Inorganic Chemistry Communications 13 (2010) 1321–1324

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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

Arene ruthenium(II) *p*-chloroacetophenone phenylthiosemicarbazone complex mediated transfer hydrogenation of ketones

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ARTICLE INFO

Article history:
Received 6 June 2010
Accepted 21 July 2010
Available online 29 July 2010

Keywords:
Synthesis
Ruthenium(II)-*p*-cymene
Phenylthiosemicarbazone ligands
Structural characterization
Transfer hydrogenation

ABSTRACT

A series of cationic half-sandwich arene ruthenium(II) complexes of general formula [Ru(η^6-*p*-cymene)Cl(L)]Cl have been synthesized from the reaction of [Ru(η^6-*p*-cymene)Cl_2]$_2$ with thiosemicarbazone derivatives (L). Characterization of the complexes were accomplished by analytical and spectral (FT-IR, UV–Vis, ^{1}H NMR) methods. Single crystal structure determination reveals the presence of a pseudooctahedral three-legged piano stool conformation. All the complexes exhibit a quasi-reversible one electron reduction in the range from −0.75 to −0.85 V. Further, the catalytic activity of the titled complex has been investigated in the transfer hydrogenation of ketones in the presence of isopropanol/NaOH.

There has been much interest in the chemistry of half-sandwich arene ruthenium(II) complexes [1,2] since the development of useful synthetic precursors with the general formula [$RuCl_2(\eta^6$-arene)]$_n$. Syntheses of new and highly active transition-metal based catalysts derived from arene ligands are used in different catalytic reactions including addition of carboxylic acids to alkynes [3], transfer hydrogenation of ketones [4], polymerization of olefins [5] and isomerization of alkenes [6]. Further, several arene ruthenium complexes are found in applications as anticancer drugs [7,8].

The reduction of carbonyl compounds is an important transformation in organic synthesis from both academic and industrial points of view [9]. Transfer hydrogenation of ketones by using an alcohol, preferably isopropyl alcohol, is an interesting alternative to the classical hydrogenation process requiring the use of dihydrogen gas [10]. Homogeneous ruthenium complexes are considered to be the most attractive catalysts for transfer hydrogenation reactions, though other metal complexes have also been used successfully [11]. Transfer hydrogenation of unsaturated compounds like ketones, imines etc. by using isopropanol/NaOH as hydrogen source is a widely investigated reaction that is promoted by many transition metal complexes [12].

Cationic arene ruthenium(II) complexes containing 2,2'-bipyrimidine ligands are used as active catalysts for transfer hydrogenation of ketones in water in the presence of HCOOH/HCOONa [13]. Similarly, asymmetric transfer hydrogenation of ketones carried out by [$RuCl_2$(*p*-cymene)]$_2$ in the presence of NaOH and *t*-BuOK has been described [14]. Bimetallic ruthenium(II) complexes bearing bis(aminophosphine) and bis(phosphinite) monodentate ligands were used as catalyst in the transfer hydrogenation of substituted acetophenone [15]. Transfer hydrogenation of benzophenone and acetophenone by arene ruthenium(II) complexes containing bis(pyrazolylazines) ligands has also been described [16]. Further, the catalytic activity of conformationally rigid diphosphine arene ruthenium(II) complexes in the transfer hydrogenation of various ketones has been reported [17]. Furthermore, transfer hydrogenation of aromatic ketones were successfully achieved by water-soluble arene ruthenium complexes containing an N,N-chelating 2,2'-dipyridylamine ligands [18].

As a part of ongoing efforts to synthesize novel ruthenium complexes and to study their catalytic efficiency in transfer hydrogenation reactions [19], herein we describe the synthesis and characterisation of a series of cationic arene ruthenium(II) complexes containing thiosemicarbazones along with their catalytic activity in transfer hydrogenation of ketones.

The substituted acetophenone thiosemicarbazone ligands (L1–L5) were prepared by modification of the reported procedure [20]. The general procedure for the preparation of the complexes is as follows. To a solution of 0.1 mmol of [{(η^6-*p*-cymene)$RuCl)_2$(μ-$Cl)_2$}] in dry benzene (25 ml) was added 0.2 mmol thiosemicarbazone ligand (mole ratio of ruthenium complex and ligand is 1:2 respectively) and the mixture was refluxed for 2–3 h (Scheme 1). The solution was concentrated to about 3 ml, pet. ether (15 ml) was added to precipitate the cationic η^6-*p*-cymene ruthenium(II)phenylthiosemicarbazone complexes. The resulting complexes were recrystallized from CH_2Cl_2/pet.ether and dried under vacuum. The overall yield obtained for all the complexes were 66–80%.

