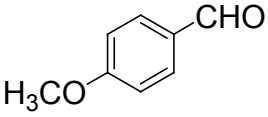
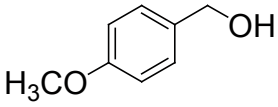
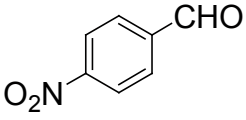
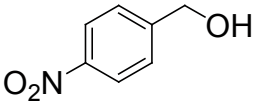
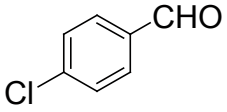
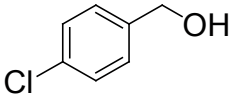
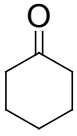
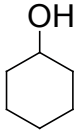
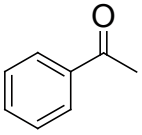
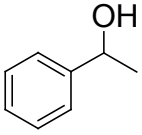
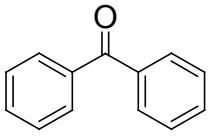
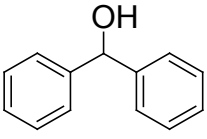
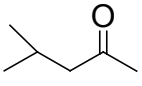
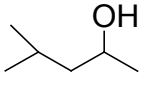


Scheme 4. Reaction of catalytic transfer hydrogenation

4. Conclusions

Several new ruthenium(II) chalcone thiosemicarbazone complexes were synthesized using chalcone

Table 7. Catalytic transfer hydrogenation of carbonyl compounds by $[Ru(CO)(AsPh_3)_2(L^1)]$ with isopropyl alcohol[a]

Entry	Substrate	Product	Time (min)	Conversion (%)[b]
1			30	91
2			30	86
3			30	89
4			30	86
5			60	88
6			60	84
7			60	95
8			240	85
9			240	82
10			240	43

[a]Conditions: reactions were carried out by heating at reflux, using 3.75 mmol of ketone (in 10 cm³ isopropyl alcohol); 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.

thiosemicarbazones formed from derivatives of 2-hydroxychalcone and thiosemicarbazide. The new complexes were characterized by analytical and spectroscopic methods. An octahedral structure was tentatively proposed for all of the complexes. The complexes showed efficient catalytic activity for the oxidation of both primary and secondary alcohols with excellent yields in short reaction time in the presence of *N*-methylmorpholine-*N*-oxide, and also for transfer hydrogenation of aldehydes and ketones with high conversions (>80%) in the presence of isopropyl alcohol and KOH as promoter.

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