Journal of Organometallic Chemistry 694 (2009) 4170–4177

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Ruthenium(II) mediated C–H activation of substituted acetophenone thiosemicarbazones: Synthesis, structural characterization, luminescence and electrochemical properties

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ARTICLE INFO

Article history:
Received 2 July 2009
Received in revised form 20 August 2009
Accepted 3 September 2009
Available online 10 September 2009

This paper is dedicated to Professor Karuppannan Natarajan on the occasion of his 60th birth anniversary.

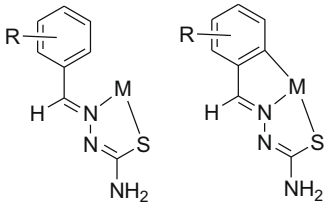
Keywords:
Thiosemicarbazone
C–H activation
Ru(II) cyclometalated complex
Crystal structure
Emission
Redox potential

ABSTRACT

Treatment of $[RuHCl(CO)(AsPh_3)_3]$ with 4′-substituted acetophenone thiosemicarbazone derivatives in methanol under reflux afford a series of air stable new ruthenium(II) cyclometalated complexes containing thiosemicarbazone of general formula $[Ru(L)(CO)(AsPh_3)_2]$. The 4′-substituted acetophenone thiosemicarbazone ligands behave as a dianionic terdentate C, N and S donors (L) and coordinates to ruthenium via aromatic carbon, the imine nitrogen and thiol sulfur. The compositions of the complexes have been established by elemental analysis, and spectral methods (FT-IR, UV–Vis, ^{1}H NMR, ESI-MS) and X-ray crystallography. In chloroform solution all the complexes exhibit metal-to-ligand charge transfer transitions (MLCT) in the visible region and are emissive at room temperature with quantum yield of 0.001–0.005. The crystal structure of one of the complexes $[Ru(4CAP\text{-}PTSC)(CO)(AsPh_3)_2]$ (**4**) has been solved by single crystal X-ray crystallography and it indicates the presence of a distorted octahedral geometry in these complexes. All the complexes exhibit a quasi reversible one electron reduction (Ru^{II}/Ru^{I}) in the range −0.83 to −0.86 V. The formal potential of all the couples correlate linearly with the Hammett constant of the para substituent in phenyl fragment of the acetophenone thiosemicarbazone ligands.

1. Introduction

Derivatives of semicarbazones and thiosemicarbazones are amongst the most widely studied nitrogen and oxygen/sulfur donor ligands [1–4]. Particularly, thiosemicarbazones have emerged as an important class of sulfur donor ligands for transition metal ions because of their mixed hard–soft donor character and versatile coordination behaviour. In particular, transition metal complexes of thiosemicarbazones have been receiving considerable interest largely because of their pharmacological (viz. antiviral, antifungal, antimicrobial, antitumour, anticancer) property [5–8]. Thiosemicarbazones are versatile ligands with a wide range of coordination modes in metal complexes. Thiosemicarbazones usually bind to a metal ion, either in the neutral thione form or in the anionic thiolate form, as bidentate N, S donor ligands forming five-membered chelate rings **1** [9,10]. However, the binding capacity of thiosemicarbazones is further increased by condensation of the thiosemicarbazide with an aldehyde or ketone containing an additional donor atom in a suitable position for chelation, normally resulting in tricoordination **2** [11,12].



Ever since, the first cyclometalated complex was synthesized [13], cyclometalation has become an important part of organometallic chemistry and several reviews covering the subject have appeared [14–16]. The intramolecular activation of aromatic C–H bonds of coordinated ligands by transition metals represents an active area of research due to their applications, such as their use in regiospecific organic and organometallic synthesis, catalysis [17–19], photochemistry [20,21], the synthesis of new metal mesogenic compounds [22] and as potential biologically active materials [23,24]. Bhattacharya et al., reported the reaction of benzaldehyde thiosemicarbazone ligands with ruthenium(II) and

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doi:10.1016/j.jorganchem.2009.09.010

osmium(II) complexes [25,26], where the thiosemicarbazone ligand behaved as a monoanionic bidentate N and S donors. Further the same research group described the different coordination modes of benzaldehyde thiosemicarbazone ligands with ruthenium in monomeric and dimeric nature [27]. Rhodium mediated C–H activation of benzaldehyde thiosemicarbazones has been achieved recently, where the ligand behaved as a dianionic terdentate ligand [28]. In addition, palladium cyclometallated complexes containing acetophenone thiosemicarbazones have been reported and thiosemicarbazone act as terdentate C, N and S donors [29]. In view of different coordination modes of these ligands, we have focused our research interest on the reaction of acetophenone thiosemicarbazone ligands with ruthenium(II) carbonyl complexes. It has been observed that, interestingly, these ligands act as terdentate C, N and S donors and generate air stable monomeric ruthenium(II) cyclometalated complexes via C–H activation.

Transition metal complexes exhibit an enormous potential for the discovery of photo redox processes for solar energy conversion [30], information storage systems [31], laser materials [32], and biosensors [33]. In particular the photophysical and the excited state chemistry of Ru(II) diimine complexes has been extensively studied [34–36]. The complex, $[Ru(bpy)_3]^{2+}$ has been studied in great detail and is one of the most used sensitizers in research laboratories due to the very favourable photochemical, photophysical and redox properties [37]. In comparison to the photophysical properties of polypyridyl complexes, the luminescent chemistry of cyclometalated ruthenium carbonyl thiosemicarbazone complexes are not well developed.

In continuation of our research on the synthesis of ruthenium cyclometalated complexes via direct C–H activation of azo or thiosemicarbazone ligands [38–42], we describe here the cyclometalation of ruthenium(II) with 4′-substituted acetophenone thiosemicarbazone ligands incorporated with triphenylarsine as ancillary ligand. All the complexes have been characterized by analytical and spectral methods. The structure of one of the complexes has been probed with the help of single crystal X-ray diffraction analysis. Further, the electrochemical behaviour of the complexes has been examined by cyclic voltammetry along with luminescence studies.

