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# Spectrochimica Acta Part A: Molecular and **Biomolecular Spectroscopy**



journal homepage: www.elsevier.com/locate/saa

## Mononuclear ruthenium(III) complexes containing chelating thiosemicarbazones: Synthesis, characterization and catalytic property

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#### ARTICLE INFO

Article history: Received 3 July 2009 Received in revised form 17 November 2009 Accepted 18 November 2009

Keywords: Chelating thiosemicarbazone Ruthenium(III) complexes Spectra Redox properties Transfer hydrogenation

### 1. Introduction

ABSTRACT

Mononuclear ruthenium(III) complexes of the type [RuX(EPh<sub>3</sub>)<sub>2</sub>(L)] (E = P or As; X = Cl or Br; L = dibasic terdentate dehydroacetic acid thiosemicarbazones) have been synthesized from the reaction of thiosemicarbazone ligands with ruthenium(III) precursors,  $[RuX_3(EPh_3)_3]$  (where E = P, X = Cl; E = As, X = Cl or Br) and [RuBr<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>OH)] in benzene. The compositions of the complexes have been established by elemental analysis, magnetic susceptibility measurement, FT-IR, UV-vis and EPR spectral data. These complexes are paramagnetic and show intense d-d and charge transfer transitions in dichloromethane. The complexes show rhombic EPR spectra at LNT which are typical of low-spin distorted octahedral ruthenium(III) species. All the complexes are redox active and display an irreversible metal centered redox processes. Complex [RuCl(PPh<sub>3</sub>)<sub>2</sub>(DHA-PTSC)] (5) was used as catalyst for transfer hydrogenation of ketones in the presence of isopropanol/KOH and was found to be the active species.

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Thiosemicarbazones have emerged as an important class of N,Sdonor ligands for transition metal ions because of their mixed

such as -PR2, -NH2, -OH, or -SH is incorporated into the ligands linked to the carbonylic carbon via one or two intervening atoms, stable complexes with D,N,S-tricoordination (IV) takes place [13,14].



hard-soft donor character and versatile coordination behavior [1–3]. Transition metal complexes of thiosemicarbazones have been receiving considerable interest largely because of their pharmacological property [4-8]. Further, structure-activity relationship studies revealed that the presence of a bulky group attached to the terminal nitrogen of the thiosemicarbazone chain strongly enhances the pharmacological activity of these compounds [9]. The possibility of modulating the cytotoxic activity by changing the structure of the complex was also proved [10,11]. Thiosemicarbazones are versatile ligands which can coordinate as neutral ligands (I) or in their tautomeric form (II) and they usually bind to a metal ion as bidentate N,S-donor ligands via dissociation of the hydrazinic proton, forming five-membered chelate rings (III) [12]. When a third donor site (D) containing donor group

Bhattacharya and co-workers reported a series of ruthenium and osmium complexes containing salicylaldehyde thiosemicarbazone complexes [15]. Further, the unusual coordination mode of the benzaldehyde thiosemicarbazone ligands with ruthenium has been studied [16]. Ruthenium(II) 1-(arylidine)thiosemicarbazone complexes have also been reported [17]. We recently reported ruthenium(II) carbonyl dehydroacetic acid thiosemicarbazone complexes in which thiosemicarbazone ligands coordinated to ruthenium through O, N and S [18].

Hydrogenation and transfer hydrogenation of carbonyl compounds are of high demand in the petrochemical, pharmaceutical and food industry. Reduction of polar organic functionalities in which carbonyl groups are converted to corresponding alcohols is one of the most fundamental transformations in organic synthesis [19]. 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 reported in recent years [20]. Ruthenium compounds have proven to serve as very efficient cat-

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alyst of transfer hydrogenation reactions [21–25]. Ruthenium(II) complexes containing diphosphine and 1,2-diamine ligands, in the presence of a base and isopropanol, are excellent catalysts for the hydrogenation of ketones under mild conditions [26,27]. van Koten and co-workers reported pincer-type aryl ruthenium(II) complexes containing the monoanionic terdentate NCN/PCP ligands as active catalysts for the transfer hydrogenation of ketones in the presence of isopropanol and KOH [28,29]. Further, several example such as ruthenium carbene complexes [30,31], ruthenium arene complexes [32,33] and ruthenium BINAP(diamine) complexes [34] have become the most prominent species for the transfer hydrogenation of ketones in an excellent yield. Though there are several complexes known as catalyst for transfer hydrogenation, only a few reports are available on ruthenium(III) complexes [35,36].