All the newly synthesized η^6-*p*-cymene ruthenium(II)phenylthiosemicarbazones complexes are colored, stable in air, non-hygroscopic in

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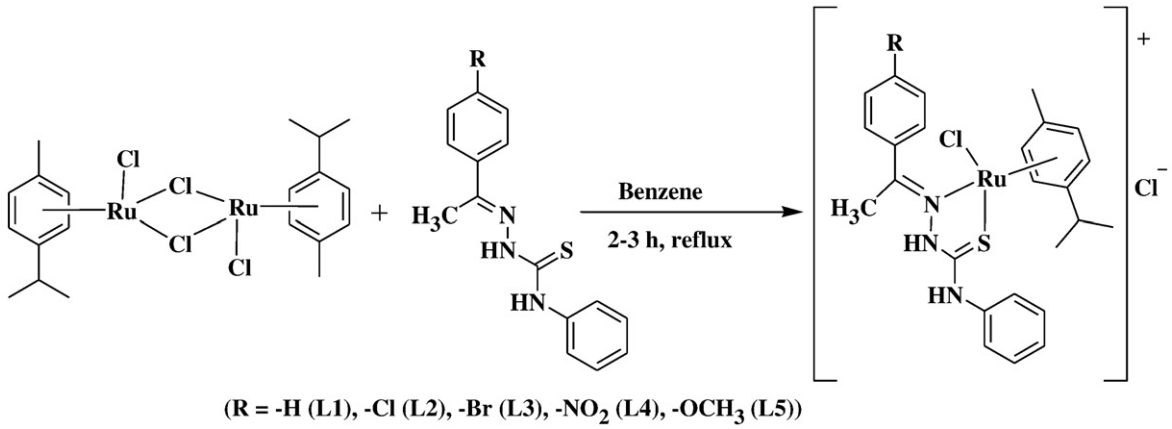
doi:10.1016/j.inoche.2010.07.026



Scheme 1. Synthesis of η^6-*p*-cymene Ru(II)phenylthiosemicarbazone complexes.

nature and highly soluble in common solvents such as dichloromethane, acetonitrile and chloroform. The elemental analyses are in good agreement with the molecular formula proposed for all the complexes (Table 1). In the IR spectra of all the complexes, the thiosemicarbazone ligands behave as neutral bidentate ligand and coordinated to the metal ions through azomethine (>C=N) nitrogen ($\nu_{C=N}$: 1606–1555 cm^{-1}) and the thione sulphur ($\nu_{C=S}$: 828–809 cm^{-1}) (Table 1). Bands in the region 464–440 cm^{-1} and 428–417 cm^{-1} are probably due to Ru–N and Ru–S bond, respectively [21]. The electronic spectra of all the complexes in chloroform at room temperature showed the medium intensity bands around 435–449 nm region due to metal to ligand charge transfer transition (MLCT) and intense n-π*, π–π* ligand-centered transitions bands with maxima in the 243–284 nm region (Table 1). The pattern of the electronic spectra of all the complexes indicates the presence of an octahedral environment around the ruthenium(II) ion [22]. The ^{1}H NMR spectra of the complexes were recorded in $CDCl_3$. The multiplet observed in the region around δ 6.8–8.4 ppm in all the listed complexes have been assigned to the aromatic protons of the phenyl group of the phenylthiosemicarbazone ligand. The singlet in the region δ 2.6–3.0 ppm is due to methyl protons nearer to coordinated azomethine group. The singlet around δ 3.8 ppm is due to methoxy protons in the complex **5**. In addition, the two isopropyl methyl protons of the *p*-cymene appeared as doublet in the region of δ 0.9–1.7 ppm and the methine protons comes in the region of δ 2.5–2.8 ppm as septet. Further, the methyl group of the *p*-cymene comes as singlet around the region of δ 1.8–1.9 ppm. Also, the hydrazinic proton and the imine (CH=N) proton of thiosemicarbazone ligands shift downfield by 0.15–0.25 ppm upon coordination to the ruthenium(II) ion. Cyclic voltammogram of these complexes exhibit one quasi reversible reduction (ΔE_p = 150–210 mV) at a scan rate of 100 mV s^{-1} and the $E_{1/2}$ lies in the range from −0.75 to −0.85 V (Ru^{III}/Ru^{II}).