2. Experimental

2.1. Materials and instrumentation

Commercially available $RuCl_3{\cdot}3H_2O$ was used as supplied from Loba Chemie Pvt. Ltd. All the reagents used were chemically pure and analar grade. The solvents were freshly distilled using the standard procedures [43]. Triphenylarsine, all substituted acetophenones and thiosemicarbazides were purchased from Aldrich. The supporting electrolyte tetrabutyl ammonium perchlorate (TBAP) was purchased from Fluka and dried in vacuum prior to use. The precursor complex, $[RuHCl(CO)(AsPh_3)_3]$, was prepared by reported literature method [44].

2.2. Physical measurements

The microanalysis of carbon, hydrogen, nitrogen and sulfur were recorded by analytic function testing Vario EL III CHNS elemental analyzer at Sophisticated Test and Instrumentation Centre (STIC), Cochin University, Kochi. Infrared spectra of complexes were recorded in KBr pellets with a Perkin–Elmer 597 spectrophotometer in the range 4000–400 cm^{-1}. The ^1H NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 with Bruker 400 MHz instrument using TMS as internal reference. Melting points were recorded in the Boetius micro heating table and are uncorrected. Electronic spectra of the complexes in chloroform solution were recorded with a Cary 300 Bio UV–Vis Varian spectrophotometer in the range 800–230 nm. Emission intensity measurements were carried out by using a Jasco FP-6500 spectrofluorimeter with 5 nm exit slit at Madurai Kamaraj University, Madurai. Electrochemical measurements were made using a Princeton EG and G-Parc model potentiostat using a glassy carbon-working electrode and $[(n\text{-}C_4H_9)_4N](ClO_4)$ (TBAP) as supporting electrolyte. All the potentials were referenced to saturated calomel electrode (SCE) and the solutions were purged with N_2 before each set of experiments.

2.3. Preparation of thiosemicarbazone ligands

The substituted acetophenone thiosemicarbazone ligands were prepared by modification of the following reported procedure [29]. A solution of 4′-substituted acetophenone (120–165 mg, 1 mmol), 4′-substituted-3-thiosemicarbazide (91–165 mg, 1 mmol) in catalytic amount of conc. HCl (0.5 ml) in methanol (20 ml) was stirred at 27 °C for 6 h. During the course of the reaction, solid formed was filtered, washed with hexane and dried in air (Scheme 1).

Spectral and analytical data for the ligands:

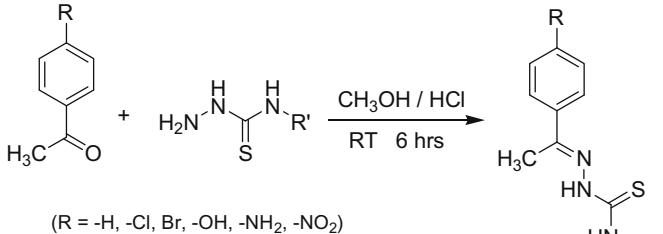
4-HAP-TSC (R = H, R′ = H): White; Yield: 90%; M.p.: 167 °C; Anal. Calc. for $C_9H_{11}N_3S$: C, 55.93; H, 5.74; N, 21.74; S, 16.59. Found: C, 55.87; H, 5.68; N, 21.64; S, 16.50%. ^1H NMR (400 MHz, $CDCl_3$) (δ ppm): 9.3 (s, 1H, NH), 8.8 (s, 2H, NH_2), 7.2–7.8 (m, 5H, aromatic), 2.3 (s, 3H, Me).

4-HAP-PTSC (R = H, R′ = Ph): White; Yield: 86%; M.p.: 169 °C; Anal. Calc. for $C_{15}H_{15}N_3S$: C, 66.88; H, 5.61; N, 15.60; S, 11.90. Found: C, 66.95; H, 5.54; N, 15.64; S, 11.82%. ^1H NMR (400 MHz, $CDCl_3$) (δ ppm): 9.3(s, 1H, NH), 8.8 (s, 1H, NHPh), 7.2–7.7 (m, 10H, aromatic), 2.3 (s, 3H, Me).

4-CAP-TSC (R = Cl, R′ = H): White; Yield: 92%; M.p.: 155 °C; Anal. Calc. for $C_9H_{10}ClN_3S$: C, 47.47; H, 4.43; N, 18.45; S, 14.08. Found: C, 47.40; H, 4.33; N, 18.53; S, 14.18%. ^1H NMR (400 MHz, $CDCl_3$) (δ ppm): 9.3 (s, 1H, NH), 8.8 (s, 2H, NH_2), 7.2–7.7 (m, 4H, aromatic), 2.3 (s, 3H, Me).

4-CAP-PTSC (R = Cl, R′ = Ph): White; Yield: 95%; M.p.: 171 °C; Anal. Calc. for $C_{15}H_{14}ClN_3S$: C, 59.30; H, 4.64; N, 13.83; S, 10.55. Found: C, 59.34; H, 4.70; N, 13.73; S, 10.50%. ^1H NMR (400 MHz, $CDCl_3$) (δ ppm): 9.3 (s, 1H, NH), 8.8 (s, 1H, NHPh), 7.2–7.7 (m, 9H, aromatic), 2.3 (s, 3H, Me).

4-MAP-TSC ($R = OCH_3$, R′ = H): White; Yield: 84%; M.p.: 160 °C; Anal. Calc. for $C_{10}H_{13}N_3OS$: C, 53.79; H, 5.87; N, 18.82; S, 14.36. Found: C, 53.89; H, 5.89; N, 18.84; S, 14.30%. ^1H NMR (400 MHz, $CDCl_3$) (δ ppm): 9.3 (s, 1H, NH), 8.8 (s, 2H, NH_2), 7.2–7.7 (m, 4H, aromatic), 3.9 (s, 3H, OMe), 2.3 (s, 3H, Me).