Hence, we focus our interest on the synthesis, characterization and catalytic application of ruthenium(III) thiosemicarbazone complexes. Herein, we describe the synthesis of a series of ruthenium(III) complexes containing dehydroacetic acid thiosemicarbazone ligands. The tridentate N, S and O combination mode of these ligands to ruthenium was confirmed by analytical and spectral methods. Further, electrochemical behavior of the complexes is monitored by cyclic voltammetric technique. Furthermore, one of the complexes, [RuCl(PPh<sub>3</sub>)<sub>2</sub>(DHA–PTSC)], (**5**) is employed as the catalyst for transfer hydrogenation of a range of aliphatic and aromatic ketones in the presence of isopropanol/KOH at 82 °C.

#### 2. Experimental

#### 2.1. Materials and physical measurements

All the reagents used were chemically pure and are of analytical reagent grade. The solvents were dried and distilled before use following the standard procedures [37]. Dehydroacetic acid (DHA) was purchased from SRL. RuCl<sub>3</sub>·3H<sub>2</sub>O was purchased from Loba-Chemie Pvt. Ltd., and was used without further purification. The ketones and tetrabutylammonium perchlorate (TBAP) were obtained from Aldrich. TBAP was dried in vacuum prior to use. Melting points were recorded with a Boetius micro-heating table and are uncorrected. The carbon, hydrogen, nitrogen and sulphur microanalysis content of each sample was determined at STIC, Cochin University of Science and Technology, Cochin, by analytic function testing VarioEL III CHNS elemental analyzer. Infrared spectra were collected using KBr pellets on a Jasco 400 Plus in the range 4000–400 cm<sup>-1</sup>. Electronic spectra of the complexes in dichloromethane were recorded on a Cary 300 Bio UV-Vis Varian spectrophotometer. Room temperature solid-state magnetic susceptibilities were measured by using an EG and G model 155 vibrating sample magnetometer at Indian Institute of Technology, Madras. Diamagnetic corrections calculated from Pascal's constant [38] were used to obtain the molar paramagnetic susceptibilities. The X-band EPR spectra of the powdered samples were recorded on JEOL JES-FA200 EPR spectrometer

at RT and LNT, the field being calibrated with 2,2-diphenyl-1picrylhydrazyl. Electrochemical studies were performed using a Princeton EG and G-PARC model potentiostat in degassed 0.001 M acetonitrile solutions of TBAP as supporting electrolyte. A threeelectrode cell was employed with carbon working electrode, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode. The precursor ruthenium(III) complexes [RuCl<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>], [RuCl<sub>3</sub>(AsPh<sub>3</sub>)<sub>3</sub>], [RuBr<sub>3</sub>(AsPh<sub>3</sub>)<sub>3</sub>], [RuBr<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>OH)] [39–42] and dehydroacetic acid thiosemicarbazone ligands [43–45] were prepared according to the literature procedures.

#### 2.2. Synthesis of ruthenium(III) DHA-TSC/PTSC complexes

All the reactions were performed under strictly anhydrous conditions and the complexes were prepared by the following general procedure. To a benzene (20 ml) solution of  $[RuX_3(EPh_3)_3]$  (0.124–0.157 g, 0.125 mmol) (E=P, X=Cl; E=As, X=Cl or Br) or  $[RuBr_3(PPh_3)_2(CH_3OH)]$  (0.112 g, 0.125 mmol) was added the appropriate Schiff base ligands (0.02–0.039 g, 0.125 mmol) (DHA–TSC, DHA–PTSC). The solution was allowed to heat under reflux for 8 h. The resulting solution was concentrated to 3 ml, cooled and light petroleum ether (60–80 °C) (5 ml) was added where upon the complex was separated. All the complexes were green in colour and were recrystallized from  $CH_2Cl_2/light$  petroleum ether mixture and dried in vacuo. The purity of the complexes was checked by TLC (yield: 65–70%).

#### 2.3. Procedure for catalytic transfer hydrogenation of ketones

Under an inert atmosphere, a mixture containing ketones (2 mmol), the ruthenium catalyst (**5**) (0.01 mmol) and KOH (0.025 mmol) was heated to reflux in isopropanol (5 ml) for 2 h. The catalyst was removed as precipitate from the reaction mixture by the addition of diethyl ether, followed by filtration and subsequent neutralization with 5 ml of 1 M HCl. Then the ether layer was passed through a short path of silica gel and the filtrate was subjected to GC analysis. The hydrogenated product was identified and determined by comparison with authentic sample.

