

# Synthesis and Characterization of Molecular Hetero Tri Metallic Fe(II) – Ru(III)-Fe(II) Complexes with PPh<sub>3</sub>: A Review on Attempting it to Synthesis of New Molecular Materials with Applications in Carcinogenic Drug & Superamolecular Material Research

Sivahari R., Syed Shabudeen P.S.

Department of Chemistry, Kumaraguru College of Technology, Coimbatore – 49  
[shabu\\_cbe@yahoo.com](mailto:shabu_cbe@yahoo.com)

## Abstract

A special emphasis is devoted to initiating, developing and combining new physical properties within the heterometallic systems enclosing cores of three different spin-carriers. The rational inclusion of 3d and/or 4f cations within the same molecular entity could generate new categories of heterotrimetallic complexes which possesses the special properties on photo magnets, luminescent or chiral compounds or with combined properties, namely magneto-luminescence or magneto-chirality. These new molecular materials open large perspectives to developing molecular “prototypes” for revolutionary optical, high-storage devices or in quantum computing. In this research the synthesis and characterization of Heterotrimetallic complexes of the type  $[RuCl(PPh_3)(L_2)]$  (where L=bidentate Schiff base ligand of ferrocenylthiosemicarbazone) was attempted by reacting  $[RuCl(PPh_3)_3]$  with bidentate Schiff base ligand of ferrocenylthiosemicarbazide. During this synthesis the complexes obtained have been characterized by Elemental analysis, IR and Electronic spectroscopy. This confirms Heterotrimetallic Fe(II)-Ru(III)-Fe(II) complex with PPh<sub>3</sub>. This complex finds its use as precursor for some carcinogenic drug and it paves the way to the area of superamolecular material research.

**Keywords:** Ru (III) complexes, IR spectroscopy, Heterotrimetallic compound

## 1. Introduction

In this work it is interested to explore the chemistry of multinuclear transition metal complexes depending on the nature of the bis (alkynyl) ferrocene transition metal fragments. In this effort, the ferrocenylthiosemicarbazone Ru(III) complexes using reactions of thiosemicarbazones of monoacetyl ferrocenes with  $[RuCl_3(PPh_3)_3]$  is attempted. In this work the basic components for the construction of multimetallic transition metal complexes were used and the metal center Fe are connected by different organic nitrogen containing  $\sigma$ -donor bridging molecules such as  $\pi$ -conjugated organonitrils, non linear  $\pi$  conjugated polypyridyl or aromatic  $\pi$ -conjugated nitrogen donor bridges. In co-ordination Chemistry, the  $\pi$ -conjugated nitrogen,  $\sigma$ -donor links are generally referred as complexing group. That can either donate or accept electrons. These links are  $\sigma$ -donor and  $\pi$  acceptor ligands. The lone pair which is available at the nitrogen atom forms as  $\sigma$  donating bond, while the  $\pi$  system can take part in the back-bonding [8]. These class of ligands stabilize soft metals, especially transition metal ions in low

oxidation states. The linking groups used in the coordination site of the bridging ligand can influence the spectroscopic data and redox properties of the metal based units and the chemical nature of the organic bridges determine the electronic communication between the donor and acceptor components of this coordination complex. They are useful in catalytic activity of organic transformations[9]. The metal – polypyridyl complexes are of the interest, because of their use in solar energy conversions and molecular devices. [9]There is an enormous scope for the studies on synthesis, reaction chemistry, solid-state structure and electrochemical studies of this complex because it might serve as new materials and it may play an important role in many industrial processes, such as homogenous and heterogeneous catalysis. Similarly these heterobimetallic compounds has found application in variety of fields such as catalysis, drug designing, environmental remediation *etc.*

In most of these studies Ruthenium which exhibits a wide range of oxidation states from +8 to -2 is used as metal and thiosemicarbazones usually to be act as chelating ligands as it enhances antibacterial, anti carcinogenic, cytotoxic activities. Very few studies have been done with heterotrimetallic complexes. The present work is focused on the synthesis and characterization of the ferrocenylthiosemicarbazone Ru(III) complexes, using the reactions of thiosemicarbazones of monoacetyl ferrocenes with  $[\text{RuCl}_3(\text{PPh}_3)_3]$ .