(R = -H, -Cl, Br, -OH, $-NH_2$, $-NO_2$)

(R' = -H, $-C_6H_5$)

4HAP-TSC: R = H, R' = H
4HAP-PTSC: R = H, R' = C_6H_5
4CAP-TSC: R = Cl, R' = H
4CAP-PTSC: R = Cl, R' = C_6H_5
4MAP-TSC: R = CH_3, R' = H
4MAP-PTSC: R = CH_3, R' = C_6H_5
4NAP-TSC: R = NO_2, R' = H
4NAP-PTSC: R = NO_2, R' = C_6H_5
4AAP-TSC: R = NH_2, R' = H
4BAP-PTSC: R = Br, R' = C_6H_5
4OHAP-TSC: R = OH, R' = H

Scheme 1. Preparation of thiosemicarbazone ligands.

4-MAP-PTSC (R = OCH_3, R′ = Ph): White; Yield: 82%; M.p.: 173 °C; Anal. Calc. for $C_{16}H_{17}N_3OS$: C, 64.19; H, 5.72; N, 14.04; S, 10.71. Found: C, 64.13; H, 5.62; N, 14.16; S, 10.75%. ^{1}H NMR (400 MHz, $CDCl_3$) (δ ppm): 9.3 (s, 1H, NH), 8.8 (s, 1H, NHPh), 7.2–7.7 (m, 9H, aromatic), 3.9 (s, 3H, OMe), 2.3 (s, 3H, Me).

4-NAP-TSC (R = NO_2, R′ = H): Yellow; Yield: 85%; M.p.: 175 °C; Anal. Calc. for $C_9H_{10}N_4O_2S$: C, 45.37; H, 4.23; N, 23.51; S, 13.46. Found: C, 45.40; H, 4.18; N, 23.61; S, 13.36%. ^{1}H NMR (400 MHz, DMSO-d_6) (δ ppm): 10.5 (s, 1H, NH), 8.7 (s, 1H, NH_2), 8.1–8.3 (m, 4H, aromatic), 2.34 (s, 3H, Me).

4-NAP-PTSC (R = NO_2, R′ = Ph): Yellow; Yield: 80%; M.p.: 180 °C; Anal. Calc. for $C_{15}H_{14}N_4O_2S$: C, 57.31; H, 4.49; N, 17.82; S, 10.20. Found: C, 57.35; H, 4.43; N, 17.92; S, 10.15%. ^{1}H NMR (400 MHz, DMSO-d_6) (δ ppm): 10.5 (s, 1H, NH), 8.7 (s, 1H, NHPh), 8.1–8.3 (m, 9H, aromatic), 2.34 (s, 3H, Me).

4-AAP-TSC (R = NH_2, R′ = H): White; Yield: 80%; M.p.: 153 °C; Anal. Calc. for $C_9H_{12}N_4S$: C, 51.90; H, 5.81; N, 26.90; S, 15.39. Found: C, 51.99; H, 5.78; N, 26.98; S, 15.42%. ^{1}H NMR (400 MHz, DMSO-d_6) (δ ppm): 9.3 (s, 1H, NH), 9.1 (s, 2H, Ar-NH_2), 8.8 (br, 2H, NH_2), 7.2–7.7 (m, 9H, aromatic), 2.3 (s, 3H, Me).

4-BAP-PTSC (R = Br, R′ = Ph): White; Yield: 86%; M.p.: 163 °C; Anal. Calc. for $C_{15}H_{14}BrN_3S$: C, 51.73; H, 4.05; N, 12.07; S, 9.21. Found: C, 51.79; H, 4.10; N, 12.14; S, 9.25%. ^{1}H NMR (400 MHz, $CDCl_3$) (δ ppm): 9.3 (s, 1H, NH), 8.8 (s, 1H, NHPh), 7.2–7.7 (m, 9H, aromatic), 2.3 (s, 3H, Me).

4-HAP-TSC (R = OH, R′ = H): White; Yield: 80%; M.p.: 164 °C; Anal. Calc. for $C_9H_{11}N_3OS$: C, 51.65; H, 5.30; N, 20.08; S, 15.32. Found: C, 51.58; H, 5.27; N, 20.13; S, 15.26%. ^{1}H NMR (400 MHz, DMSO-d_6) (δ ppm): 10.1 (s, 1H, NH), 9.7 (s, 1H, NH_2), 7.2–7.7 (m, 9H, aromatic), 6.7 (s, 1H, Ar-OH), 2.3 (s, 3H, Me).

2.4. Synthesis of Ru(II) cyclometalated thiosemicarbazone complexes

All the reactions were carried out under anhydrous conditions under nitrogen atmosphere and the ruthenium complexes were prepared by the following general procedure: to a methanolic solution (20 ml) of [RuHCl(CO)($AsPh_3$)$_3$] (100 mg, 0.092 mmol) was added appropriate thiosemicarbazone ligand (17.8–35.7 mg, 0.092 mmol), lithium bromide (16 mg, 0.184 mmol) and sodium acetate (15.1 mg, 0.184 mmol). The reaction mixture was then refluxed for 6 h. During the course of the reaction solid was formed. The solvent was evaporated, the residue was washed with light petroleum ether (60–80 °C) recrystallized from CH_2Cl_2/CH_3OH and dried under vacuum (Scheme 2). (Yield: 65–75%). The ^{1}H NMR spectra for a representative complex is shown in Fig. 1. The analytical data of all the Ru(II) cyclometalated thiosemicarbazone complexes is given in Table S1 (Supplementary material).