#### 3. Results and discussion

The reactions of  $[RuX_3(EPh_3)_3]$  (E=P, X=Cl; E=As, X=Cl or Br) or  $[RuBr_3(PPh_3)_2(CH_3OH)]$  with Schiff base ligands (DHA–TSC, DHA–PTSC) in 1:1 molar ratio in dry benzene afforded new hexa-coordinated low-spin ruthenium(III) thiosemicarbazone complexes (Scheme 1). The analytical data (Table 1) are in good agreement with the general molecular formula proposed. In all the reactions, the Schiff base ligand behaves as tridentate ligand by replacing one triphenylphosphine or triphenylarsine molecule, two chloride or bromide ions and one methanol from the precursors. All the complexes are air-stable, non-hygroscopic in nature, insoluble in water and highly soluble in common solvents such as chloroform, dichloromethane, acetonitrile and dimethyl sulphoxide producing intense green solutions. Attempts made to grow single crystal were



Table	1
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Analytical data of ruthenium(III) DHA-thiosemicarbazone complexes.

Sl. no.	Complex	Empirical formula	m.p <sup>a</sup> (°C)	Calculated (found) %			
				С	Н	N	S
1	[RuCl(PPh <sub>3</sub> ) <sub>2</sub> (DHA-TSC)]	C45H39CIN3O3P2RuS	176	60.03(59.89)	4.37(4.23)	4.67(4.54)	3.56(3.51)
2	[RuCl(AsPh <sub>3</sub> ) <sub>2</sub> (DHA–TSC)]	C45H39ClN3O3As2RuS	233	54.69(54.76)	3.98(3.87)	4.25(4.43)	3.24(3.44)
3	[RuBr(PPh <sub>3</sub> ) <sub>2</sub> (DHA–TSC)]	$C_{45}H_{39}BrN_3O_3P_2RuS$	167	57.21(57.60)	4.16(4.59)	4.45(4.21)	3.39(3.19)
4	[RuBr(AsPh <sub>3</sub> ) <sub>2</sub> (DHA–TSC)]	C45H39BrN3O3As2RuS	230	52.34(52.37)	3.81(3.55)	4.07(3.98)	3.10(2.98.)
5	[RuCl(PPh <sub>3</sub> ) <sub>2</sub> (DHA-PTSC)]	C <sub>51</sub> H <sub>43</sub> ClN <sub>3</sub> O <sub>3</sub> P <sub>2</sub> RuS	210	62.73(62.53)	4.44(4.35)	4.30(4.72)	3.28(3.39)
6	[RuCl(AsPh <sub>3</sub> ) <sub>2</sub> (DHA–PTSC)]	C <sub>51</sub> H <sub>43</sub> ClN <sub>3</sub> O <sub>3</sub> As <sub>2</sub> RuS	260	57.55(57.57)	4.07(3.90)	3.95(3.99)	3.01(2.89)
7	[RuBr(PPh <sub>3</sub> ) <sub>2</sub> (DHA-PTSC)]	C <sub>51</sub> H <sub>43</sub> BrN <sub>3</sub> O <sub>3</sub> P <sub>2</sub> RuS	196	60.00(59.67)	4.25(4.64)	4.12(4.10)	3.14(3.02)
8	[RuBr(AsPh <sub>3</sub> ) <sub>2</sub> (DHA–PTSC)]	$C_{51}H_{43}BrN_3O_3As_2RuS$	190	55.24(55.46)	3.91(3.98)	3.79(3.58)	2.89(2.97)

<sup>a</sup> Decomposition temperature.

unsuccessful. Based on our previous report on the crystal structure of the ruthenium(II) DHA–thiosemicarbazone complexes [18], the trans-meridional structure is confirmed for the present complexes rather than a facial structure. Further, the trans-meridional structure is more favoured structure than a cis meridional, due to the bulky nature of two PPh<sub>3</sub> groups and the presence of conjugation in DHA–thiosemicarbazone ligands.