The complex [Ru(η^6-*p*-cymene)Cl(L**2**)]Cl (**2**) has been structurally characterized by X-ray crystallography. The coordination sphere around ruthenium consists of the η^6-*p*-cymene ring, sulphur, nitrogen of thiosemicarbazone and a chloride and all are disposed in a classical pseudooctahedral three-legged piano-stool geometry, similar to that of other ruthenium(II)-*p*-cymene complexes (Fig. 1) [23]. The phenylthiosemicarbazone ligands bind the metal center at S and N forming the five membered chelate ring with bite angle around Ru(II) ion being 81.13(9) for S(1)–Ru(1)–N(1) and bond lengths for Ru(1)–S(1) and Ru(1)–N(1) are 2.3376(12) Å and 2.130(3) Å respectively. The Ru–Cl bond length is found to be 2.4218(12) Å. Ruthenium(II) ion is therefore sitting in a SNCl(η^6-*p*-cymene) coordination environment, which is pseudooctahedral in nature as reflected in all the bond parameters around Ru(II) ion. As all the complexes display similar spectral and electrochemical properties, the other four complexes are assumed to have similar structure to that of complex [Ru(η^6-*p*-cymene)Cl(L**2**)]Cl.

One of the complexes [Ru(η^6-*p*-cymene)Cl(L**2**)]Cl is taken as model catalyst and the catalytic activity in transfer hydrogenation of aliphatic and aromatic ketones in the presence of isopropanol as hydrogen source and base as promoter has been explored (Scheme 2). In the transfer hydrogenation reaction, the base facilitates the formation of ruthenium alkoxide by abstracting proton from the alcohol and subsequently alkoxide undergoes β-elimination to give ruthenium hydride, which is an active species in this reaction. This is the mechanism proposed by several workers on the studies of ruthenium catalyzed transfer hydrogenation reaction by metal hydride intermediates [24].

Since the base facilitates the formation of a ruthenium alkoxide by abstracting the proton from isopropanol, different bases were used as promoters in the transfer hydrogenation of ketones (Table 2). Acetophenone was kept as a test substrate and allowed it to react in isopropanol with catalytic quantities of complex **2** in the presence of different bases like NaOH, KOH, *t*-BuOK and NaOAc. It has been observed that NaOH and KOH are shown to have good conversions

Table 1
Analytical, IR and UV–Vis spectral data of η^6-*p*-cymene ruthenium(II)phenylthiosemicarbazone complexes.

Complexes	Found (calculated) %				$\nu_{C=N}$ (cm^{-1})	$\nu_{C=S}$ (cm^{-1})	λ_{max}, nm (ε, M^{-1} cm^{-1})
	C	H	N	S			
(1) [Ru(η^6-*p*-cymene)(Cl)(L**1**)]Cl	55.69 (55.62)	5.23 (5.27)	7.79 (7.83)	5.95 (5.92)	1557	810	449[a] (492), 282[b] (13180), 244[c] (13666)
(2) [Ru(η^6-*p*-cymene)(Cl)(L**2**)]Cl	52.35 (52.32)	4.74 (4.78)	7.33 (7.29)	5.59 (5.60)	1606	828	440[a] (538), 282[b] (13408), 243[c] (14577)
(3) [Ru(η^6-*p*-cymene)(Cl)(L**3**)]Cl	48.59 (48.56)	4.40 (4.46)	6.80 (6.75)	5.19 (5.18)	1555	821	435[a] (499), 283[b] (13185), 245[c] (13743)
(4) [Ru(η^6-*p*-cymene)(Cl)(L**4**)]Cl	51.40 (51.41)	4.66 (4.68)	9.59 (9.63)	5.49 (5.53)	1595	809	442[a] (521), 278[b] (13664), 251[c] (14504)
(5) [Ru(η^6-*p*-cymene)(Cl)(L**5**)]Cl	54.87 (54.79)	5.31 (5.37)	7.38 (7.25)	5.63 (5.59)	1604	825	445[a] (495), 284[b] (13560), 248[c] (13050)

[a] MLCT.
[b] $n-\pi^*$.
[c] $\pi-\pi^*$.