## 2. Methodology

The reagents used for the study were of AR grade. Ruthenium trichloridetrihydrate ( $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ ), procured and it is used in the purified form. The purified solvents by standard procedure<sup>1</sup> were analyzed for the elements C, H and N by Vario EL III elemental analyzer. The IR Spectra of the ligands and of their complexes have been recorded in KBr pellets with a Shimadzu/Nicolet instrument in the  $4000\text{-}400\text{ cm}^{-1}$  range. Electronic spectra of the complex have been recorded in  $\text{CH}_2\text{Cl}_2$  using a **Systronics 119 spectrophotometer** in the 800- 200 nm range. The Melting points were recorded on Loba India melting point apparatus.

### 2.1. Preparation of Acetyl Ferrocene

The Acetyl ferrocene was prepared according to the standard procedure (2), A solution of 5gm (0.027 mol) of ferrocene and 5.5 gm (0.054 mol) of acetic anhydride in  $45\text{ cm}^3$  of  $\text{CH}_2\text{Cl}_2$  is stirred well and cooled in an ice bath, and saturated with gaseous Borontrifluoride (copious evolution of white fumes). An amber coloured solution was obtained and it soon becomes deep purple coloured solution. After stirring for 0.5 h, the reaction mixture was allowed to attain room temperature and kept intact for 4 h. Excess of sodium acetate solution was then added with stirring, whereby two layers were separated. The dichloromethane layer was washed with water, followed by the saturated solution sodium bicarbonate and dried over magnesium sulphate. After filtration the solvent was removed and the residue recrystallized from hexane to give 3 gm (60%) of orange needles of acetylferrocene whose Melting point is determined and it is found to be  $85 - 86^\circ\text{C}$ .

### 2.2. Preparation of Bidentate Schiff Base Ligands

Schiff bases of the following general structure was prepared and reacted with starting complexes to yield new complexes. The names of the abbreviations of the Schiff base are given below.(2.3,2.4)

**Table 1. Nomenclature**

<b>R</b>	<b>Name of the Ligand</b>	<b>Abbreviations</b>
H	1- Acetylferrocene thiosemicarbozone	HAFTSC
C <sub>6</sub> H <sub>5</sub>	1- Acetylferrocene-4-phenylthiosemicarbozone	HAFPTSC

### 2.3. Preparation of 1- Acetylferrocene thiosemicarbozone (HAFTSC)

HAFTSC was prepared by refluxing a mixture of acetylferrocene and thiosemicarbozone in a 1:1 molar ratio in anhydrous ethanol for 5 H. A few drops of glacial acetic acid were then added and the contents were again refluxed for 1H. The resulting content was cooled and poured into ice to obtain a granular product. This is filtered and recrystallized from absolute ethanol and finally dried under vacuum. The Melting Point of HAFTSE was determined and it was 130 °C.with an yield of 75%.

### 2.4. Preparation of 1- Acetylferrocene -4 Phenylthiosemicarbozone(HAFPTSC)

HAFPTSC was prepared by refluxing a mixture of acetylferrocene and 4-phenyl thiosemicarbozone in a 1:1 molar ratio in anhydrous ethanol for 5 h. A few drops of glacial acetic acid were then added and content were again refluxed for 1 hour. The resulting content was cooled and poured into ice. The granular product amount of petroleum ether (60-80 °C).The resulting complex was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> or petroleum ether (60-80 °C) and dried under vacuum. The Melting Point is175°C and its Yield is 68 %.

### 2.5. Preparation of trichlorotris (triphenylphosphine) ruthenium(III) [RuCl<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>]

Ruthenium trichloride trihydrate (0.2 g) was taken in ethanol (20 cm<sup>3</sup>) and concentrated Hydrochloric acid (2cm<sup>3</sup>) was added to this. To the above solution triphenylphosphine (0.8 g) was added. The solution was heated under reflux for about 5 minutes and then cooled. The resulting reddish brown compound (6) was separated, washed with ether and dried under vacuum and its melting Point is158°C

### 2.6. Preparation of new Ruthenium(III) complexes:- [RuCl(PPh<sub>3</sub>)(FTSC)<sub>2</sub>]

The Schiff solution was added with HAFPTSC 0.060g (0.020mmol) and made a solution of [RuCl<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>] (0.095g; 0.1 mmol) in dry benzene (20 cm<sup>3</sup>). The above mixture was refluxed for 6 h. A brown colour solution obtained was concentrated. The complex was separated by the addition of a small amount of petroleum ether

at (60-80 °C). The resulting complex was re-crystallized from CH<sub>2</sub>Cl<sub>2</sub>/ petroleum ether (60-80 °C) and dried under vacuum. The Colour is brown and its melting point is > 300°C and its yield is 70 %.