#### 3.1. Spectroscopic characterization

The important IR absorption frequencies of the synthesized complexes are shown in Table 2. The free ligand displays  $v_{(C=S)}$ and  $\nu_{(N-H)}$  absorptions at 788 and 3181 cm<sup>-1</sup>, respectively and were disappeared upon complexation. These observations may be attributed to the enolization of -NH-C=S and subsequent coordination through the deprotonated sulphur [46]. The azomethine nitrogen  $v_{(C=N)}$  stretching frequency in the free ligands (DHA-TSC and DHA-PTSC) appear around 1624-1643 cm<sup>-1</sup>. This frequency has been shifted to lower wave numbers in the range 1562–1589 cm<sup>-1</sup> in accordance with the coordination of the azomethine function to the metal ion for all the complexes [47] and this lowering of the wave number may be attributed to the decrease in electron density on the nitrogen atom of the azomethine group. The enolic  $v_{(C-O)}$  stretching frequency of the free ligand (DHA–TSC and DHA-PTSC) appears around 1235-1250 cm<sup>-1</sup>. On complexation this frequency is shifted to higher frequency in the range 1244–1279 cm<sup>-1</sup> for all the complexes. This is further supported by the disappearance of the  $v_{OH}$  in the range 3400–3440 cm<sup>-1</sup> in all the complexes indicating deprotonation of the enolic proton prior to coordination [48]. The spectra of the free DHA-TSC ligand show strong stretch around 1682 and 3380 cm<sup>-1</sup> due to the presence of lactone carbonyl  $\nu_{(C=0)}$  and NH<sub>2</sub> groups, respectively [49]. These frequencies remain same even after the coordination indicating that the groups are not involved in coordination. Further, the bands were observed in the region 500-550, 441-476 and  $406-417 \, \text{cm}^{-1}$  which are probably due to the formation of M–O, M–N and M–S bonds, respectively [50]. All the ruthenium(III)

Table 2

IR and electronic spectral data of ruthenium(III) DHA-thiosemicarbazone complexes.

thiosemicarbazone complexes show strong vibrations near 530, 690, 745 and  $1550 \text{ cm}^{-1}$  which are attributed to PPh<sub>3</sub>/AsPh<sub>3</sub> [51].

The electronic spectra of the complexes were recorded in dichloromethane solution in the region 800–200 nm (Table 2). The ground state of ruthenium(III) is  ${}^{2}T_{2g}$  and the first excited doublet levels in the order of increasing energy are  ${}^{2}A_{2g}$  and  ${}^{2}A_{1g}$ , which arise from  $t_{2g}^{4}e_{g}^{1}$  configuration [52]. All the ruthenium(III) complexes display strong band in the visible region in the range 584–534 nm followed by a weak shoulder in the range 450–493 nm which are assigned as d–d and LMCT transitions, respectively. The bands in the 325–369 nm regions are due to  $n-\pi^{*}$  transition of non-bonding electrons present on the nitrogen of the azomethine group in the ruthenium(III) complexes. The band observed around 230–286 nm is as assigned to  $\pi-\pi^{*}$  transitions of the ligand. The pattern of the electronic spectra of all the complexes indicates the presence of an octahedral environment around the ruthenium(III) ion [53].

#### 3.2. Magnetic moments and EPR spectra

The room temperature magnetic susceptibility measurements show that these complexes are paramagnetic corresponding to one unpaired electron (1.85-1.92 BM), which supports the trivalent state of ruthenium (low-spin Ru<sup>III</sup>,  $t_{2\sigma}^5$ ) in an octahedral environment. All the complexes exhibit well-defined single isotropic lines with 'g' values in the range 2.08-2.26. Isotropic lines are observed as a result of either intermolecular spin exchange (which can broaden the lines) or occupancy of the unpaired electron in a degenerate orbital. However, the EPR spectra of the complexes, [RuCl(PPh<sub>3</sub>)<sub>2</sub>(DHA-TSC)] (1), [RuCl(PPh<sub>3</sub>)<sub>2</sub>(DHA-PTSC)] (5) and [RuBr(AsPh<sub>3</sub>)<sub>2</sub>(DHA-PTSC)] (8) recorded in toluene at 77 K shows rhombic spectra with three different 'g' values  $g_x = 2.19$ ,  $g_y = 2.08$ ,  $g_z = 1.98$  (1),  $g_x = 2.24$ ,  $g_y = 2.08$ ,  $g_z = 1.97$  for (5) and  $g_x = 2.21$ ,  $g_y = 2.13, g_z = 1.99$  for (8)  $(g_x \neq g_y \neq g_z)$ , respectively (Fig. 1) The rhombicity of the spectra reflects the asymmetry of the electronic environment around the ruthenium in these complexes [54].