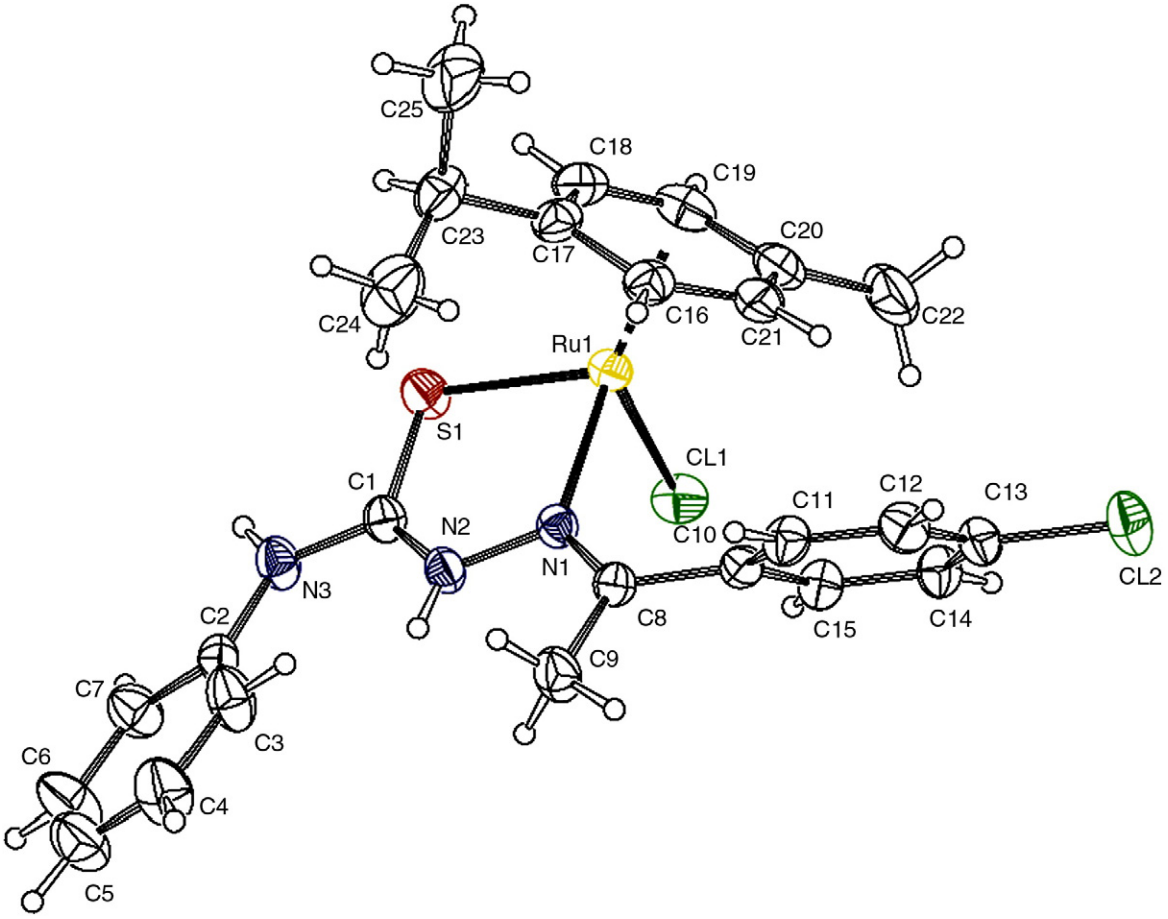
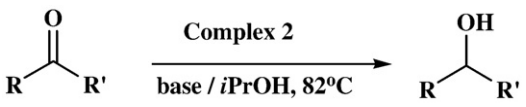


Fig. 1. ORTEP view of the complex [Ru(η^6-*p*-cymene)Cl(L**2**)]Cl. Selected bond lengths (Å) and bond angles (°): Ru(1)–N(1) 2.130(3), Ru(1)–S(1) 2.3376(12), Ru(1)–Cl(1) 2.4218 (12) and N(1)–Ru(1)–S(1) 81.13(9), N(1)–Ru(1)–Cl(1) 86.00(9), S(1)–Ru(1)–Cl(1) 85.57(5).

when compared to the *t*-BuOK and NaOAc in the hydrogenation reactions and the influence of bases in hydrogen promotion is in the order of NaOH>KOH>*t*-BuOK>NaOAc. Hence, it is decided that base NaOH is the best compromise between optimum reaction rate in isopropanol and reaching 99% conversion for acetophenone within 20 h. Under the same experimental condition, transfer hydrogenation of a series of aliphatic and aromatic ketones was explored by means of complex **2** as catalyst.