2.5. X-ray crystallography

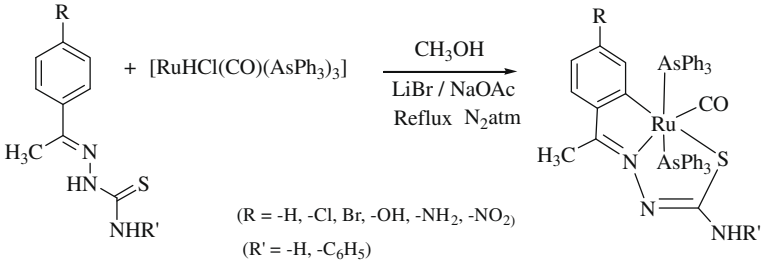
Single crystals of [Ru(4CAP-PTSC)(CO)($AsPh_3$)$_2$] (**4**) were grown by slow evaporation of methanol solution at room temperature. The data collection was carried out using Bruker AXS Kappa APEX II single crystal X-ray diffractometer using monochromated Mo Kα radiation (kI = 0.71073 Å). Data were collected at 293 K. the unit cell parameters were determined by the method of difference vectors using reflections scanned from three different zones of the reciprocal lattice. The intensity data were measured using ω and φ scan with a frame width of 0.5°. Frame integration and data reduction were performed using the Bruker SAINT-Plus (Version 7.06a) software. The multi-scan absorption corrections were applied to the data using SADABS software.

3. Results and discussion

The new ruthenium(II) cyclometalated thiosemicarbazone complexes of 4′-substituted acetophenone thiosemicarbazone of the type [Ru(L)(CO)($AsPh_3$)$_2$] (Scheme 2) have been obtained in good yield via C–H activation of 4′-substituted acetophenone thiosemicarbazone ligand by [RuHCl(CO)($AsPh_3$)$_3$] in dry methanol in 1:1 molar ratio in the presence of lithium bromide and sodium acetate. The addition of lithium bromide in basic medium to the reaction mixture was used to abstract proton and cyclometalation was achieved [29]. It has been observed that the ligands behave as dianionic terdentate and replaces one hydride, one chloride and one triphenylarsine from the ruthenium(II) precursor and the oxidation state of ruthenium remain unchanged during the formation of cyclometalated species. All the complexes are found to be air stable in both the solid and the liquid states at room temperature and are non-hygroscopic in nature. The synthesized ruthenium(II) complexes are soluble in common solvents such as chloroform, dichloromethane, acetonitrile, DMF and DMSO producing intense coloured solutions. The analytical data of all the ruthenium(II) cyclometallated thiosemicarbazone complexes are given in Table S1 and are in good agreement with the molecular structure proposed.

3.1. Characterization

The important IR absorption bands for all the synthesized complexes are given in Table 1. The observed bands may be classified into those originating from the ligands and those arising from the bonds formed between Ru(II) and the coordinating sites. The free ligand displays $\nu_{C=S}$ absorptions at 834 cm^{-1} and was disappeared upon complexation. This observation may be attributed to the enolization of –NH–C=S and subsequent coordination through the deprotonated sulfur [45]. The band observed in the region 1302–1324 cm^{-1} due to ν_{C-S}, further confirms the coordination through the deprotonated sulfur. The ligand showed a strong band at 1611 cm^{-1} which is characteristic of the azomethine group (>C=N). Coordination of the ligand to the ruthenium ion through azomethine nitrogen atom is expected to reduce the electron density in the azomethine link and thus lowers the $\nu_{C=N}$ absorption frequency in the region 1559–1584 cm^{-1} after complexation indicating the coordination of azomethine nitrogen [46] to ruthenium



Scheme 2. Synthesis of Ru(II) cyclometalated thiosemicarbazone complexes.