Complex	$\nu_{(C=N)} (cm^{-1})$	$v_{(C-0)} + v_{(C-S)} (cm^{-1})$	$\lambda_{max}$ , nm ( $\varepsilon$ , dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> )
1	1568	1262	534 <sup>a</sup> (690), 451 <sup>b</sup> (1959), 369 <sup>c</sup> (8154), 230 <sup>d</sup> (16,605)
2	1565	1275	536 <sup>a</sup> (2184), 450 <sup>b</sup> (4281), 361 <sup>c</sup> (14,481), 280 <sup>d</sup> (29,026)
3	1564	1264	584 <sup>a</sup> (1125), 457 <sup>b</sup> (2284), 325 <sup>c</sup> (9047), 241 <sup>d</sup> (21,739)
4	1571	1264	582 <sup>a</sup> (2612), 453 <sup>b</sup> (4208), 369 <sup>c</sup> (7587), 231 <sup>d</sup> (24,429)
5	1564	1250	537 <sup>a</sup> (2189), 451 <sup>b</sup> (6009), 363 <sup>c</sup> (14,531), 283 <sup>d</sup> (29,182)
6	1581	1261	541 <sup>a</sup> (473), 467 <sup>b</sup> (1151), 369 <sup>c</sup> (5390), 241 <sup>d</sup> (18,420)
7	1581	1271	573 <sup>a</sup> (1854), 493 <sup>b</sup> (2872), 368 <sup>c</sup> (18,076), 283 <sup>d</sup> (28,602)
8	1589	1279	543 <sup>a</sup> (418), 487 <sup>b</sup> (1607), 355 <sup>c</sup> (5046), 286 <sup>d</sup> (28,095)

<sup>a</sup> d–d transition.

b LMCT.

 $c n-\pi^*$ .

 $d \pi - \pi^*$ .



Fig. 1. EPR spectrum of [RuCl(PPh<sub>3</sub>)<sub>2</sub>(DHA–PTSC)] (5) at 77 K.

#### 3.3. Redox properties

The redox behavior of the ruthenium(III) thiosemicarbazone complexes has been examined by cyclic voltammetric technique at glassy carbon electrode in degassed acetonitrile solution and the redox potentials are expressed with reference to Ag/AgCl. The potentials are summarized in Table 3 and a representative voltammogram of complex (**5**) is shown in Fig. 2. The cyclic voltammogram of all the complexes exhibit an irreversible oxidation and an irreversible reduction at the scan rate of 100 mV s<sup>-1</sup>. The redox potential of the complexes is characterized by well-defined waves in the range +0.74 to +0.98 V (oxidation) and -0.94 to -1.06 V (reduction). The irreversible redox processes observed for these complexes may be due to short-lived oxidized/reduced state of the metal ion [55]. There is not much variation in the redox potential due to the replacement of chloride by bromide and triphenylphosphine by triphenylarsine.

#### 3.4. Catalytic transfer hydrogenation of ketones

Ruthenium mediated transfer hydrogenation reactions are found to be effective catalytic systems in which hydrogen is transferred from one organic molecule to another and this made us to carry out this type of reactions. One of the complexes [RuCl(PPh<sub>3</sub>)<sub>2</sub>(DHA–PTSC)] (**5**) is taken as model catalyst and the catalytic activity in the transfer hydrogenation of various aliphatic and aromatic ketones in the presence of isopropanol and KOH has

Table 3

Electrochemical data of ruthenium(III) DHA-thiosemicarbazone comple	xes.
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Complex	Ru(III)/Ru(IV) E <sub>pa</sub> (V)	Ru(III)/Ru(II) $E_{pc}(V)$
1	0.98	-1.01
2	0.76	-1.01
3	0.83	-1.01
4	0.77	-1.02
5	0.74	-1.05
6	0.96	-1.02
7	0.89	-1.02
8	0.75	-1.06

Solvent: acetonitrile; supporting electrolyte: 0.001 M [NBu<sub>4</sub>]ClO<sub>4</sub>; concentration of the complex: 0.001 M; scan rate:  $100 \text{ mV s}^{-1}$ .  $E_{pa}$  and  $E_{pc}$  are anodic and cathodic potentials, respectively.

abl	e	4	
	•		

Transfer hydrogenation of ketones by  $[RuCl(PPh_3)_2(DHA-PTSC)]$  (5) with isopropanol/KOH<sup>a</sup>.

