

**CHEMISTRY OF ALKYNYL AND DIPYRROMETHANE
DERIVATIVES OF FERROCENE AND THE COBALT
SANDWICH COMPOUND (η^5 -Cp)Co(η^4 -C₄Ph₄)**

by

KARUNESH KESHAV

Department of Chemistry

Submitted

in fulfillment of the requirement

of the degree of

Doctor of Philosophy

to the



Indian Institute of Technology Delhi, India

April, 2013

Dedicated

to

My parents

CERTIFICATE

This is to certify that the thesis entitled “**Chemistry of alkynyl and dipyrromethane derivatives of ferrocene and the cobalt sandwich compound $[\eta^5\text{-CpCo}(\eta^4\text{-C}_4\text{Ph}_4)]$** ”, being submitted by Mr. Karunesh Keshav to Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by him. Mr. Karunesh Keshav has worked under my supervision and guidance and has fulfilled all the requirements for the submission of a Ph.D. thesis, which to my knowledge has reached the requisite standard and is worthy of consideration for the award of Ph.D. degree.

The work embodied in this thesis has not been submitted, in part or full, to other University or Institute for the award of any degree or diploma.

Dr. Anil J. Elias

Thesis Supervisor

Professor

Department of Chemistry

Indian Institute of Technology Delhi

Hauz Khas, New Delhi-110016, India.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor **Prof. Anil J. Elias**, whose expertise, understanding and patience, added considerably to my research experience. I appreciate his vast knowledge and skill in many areas (synthesis, characterization and mechanism study) and his assistance in writing scientific papers. It was through his persistence, understanding and encouragement that I completed my doctoral degree. I would also like to thank him for being an open person to new ideas, and for encouraging and helping me to shape my research interests and ideas.

I express my gratitude to members of my student research committee, Prof. A. Ramanan, Dr. S. Nagendran and Dr. J. Jacob for their help and suggestions.

I thank the present and previous heads of the department of chemistry for providing the necessary departmental facilities to carry out my research work.

I express my gratitude to my seniors, Dr. Senthil, Dr. Behera and Dr. Nem for helping me in the initial stage of learning laboratory techniques. I thank my current labmates for providing a friendly atmosphere in the laboratory and for their assistance.

Finally, I wish to thank CSIR, India for giving me JRF and SRF. I also thank DST, CSIR and IIT Delhi for providing financial assistance for carrying out this research work.

Karunesh Keshav

ABSTRACT

The thesis entitled “Chemistry of alkynyl and dipyrromethane derivatives of ferrocene and the cobalt sandwich compound $(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$.” presents the results obtained from the research work carried out on the synthesis, characterization and exploration of the chemistry of alkynyl derived ferrocene and $(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$ and the dipyrromethane derivative of $(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$. The accomplished research work has been divided into six chapters.

Chapter 1 is a general introduction providing the back ground and literature required to follow up the actual experiments carried out and presented in the subsequent chapters. As the first part of the work described in the thesis is centered on cyclophosphazenes, salient features of cyclophosphazenes have been discussed with relevant literature background. This is followed by a general introduction to organometallic sandwich compounds. An account of the chemistry of $(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$ known so far is described in particular.

Ethynyl derived organometallic sandwich compounds are interesting structural motifs for synthesizing a variety of carbon-rich organometallic compounds such as dehydroannulenes, metallocene derived polymers, metallocenophanes and sandwich based catalysts. Salient aspects of the literature known of ethynyl metallocenes with emphasis on ethynyl ferrocene is therefore consolidated in this chapter. Dipyrromethane derived compounds have gained considerable attention in recent years because of their potential application in the design of molecular sensors, magnetic and nonlinear optical materials, coordination polymers and as ligands in homogeneous catalysis. As the work described in the thesis also encompass the chemistry of dipyrromethanes and porphyrins, the relevant literature needed to introduce the chemistry of these compounds has been reviewed. The chapter ends with scope of the present work carried out and reported in the thesis.