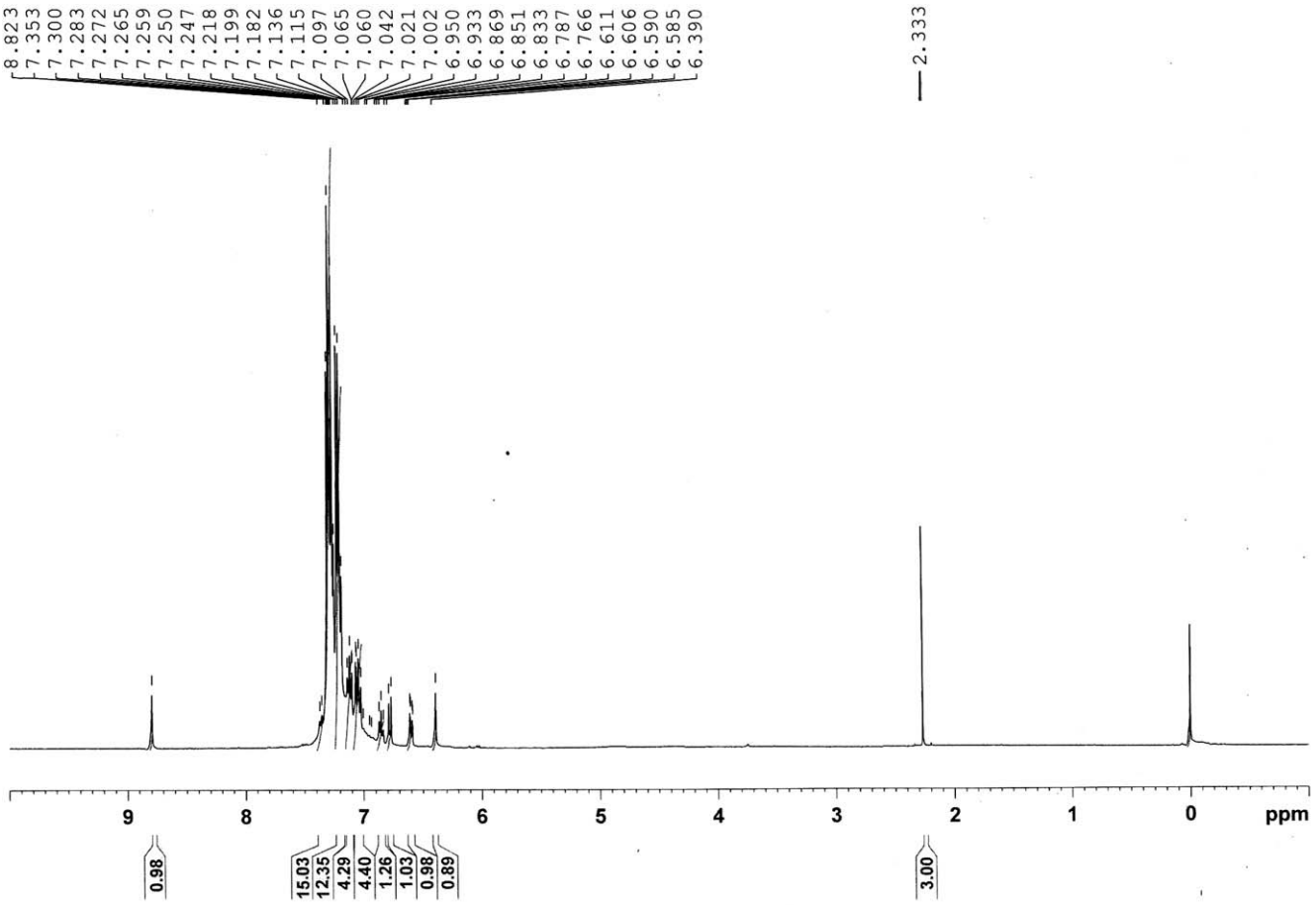


Fig. 1. ^{1}H NMR spectrum of complex **4**.

Table 1
IR data of ruthenium(II) cyclometalated thiosemicarbazone complexes.

Sl. no.	Complexes	$\nu_{(C=O)}$ (cm^{-1})	$\nu_{(C=N)}$ (cm^{-1})	$\nu_{(C-S)}$ (cm^{-1})
1	[Ru(4-HAP-TSC)(CO)($AsPh_3$)$_2$]	1916	1568	1317
2	[Ru(4-HAP-PTSC)(CO)($AsPh_3$)$_2$]	1914	1567	1315
3	[Ru(4-CAP-TSC)(CO)($AsPh_3$)$_2$]	1929	1567	1324
4	[Ru(4-CAP-PTSC)(CO)($AsPh_3$)$_2$]	1921	1564	1309
5	[Ru(4-MAP-TSC)(CO)($AsPh_3$)$_2$]	1916	1566	1312
6	[Ru(4-MAP-PTSC)(CO)($AsPh_3$)$_2$]	1916	1577	1302
7	[Ru(4-NAP-TSC)(CO)($AsPh_3$)$_2$]	1926	1574	1310
8	[Ru(4-NAP-PTSC)(CO)($AsPh_3$)$_2$]	1928	1580	1313
9	[Ru(4-AAP-TSC)(CO)($AsPh_3$)$_2$]	1912	1584	1310
10	[Ru(4-BAP-PTSC)(CO)($AsPh_3$)$_2$]	1926	1559	1311
11	[Ru(4-OHAP-TSC)(CO)($AsPh_3$)$_2$]	1926	1578	1315

ion. For all complexes, a strong band in the region 1912–1929 cm^{-1} is due to the terminally coordinated carbonyl group and is observed at higher frequency than in the precursor complexes. In addition, other characteristic bands due to triphenylarsine are also present at 1480 cm^{-1} in the spectra of all the complexes.

The electronic absorption spectra of all the complexes in chloroform showed three to four bands in the region 242–580 nm (Table 2). All the ruthenium(II) 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_{2g}^6 configuration, and the excited states corresponding to the $t_{2g}^5e_g^1$ 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 the increasing energy. The low energy bands in the visible region are assigned to the charge transfer (CT) transitions. The charge transfer bands observed in all the complexes due to M → L transitions are possible in the visible region in the range of 457–580 nm [47–49]. The other high intensity bands in the region 242–398 nm region were assignable to ligand-centered (LC) transitions and have been designated as π–π^* and n–π^* transitions. The absorption spectrum of a repre-

Table 2
Absorption and luminescence data of ruthenium(II) cyclometalated thiosemicarbazone complexes.

Complexes	λ_{max} (nm)[a]; ε ($dm^3\ mol^{-1}\ cm^{-1}$)	Luminescence data	
		λ_{max} (nm)[b]	ϕ_{em}[c]
1	476(2,030), 307(16,400), 242(45,100)	594	0.0034
2	481(1,990), 339(22,370), 245(44,300)	594	0.0029
3	478(3,090), 309(25,490), 243(46,400)	596	0.0046
4	480(1,390), 331(20,720), 249(45,800)	596	0.0032
5	462(4,150), 344(10,110), 249(46,700)	590	0.0022
6	470(3,920), 328(28,130), 250(44,250)	590	0.0027
7	580(3,520), 398(12,650), 242(49,320)	598	0.0042
8	573(2,690), 398(15,520), 245(48,670)	598	0.0050
9	457(4,140), 349(13,110), 243(42,670)	590	0.0017
10	480(1,380), 331(20,620), 249(45,570)	596	0.0042
11	459(3,320), 303(25,340), 242(44,530)	590	0.0015

[a] Linear absorption maximum in $CHCl_3$ solution.
[b] Room temperature emission maximum in $CHCl_3$ (10^{-4} M) solution (λ_{ex} = 450 nm).
[c] Room temperature emission quantum yield in $CHCl_3$ solution using $[Ru(bpy)_3]^{2+}$ in acetonitrile as standard, with ϕ_{em} = 0.062.

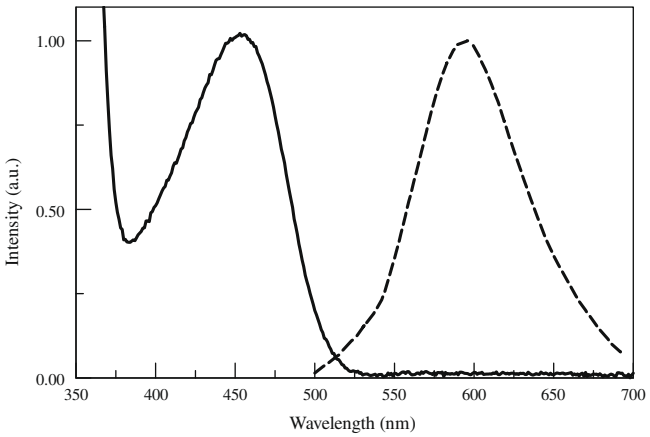


Fig. 2. Normalised lowest energy absorption band (—) and luminescence (- - -) spectra of complex **4** (10^{-4} M) at 298 K in chloroform and deaerated chloroform, respectively, with 450 nm as the excitation wavelength.