In all the reactions, this complex catalyzes the reduction of ketones to the corresponding alcohols via hydrogen transfer from isopropanol. In a typical experiment, the ketone (3.75 mmol), arene ruthenium(II) complex (0.0125 mmol) and NaOH (0.03 mmol) in 5 ml of isopropanol (catalyst/substrate/base molar ratio 1:300:2.5) were taken into the round bottom flask and are heated to reflux for 20 h at 82 °C. The catalyst was removed from the reaction mixture by the addition of ether followed by filtration and subsequent neutralization with 1 M HCl. The organic layer was filtered through the short path of silica gel by column chromatography and is subjected to GC analysis. The catalyst **2** performed efficiently in the conversion of ketones to alcohols in 71 to 99% and the results of this organic transformation are presented in (Table 3). The conversion of ketone to secondary alcohol in the case of acetophenone was 99% (20 h) (entry 1), which takes place at a faster rate than that for 4-methoxy acetophenone (88%). The presence of electron withdrawing (Cl) or electron donating (OCH_3) substituent on acetophenone (entry 2 and 3) has significant effect on the reduction of ketones to their corresponding alcohols. The maximum conversion of 4-chloro acetophenone to corresponding alcohol was achieved over a period of 20 h. 4-methoxy acetophenone was converted to its corresponding alcohol in 88% conversion (entry 3). Interestingly, this catalyst shows excellent activity for the conversions of six, seven and eight membered cyclic ketones (entries 4–7) to their corresponding alcohols with 71 to 80% conversions. No transfer hydrogenation was observed in the absence of base. The work up process is very simple for this catalytic system and as the catalyst is stable in all organic solvents and it can be recovered. The catalytic efficiency of the present complex is less when compared to the ruthenium complexes containing Schiff base, aryl azo and pincer ligands [25]. However, it has been found that the



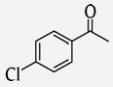
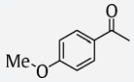
Scheme 2. Catalytic transfer hydrogenation of ketones.

Table 2
Catalytic transfer hydrogenation of acetopheneone by [Ru(η^6-*p*-cymene)Cl(L**2**)]Cl with *i*-PrOH.[a]

Entry	Bases	Time (h)	Conversion (%)	TON
1.	NaOH	5	83	249
2.	KOH	5	78	234
3.	t-BuOK	5	48	144
4.	AcONa	5	9	27

[a] Conditions: reactions were carried out at 82 °C using 3.75 mmol of acetophenone (5 ml isopropanol); catalyst/ketone/base ratio 1: 300: 2.5. TON = ratio of moles of product obtained to the moles of catalyst used.

Table 3
Catalytic transfer hydrogenation of ketones by [Ru(η⁶-*p*-cymene)Cl(L**2**)]Cl with *i*-PrOH/NaOH.[a]

Entry	Ketone	Time (h)	Conversion (%)	TON
1		5/20	83/99	249/297
2		5/20	79/99	237/297
3		5/20	51/88	153/264
4		5/20	41/78	123/234
5		5/20	45/80	135/240
6		5/20	36/71	108/213
7		5/20	38/79	114/237

[a] Conditions: reactions were carried out at 82 °C using 3.75 mmol of ketone (5 ml isopropanol); catalyst/ketone/NaOH ratio 1: 300: 2.5; Yield of product was determined using a HP 6890 series GC-FID with a DP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness and by comparison with authentic samples. TON = ratio of moles of product obtained to the moles of catalyst used.

titled complex shows better catalytic activity than the other reported arene ruthenium(II) complexes [26].

Conclusion

In conclusion, we have synthesized and characterized arene ruthenium(II) half-sandwich complexes bearing thiosemicarbazone ligands. X-ray diffraction study of complex confirms the azomethine nitrogen and thione sulphur coordination mode of phenylthiosemicarbazone ligands and indicates the presence of pseudooctahedral geometry. Further, the complex [Ru(η⁶-*p*-cymene)Cl(L**2**)]Cl efficiently catalyze the transfer hydrogenation of ketones in the presence of isopropanol/NaOH up to 99%.

Acknowledgements

We gratefully acknowledge financial support from the Department of Science and Technology (DST Ref No: SR/S1/IC-03/2007) New Delhi, India. MUR thanks DST for the award of Senior Research Fellowship (SRF). We thank D.S.T-India (F.I.S.T programme) for the use of Bruker Smart APEX II diffractometer at the School of Chemistry, Bharathidasan University.

Appendix A. Supplementary data

CCDC 760991 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.07.026.

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