Entry	Substrates	Products	Conversion <sup>b</sup> %	TON <sup>c</sup>
1		OH	67.6	135
2	CI	CI	89.2	178
3		OH	83.0	166
4	0 L	OH	97.5	195
5	° V	OH	96.6	193
6		OH	79.1	158
7	°.	OH	86.2	172
8	⊂,°	ОН	66.3	132
9	0	ОН	94.6	189

<sup>a</sup> Reaction condition: reactions were carried out at 82 °C using substrate (2 mmol), catalyst (0.01 mmol) in 5 ml of isopropanol, KOH (0.025 mmol); catalyst/ketone/KOH ratio 1:200:2.5.

 $^b$  Conversion of the product after 2 h was determined with authentic samples using HP 6890 series GC-FID with a DP-5 column of 30 m length, 0.32 mm diameter and 0.25  $\mu m$  film thickness.

<sup>c</sup> TON = moles of product/moles of catalyst.

been explored.



(R or R' = alkyl or aryl)

The complex catalyzes the conversion of ketones to their corresponding alcohols with reasonable conversions in all the cases (Table 4). The alcohols formed were determined by GC by comparison with authentic samples. In this method, it is believed that the base facilitates the formation of a ruthenium alkoxide by abstracting the proton of the alcohol, which then undergoes  $\beta$ -elimination to give a ruthenium-hydride which is the active catalyst. This classical mechanism is proposed by several workers on the studies of ruthenium complexes catalyzed transfer hydrogenation reaction by metal hydrides [56,57].

The conversion in case of acetophenone is 67.6%. 4-Chloro acetophenone is converted to corresponding alcohol with 89.2% conversion and in the case of 4-methoxy acetophenone the con-



Fig. 2. Cyclic voltammogram of [RuCl(PPh<sub>3</sub>)<sub>2</sub>(DHA-PTSC)] (5).

version is 83.0%. The presence of electron withdrawing (Cl) and electron donating (OCH<sub>3</sub>) substituents on the substrates (entries 2 and 3) has marginal effect on the catalytic transfer hydrogenation of ketones. Though the effect is minimal, the greater conversion in case of 4-chloro acetophenone compared to 4-methoxy acetophenone may be due to the fact that reduction involves the substrate gaining electrons and this would be more facile at an electron deficient center [58]. The complex efficiently catalyzed the reduction of aliphatic ketones such as methyl propyl ketone and diethyl ketone to their corresponding alcohols with 97.5% and 96.5% conversions, respectively (entries 4 and 5). Moreover, this catalyst efficiently catalyzes the reduction of cyclopentanone and cyclohexanone to cyclopentanol and cyclohexanol with 79.1% and 86.2% conversions, respectively (entries 6 and 7). The complex shows good catalytic activity for seven and eight membered cyclic ketones, cycloheptanone and cyclooctanone, with 66.3% and 94.6% conversions, respectively (entries 8 and 9). The presence of a catalytic amount of base is necessary for the transfer hydrogenation of ketones. Acetone was identified as only byproduct in all the cases. As the catalyst is stable in all organic solvents and it can be recovered and the work up process is also very simple for this catalytic system. Although the present catalyst has less catalytic efficiency compared to ruthenium pincer [59] or azo [60] complexes, they possesses better catalytic activity than the ruthenium complexes recently reported in the literature [61–64].

#### 4. Conclusion

In conclusion, we have described the synthesis and characterization of a series of ruthenium(III) complexes containing tridentate thiosemicarbazone, halides and triphenyl phosphine/arsine. A distorted octahedral geometry has been proposed around the ruthenium ion. The complex (**5**), [RuCl(PPh<sub>3</sub>)<sub>2</sub>(DHA–PTSC)], has been tested as catalyst in transfer hydrogenation of aliphatic and aromatic ketones to the corresponding secondary alcohols in the presence isopropanol/KOH at 82 °C.

#### Acknowledgements

One of the authors (N.R.) thanks University Grants Commission (UGC), New Delhi for the award of UGC-SAP RFMS Scholarship. We thank Prof. P. Sambasiva Rao, Department of Chemistry, Pondicherry University, for providing the EPR facility. We express our sincere thanks to Prof. P.R. Athappan, School of Chemistry, Madurai Kamaraj University, for providing cyclic voltammetric facility.

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