Table 3
^{1}H NMR data of ruthenium(II) cyclometalated thiosemicarbazone complexes.

Complexes	^{1}H NMR data (ppm)			
	NH–R′ (s)	Ar–H (m)	CH_3 (s)	R
1	8.8	6.4–7.7	2.1	7.4
2	8.8	6.4–7.9	2.3	7.4
3	8.8	6.4–7.7	2.3	–
4	8.8	6.4–7.8	2.3	–
5	8.8	6.4–7.8	2.2	3.9
6	8.8	6.4–7.8	2.3	3.9
7	8.7	6.4–7.7	2.1	–
8	8.7	6.4–7.7	2.3	–
9	8.7	6.4–7.7	2.2	10.2
10	8.8	6.4–7.7	2.3	–
11	8.8	6.4–7.9	2.2	8.3

sentative complex is shown in Fig. 2. The pattern of the electronic spectra of all the complexes indicated the presence of an octahedral environment around the ruthenium(II) ion, similar to that of other ruthenium(II) octahedral complexes [50,51].

The ^{1}H NMR spectra of all the complexes were recorded to confirm the binding of the thiosemicarbazone ligands to the ruthenium(II) ion (Table 3). Multiplets are observed in the region δ 6.4–7.9 ppm in all the complexes and have been assigned to the aromatic protons of triphenylarsine and thiosemicarbazone ligands [52]. The CH_3 protons of azomethine group appeared as a singlet at δ 2.1–2.3 ppm. All the complexes showed a singlet at δ 8.7–8.8, which has been assigned to NH_2 or NH–R protons. The HN–C=S, protons present in the ligand are absent in the complexes. The ^{1}H NMR spectra of all the complexes are therefore consistent with their composition.

3.2. Luminescence property

All the complexes are diamagnetic with the bivalent nature of ruthenium in low-spin d^6 in these complexes. The light emitting property of all the complexes (10^{-4} M) was investigated in degassed chloroform at room temperature (Table 2) with 450 nm as the excitation wavelength. The emission maxima fall in the range 590–598 nm for the complexes. The luminescence spectrum of a representative complex is shown in Fig. 2. It is likely that the emission originates from the lowest energy metal-to-ligand charge transfer (MLCT) state, probably derived from the excitation involving $d\pi(Ru) \rightarrow \pi^*$ (ligand) transitions, similar to the MLCT observed in Ru(II) bipyridyl complexes [53,54]. All the complexes are weakly emissive at room temperature in chloroform with a quantum yield of 0.001–0.005 (using $[Ru(bpy)_3]^{2+}$ in acetonitrile as standard, with $\phi_{em} = 0.062$ [55]). The present result shows that the cyclometalated Ru(II) carbonyl thiosemicarbazone complexes have low emission intensity/quantum yield, when compared to other ruthenium(II) bipyridyl complexes.

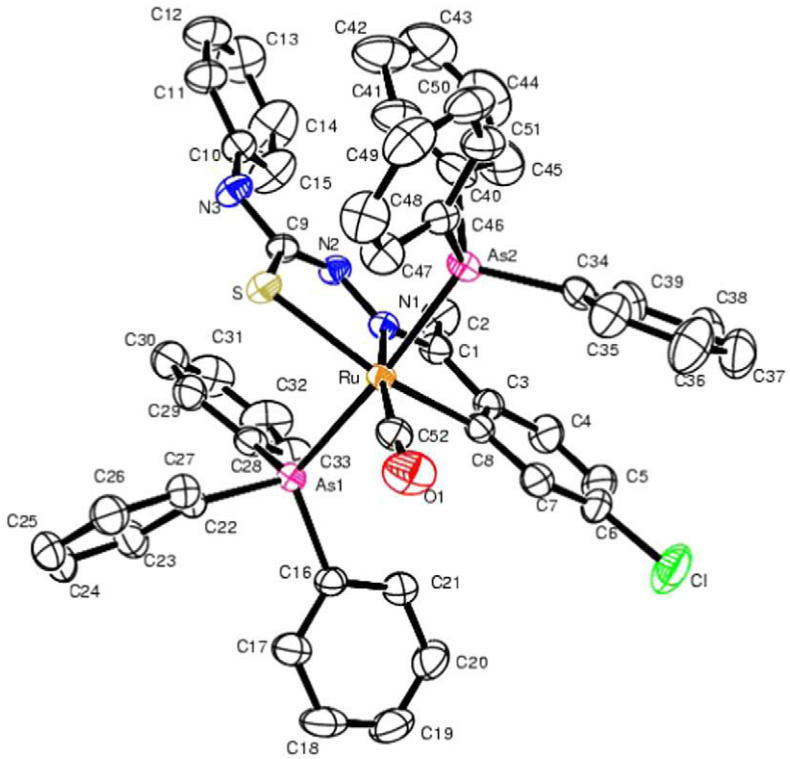


Fig. 3. The ORTEP diagram of the complex $[Ru(4CAP\text{-}PTSC)(CO)(AsPh_3)_2]$ (**4**). For reasons of clarity, hydrogen atoms have been omitted.

3.3. X-ray structure

The molecular structure of one of the complexes [Ru(4CAP-PTSC)(CO)($AsPh_3$)$_2$] (**4**) has been determined by single crystal X-ray diffraction to find out the coordination mode of the acetophenone thiosemicarbazone in the complexes and stereochemistry of the complexes. The ORTEP view of complex **4** is shown in Fig. 3.

Table 4
Crystal data and structure refinement for complex **4**.