### 2.7. [RuCl(PPh<sub>3</sub>)(FPTSC)<sub>2</sub>]

The Schiff base HAFPTSC (0.064 g; 0.2 mmol) was added to the solution of [RuCl<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>](0.095 g; 0.1 mmol) in dry benzene (20 cm<sup>3</sup>). The above mixture is refluxed for six hours. A black colour solution obtained was concentrated to about 3 cm<sup>3</sup>. The complex was separated by the addition of a small complex and new band in the region 722–739 cm<sup>-1</sup> appeared in all the new trimetallic complex[1]. This indicate that the other coordination is through the Sulphur atom of the ligand takes place after the enolisation of NHC=S group of the ligand and coordination through the S atom after de-protonation. Characteristic bands due to triphenylphosphine are also present in the expected region it is shown in Table 2 and 3.

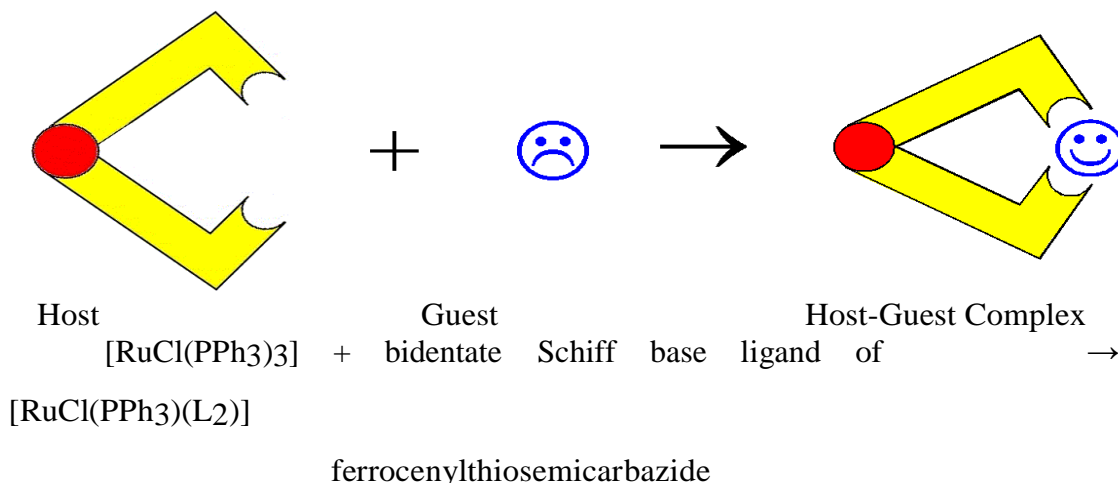
**Table 2. Analytical Data of Ru(II) Schiff Base Complexes**

Complex	Colour	Melting point	Elemental Analyses calculated (found)			
			C(%)	H(%)	N(%)	S(%)
[RuCl(PPh <sub>3</sub> )(FTSC) <sub>2</sub> ]	Brown	>300	52.87	4.34	8.41	6.42
[RuCl(PPh <sub>3</sub> )(FPTSC) <sub>2</sub> ]	Brown	>300	58.39	4.46	7.30	5.57

**Table-3. IR Spectral Data of Ru(III) Schiff Base Complexes**

Complex	$\nu_{C=N}$ (cm <sup>-1</sup> )	$\nu_{C=S}$ (cm <sup>-1</sup> )	$\nu_{C=N} + \nu_{C=C}$	Bands for PPh <sub>3</sub> (cm <sup>-1</sup> )
HAFTC	1651	821	-	-
HAFPTSC	1650	815	-	-
[RuClPPh <sub>3</sub> (FTSC) <sub>2</sub> ]	1631	722	1540	1433,1093,693
[RuClPPh <sub>3</sub> (FPTSC) <sub>2</sub> ]	1620	739	1541	1434,1094,695