Chapter 2 describes general experimental procedures adopted in the synthesis of new compounds and details of characterization techniques utilized. Specific synthetic details of some of the starting materials used in the work described in the thesis are also presented.

Chapter 3 begins with the synthesis of ethynylferrocene substituted cyclophosphazenes. The reactions of lithiated ethynylferrocene with hexafluoro and hexachlorocyclotriphosphazenes were carried out at -78 °C with the formation of monoethynylferrocene and geminal bisethynylferrocene derived fluoro- and chlorophosphazenes. The second part of this chapter deals with the reactions of these ethynylferrocene substituted phosphazenes with CpCo(COD) and benzyl azide. The ethynylferrocene substituted fluorotriphosphazene with CpCoCOD under toluene reflux conditions gave both *cis* and *trans* products, while reaction of ethynylferrocene substituted chlorotriphosphazene with CpCoCOD under the same reaction conditions gave only the *trans* substituted product. In order to observe the reactivity of these ethynylferrocene substituted phosphazene towards organic azide, mono(ethynylferrocenyl) cyclofluorophosphazene was refluxed with benzyl azide in toluene which gave two different positional isomers of the 1, 2, 3-triazoles (1-PhCH₂, 4-Fc, 5-P₃N₃F₅)C₂N₃ and (1-PhCH₂, 4-P₃N₃F₅, 5-Fc)C₂N₃. The triazole compounds having the benzyl group in the vicinity of ferrocenyl unit was obtained as the major product. A similar reaction of the geminal bis(ethynylferrocene)-substituted chlorophosphazene with benzyl azide gave five different products having triazole units which were carefully separated, purified, and structurally characterized. We were keen to explore the possibility of using the phosphazene and ferrocene-derived 1, 2, 3-triazoles as ligands in coordination chemistry. A 2:1 molar reaction of one of the fluorophosphazene-derived triazoles with PdCl₂(PhCN)₂ resulted in the exclusive formation of a square-planar palladium complex, trans-[(1-PhCH₂-4-P₃N₃F₅-5-Fc)C₂N₃]₂PdCl₂ which was structurally characterized.

Chapter 4 deals with the synthesis of sterically hindered porphyrins substituted with sandwich units of $\eta^5\text{-CpCo}(\eta^4\text{-C}_4\text{Ph}_4)$ at their meso positions. Reaction of the carboxaldehyde derivative $[(\eta^5\text{-C}_5\text{H}_4(\text{CHO}))\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)]$ with excess of pyrrole in the presence of trifluoroacetic acid gave the dipyrromethane $\{\eta^5\text{-}[(\text{C}_4\text{H}_4\text{N})_2\text{CH}]\text{C}_5\text{H}_4\}\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$. Reaction of this dipyrromethane with dimethylformamide under Vilsmeier condition yielded the 1, 9-bisformyldipyrromethane derivative. Metal templated condensation of 1, 9-bisformyldipyrromethane derived $\eta^5\text{-CpCo}(\eta^4\text{-C}_4\text{Ph}_4)$ with ferrocenyl and aryl dipyrromethanes in the presence of $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$, KOH and ethanol as a solvent under reflux condition gave the *trans*-AB porphyrins having cobalt and iron sandwich units trans to each other. Reactions of the aldehyde $[(\eta^5\text{-C}_5\text{H}_4(\text{CHO}))\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)]$ with sterically hindered dipyrromethane derivatives under acid mediated condensation gave *trans*-A₂B₂ type porphyrins [where A = $\eta^5\text{-CpCo}(\eta^4\text{-C}_4\text{Ph}_4)$ and B = C₆F₅, mesityl] while with sterically unhindered dipyrromethanes, AB₃ and *cis*-A₂B₂ type porphyrins (where A = $\eta^5\text{-CpCo}(\eta^4\text{-C}_4\text{Ph}_4)$ and B = [(4-*t*-butyl)C₆H₄]) were found to form as a result of extensive rearrangement.