Empirical formula	$C_{52}H_{42}As_2ClN_3ORuS$
Formula weight	1043.31
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, *P*21/*n*
Unit cell dimensions	
a (Å)	12.4945(4)
b (Å)	28.4182(11)
c (Å)	13.7331(5)
α (°)	90
β (°)	113.174(2)
γ (°)	90
Volume (Å^3)	4482.8(3)
Z, calculated density (Mg/m^3)	4, 1.546
Absorption coefficient (mm^{-1})	1.964
F(0 0 0)	2104
Crystal size (mm)	0.30 × 0.20 × 0.20
Theta range for data collection (°)	1.43 to 31.15
Limiting indices	$-18 \le h \le 17$, $-40 \le k \le 38$, $-19 \le l \le 16$
Reflections collected/unique [$R_{(int)}$]	59 554/14 141 [0.0381]
Completeness to theta = 25.00	100.0%
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	0.68 and 0.55
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	14141/1/556
Goodness-of-fit (GOF) on F^2	1.067
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0387, wR_2 = 0.0893
R indices (all data)	R_1 = 0.0754, wR_2 = 0.1099
Extinction coefficient	0.00158(12)
Largest difference peak and hole (e A^{-3})	1.071 and −0.519

Table 5
Selected bond lengths (Å) and angles (°) for complex **4**.

Bond lengths (Å)		Bond angles (°)	
Ru–As	1 2.4695(3)	S–Ru–As	1 87.191(18)
Ru–As	2 2.4379(3)	S–Ru–As2	88.078(19)
Ru–C8	2.061(3)	S–Ru–C8	157.42(7)
Ru–N1	2.0732(19)	S–Ru–N1	79.05(6)
Ru–S	2.4641(7)	S–Ru–C52	110.30(9)
Ru–C52	1.838(3)	As1–Ru–As2	175.180(13)
As1–C16	1.953(3)	As1–Ru–C8	93.59(6)
As1–C22	1.942(3)	As1–Ru–N1	88.81(5)
As1–C28	1.944(3)	As1–Ru–C52	92.16(8)
As2–C34	1.944(3)	As2–Ru–C8	90.43(6)
As2–C40	1.947(3)	As2–Ru–N1	89.39(5)
As2–C46	1.945(3)	As2–Ru–C52	90.34(8)
C1–C3	1.443(4)	C8–Ru–N1	78.41(9)
C3–C8	1.424(3)	C8–Ru–C52	92.23(11)
C6–Cl	1.739(3)	N1–Ru–C52	170.64(11)
C9–S	1.755(2)	Ru–S–C9	94.81(9)
C52–O1	1.146(3)	Ru–N1–N2	125.34(15)
N1–N2	1.377(3)	Ru–N1–C1	118.15(18)
N1–C1	1.301(3)	N2–N1–C1	116.5(2)
N2–C9	1.292(3)	N1–N2–C9	114.0(2)
N3–C9	1.363(3)	Ru–C52–O1	174.6(3)
		N1–C1–C3	114.3(2)
		S–C9–N2	126.6(2)
		S–C9–N3	115.3(2)
		N2–C9–N3	118.1(2)

ESD in parenthesis.

The summary of the data collection and refinement parameters are given in Table 4 where as selected bond lengths and bond angles are given in Table 5. The complex crystallizes in *P*21/*n* space group. The thiosemicarbazone ligand coordinates in a terdentate manner to the ruthenium(II) ion via thiolate sulfur, azomethine nitrogen and one ortho carbon of the phenyl ring in the acetophenone fragment in addition to two $AsPh_3$ and one carbonyl ligands. Ruthenium is therefore sitting in a C_2NSAs_2 coordination environment, which is distorted octahedral in nature as reflected in all the bond parameters around ruthenium. The bite angles around Ru(II) are S–Ru–N(1) = 79.05(6)°, C(8)–Ru–N(1)= 78.41(9)°, C(8)–Ru–C(52) = 92.23(11)° and S–Ru–C(52) = 110.30(9)°, and bond lengths of 2.061(3) Å Ru–C(8), 2.0732(19) Å Ru–N(1), 2.4641(7) Å Ru–S and 1.838(3) Å Ru–C(52). The thiosemicarbazone ligand binds the metal center at C, N and S forming two five-membered chelate rings. The coordinated acetophenone thiosemicarbazone ligand and carbonyl ligand constitute one equatorial plane with the metal at the center where the carbonyl ligand is trans to the azomethine (>C=N) nitrogen. The two $AsPh_3$ ligands are mutually trans to each other. Usually the $AsPh_3$ ligands prefer to occupy mutually cis positions for better π-interaction [56]. However, in these complexes the presence of CO, which is stronger π-acidic ligand, has probably forced the bulky $AsPh_3$ to take up mutually trans position for steric reasons.

3.4. Electrochemical study

Electrochemical study was carried out for all the free ligands and the Ru(II) carbonyl thiosemicarbazone complexes in acetonitrile solution under N_2 atmosphere in the potential range of 0 to −1.5 V. The supporting electrolyte used was 0.05 M tetrabutyl ammonium perchlorate (TBAP) and the concentration of the complex was 10^{-3} M. We have not observed any redox waves within the potential limits of 0 to −1.5 V for free ligands and whatever the reductive responses observed within this potential limits were due to metal center only. All the complexes display a quasi reversible reduction at a scan rate of 100 mV s^{-1} and the one electron nature of reduction has been confirmed by comparing its current height with that of a standard ferrocene–ferrocenium couple under identical experimental conditions. The potentials are summarized in Table 6 and cyclic voltammogram of complex **4** is shown in Fig. 4. All the complexes show well-defined waves, with $E_{1/2}$ in the range of −0.82 to −0.86 V. The redox processes are quasi-reversible in nature, characterized by a rather large peak-to-peak separation (ΔE_p) of 100–140 mV [57]. The redox potentials are virtually independent of scan rates, indicating quasi-reversibility.

The potentials of reduction (Ru^{II}/Ru^{I}) have been found to be sensitive to the nature of the substituent (R) in the acetophenone

Table 6
Electrochemical data of ruthenium(II) cyclometallated thiosemicarbazone complexes.