Based on analytical and spectral (IR and UV) an octahedral structure was tentatively proposed for all the new trimetallic complexes. Thus heterotrimetallic complexes of the type [RuCl(PPh<sub>3</sub>)(L<sub>2</sub>)](where L = bidentate Schiff base ligand of ferrocenylthiosemi carbazone) can be synthesized by reacting [RuCl(PPh<sub>3</sub>)<sub>3</sub>] with bidentate Schiff base ligand of ferrocenylthiosemicarbazide.



This new tri metallic complex could be investigated as precursor for organometallic ruthenium (II) complexes of general formula  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PP})\text{L}]\text{CF}_3\text{SO}_3$ ].

### 3. Results and Discussions

Inhibition of the growth of LoVo human colon adenocarcinoma and MiaPaCa pancreatic cancer cell lines by two new organometallic ruthenium (II) complexes of general formula  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PP})\text{L}]\text{CF}_3\text{SO}_3$  ] where PP is 1,2 bis (diphenyl phosphino)ethane and L is 1,3,5-triazine (Tzn) 1 or PP is 2xtriphenyl phosphine and L is pyridine 9Pyd) has been investigated and reported. (10) In the report it is stated the above two organic metallic Ru(II) complexes involve the following mechanisms of interaction with plasmid pBR 322DNA while the mode of binding of compound 1 could be intercalation between base pairs of DNA, compound 2 might be involved in a covalent bond formation within from the purine base.

Ruthenium Vs Osmium complexes as catalyst for Atom Transfer Radical Addition Reaction [11] are reported. The catalytic activity of complexes  $[\text{Cp}^*\text{OsBr}_2(\text{PPh}_3)]$  and  $[\text{Cp}^*\text{RuCl}_2(\text{PPh}_3)]$  in conjugation with Mg has been evaluated for atom transfer radical addition(ATRA) reactions and for atom transfer radical cyclization (ATRC) reactions.

The rational inclusion of 3d and/or 4f cations within the same molecular entity could generate new categories of heterotrimetallic complexes which possess the special properties on photo magnets, luminescent or chiral compounds or with combined properties, namely magneto-luminescence or magneto-chirality. These new molecular materials open large perspectives to developing molecular “prototypes” for revolutionary optical, high-storage devices or in quantum computing as well as in drug discovery.

## References

- [1] A.I. Vogel "Textbook of practical organic chemistry" 5<sup>th</sup> Edition, Longman, London, (1989).
- [2] C.R. Hauser and J.K. Lindsay, J. Am. Chem. Soc., 22, 482 (1957).
- [3] B.S. Garg and L. Kapur, Inorg. Chem. Acta, 170, 177 (1990).
- [4] B.S. Garg and L. Kapur, Inorg. Chem. Acta, 173, 223 (1990).
- [5] Z. Xiaoxim, L. Youngmin, N. Fajun and M. Youngxiang, Polyhedron, 11, 44 ,(1990).
- [6] J.Chatt,G.J.Leigh, D.M.P. Mongos and R.J. Paske, J. Chem. Soc. (A), 2636 (1968).
- [7] R.K. Poddar, I.P. Khulla and U. Agarwala, Inorg. Nucl. Chem. Lett., 10, 221, (1974).
- [8] M. Pizzotti, R. Ugo, D. Roberto, S. Bruni, Organometallic 21 5830,(2002).
- [9] M.R. Waterland, T. J. Simpson, K. C. Gordon, A. K. Burrell, J. Chem. Soc. Dalton Trans. (1998) 185. (b) G.K Petra, I. Goldberg, Eur. J. Inorg. Chem 969. (2003).
- [10] M.Helena Garcia et al., Inhibition of cancer cell growth by Ruthenium (II)cyclo Rentadienyl derivative complex with hetero aromatic ligands.
- [11] A Mariano Fernandez –zumel et al, European journal of inorganic chemistry, Aug, 23,P-3596-3601,(2010).