Complexes	(RuII/RuI)			
	E_{pc} (V)	E_{pa} (V)	$E_{1/2}$ (V)	ΔE_p (mV)
1	−0.91	−0.77	−0.84	140
2	−0.89	−0.79	−0.84	100
3	−0.93	−0.81	−0.87	120
4	−0.94	−0.80	−0.87	140
5	−0.91	−0.79	−0.85	120
6	−0.90	−0.80	−0.85	100
7	−0.95	−0.83	−0.89	120
8	−0.96	−0.83	−0.89	130
9	−0.89	−0.77	−0.83	120
10	−0.95	−0.81	−0.88	140
11	−0.90	−0.78	−0.84	120

Supporting electrolyte: [Bu_4N](ClO_4) (0.05 M); solvent = acetonitrile; all potentials referenced to SCE; $E_{1/2} = 0.5(E_{pc} + E_{pa})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; $\Delta E_p = (E_{pc} + E_{pa})$; scan rate: 100 mV s^{-1}.

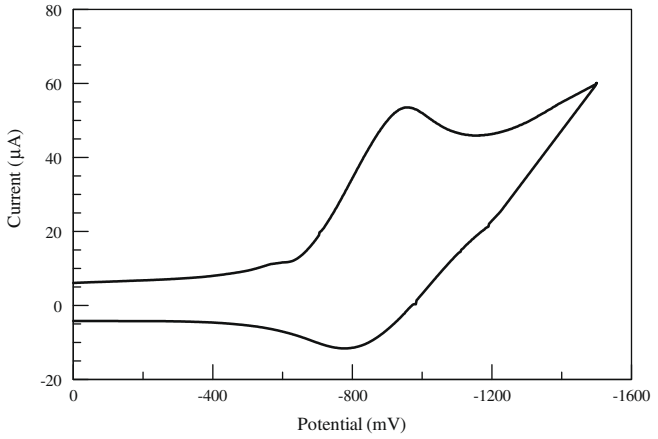


Fig. 4. Cyclic voltammogram of complex **4**. Supporting electrolyte: $[Bu_4N](ClO_4)$ (0.05 M); solvent = acetonitrile; scan rate: 100 mV s^{-1}.

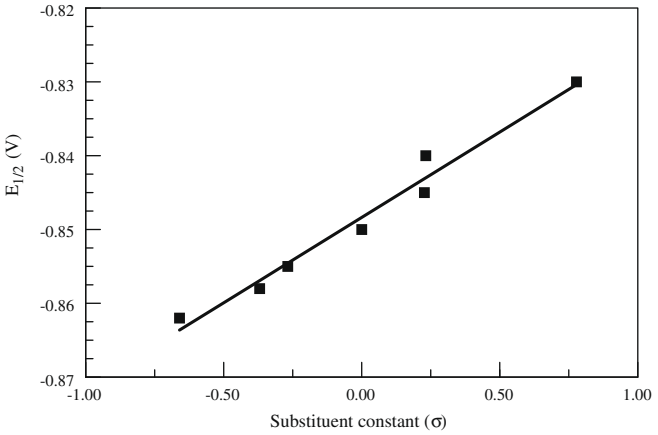


Fig. 5. Least square plot of $E_{1/2}$ values reduction (Ru^{II}/Ru^{I}) potentials vs. σ.

thiosemicarbazide ligand which perturbs the metal reduction. The potential increases linearly with increasing electron-withdrawing character of R. The half wave potentials ($E_{1/2}$) moves to negative value with electron donating substituent(s) in the aryl ring and reverse movement is observed for electron-withdrawing group. The plot of formal potentials $E_{1/2}$ versus σ (where σ is Hammett para substituent constant of R [58]; R: $NH_2 = -0.66$, $OH = -0.37$, $OCH_3 = -0.27$, $CH_3 = -0.17$, $H = 0.00$, $Cl = +0.23$, $Br = +0.23$, $NO_2 = 0.78$) is found to be linear for the reduction couples (Fig. 5).

The slope of the line which is known as the reaction constant ρ [59] is a measure of the sensitivity of $E_{1/2}$ with the substituent (R) for the Ru^{II}/Ru^{I} couple. This shows that the nature of the para substituent R on the acetophenone thiosemicarbazide ligands can still influence the metal-centered potentials in a predictable manner. Hence, it is inferred from the electrochemical data that the present ligand system is ideally suitable for stabilizing the higher oxidation state of ruthenium ion and the electron transfer reactions take place without gross changes in the stereochemistry of the complexes [60].

4. Conclusion

A series of carbonyl ruthenium(II) cyclometalated complexes containing 4′-substituted acetophenone thiosemicarbazone of the general formula $[Ru(L)(CO)(AsPh_3)_2]$ (where L = 4′-substituted acetophenone thiosemicarbazone ligands behaving as dianionic terdentate C, N and S donors) have been synthesized from the reactions of $[RuHCl(CO)(AsPh_3)_3]$ with 4′-substituted acetophenone thiosemicarbazone ligand. The characterization of the complexes were accomplished by analytical and spectral (IR, UV–Vis, ^1H NMR) methods. X-ray diffraction study of complex **4** confirms the C, N and S coordination mode of acetophenone thiosemicarbazone ligands and reveals the presence of a distorted octahedral geometry around Ru(II) ion. The present result shows that the terdentate C, N and S coordination mode of acetophenone thiosemicarbazone to ruthenium(II) ion via C–H activation. All the complexes are luminescent but have low quantum yield, when compared to other ruthenium(II) bipyridyl complexes. All the complexes show one electron nature of reduction and the electronic effects of the substituents (R) have direct influence on the redox potential.

Acknowledgements

We sincerely thank Council of Scientific and Industrial Research (CSIR), New Delhi for financial support [Scheme. No. 10-2(5)/426 2007(i)-E.U.II; 01(2156)/07/EMR-II] and for Junior Research Fellowship to R.N.P. We express sincere thanks to SAIF, Indian Institute of Technology – Madras, for single crystal X-ray crystallographic studies.

Appendix A. Supplementary material

CCDC 703225 contains the supplementary crystallographic data for complex **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.09.010.

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