Chapter 5 describes with synthesis of metal sandwich derived 2-pyridones. Reaction of ferrocenyl alkynyl carboxaldehyde with *p*-anisidine forms a Schiff's base which was further reacted with dialkyl malonate under basic conditions to give the metal sandwich derived 2-pyridone. Here 1, 4- addition reaction of dialkyl sodiomalonate to alkynyl imine generates metalloallenamine which in turn isomerizes into metalloenamine and finally undergoes cyclization to give the 2-pyridone. A similar reaction of the alkynyl carboxaldehyde of $(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$ gave the first example of a $(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$ substituted 2-pyridone which was also characterized by HRMS and NMR techniques.

Chapter 6 gives the overall conclusions of the entire work carried out in the present study.

TABLE OF CONTENTS

	Page
CERTIFICATE	I
ACKNOWLEDGEMENTS	II
ABSTARCT	III
TABLE OF CONTENTS	VI
LIST OF FIGURES	XI
LIST OF TABLES	XVII
ABBREVIATIONS	XX
CHAPTER 1 Introduction	1
1.1.1. Halogenated cyclic phosphazenes	1
1.1.2. Chloro vs fluorocyclophosphazenes	8
1.1.3. Synthesis, spectra and structure of fluorophosphazenes	9
1.1.4. Alkynyl derived cyclophosphazenes	12
1.2.1. Metal sandwich compounds	16
1.2.2. Physical properties and structural aspects of metal sandwich complexes	21
1.2.3. General applications of metal sandwich compounds	23
1.2.4. Reactions of metal sandwich compounds	25
1.2.5. Sandwich compounds having bulky substituted cyclopentadienyl rings	25

1.2.6.	Metallocene bound phosphazenes	27
1.2.7.	Cobalt based stable sandwich compounds	30
1.2.8.	Cobalt sandwich compounds of the type (η^5 -Cp)Co(η^4 -C ₄ Ph ₄) with varying substituents on the cyclobutadiene ring	36
1.2.9.	RCp)Co(η^4 -C ₄ Ph ₄) with varying substituents on the cyclopentadienyl ring	42
1.2.10.	Applications of cobalt based sandwich compounds	48
1.3.1.	Ethynyl derived organometallic sandwich and half sandwich compounds	49
1.3.2.	Synthesis of ethynyl derived sandwich compounds	50
1.3.3.	Synthesis of ethynyl bounded half sandwich compounds	53
1.3.4.	Reactions of ethynylferrocene	56
1.3.5.	Reactions of 1, 2 diethynyl ferrocene	57
1.3.6.	Reactions of 1, 1' diethynyl ferrocene	58
1.3.7.	Reactions of ethynyl substituted (η^5 -Cp)Co(η^4 -C ₄ Ph ₄)	59
1.4.1.	Dipyrromethane substituted metal sandwich compounds	60
1.4.2.	Boron dipyrromethane compounds	61
1.4.3.	Synthesis of metallocene substituted dipyrromethane and BODIPY compounds	62

	1.4.4.	Peripherally metallated porphyrins	63
	1.4.5.	General methods for the synthesis of peripherally metallated porphyrins	63
	1.4.6.	Application of peripherally metallated porphyrins	65
	1.4.7.	Synthesis of peripherally metallated porphyrins	67
	1.4.8.	Distortion in porphyrins	72
	1.4.9	Scope of the work	72
CHAPTER	2	Experimental (reagents and techniques)	76
	2.1.	Preparation, purification and characterization of starting materials	76
	2.2.	Purification and drying of solvents and reagents used in the Study	90
	2.3.	Experimental techniques	91
	2.4.	Characterization technique	92
CHAPTER	3	Synthesis and reactions of ethynylferrocene-derived fluoro- and chlorocyclotriphosphazenes	94
	3.1.	Introduction	94
	3.2.	Results and discussion	95
	3.3.	Spectral studies of compounds 19--34	101
	3.4.	Electrochemical studies	109
	3.5.	Structural studies of compounds 19-29 and 31-34	111
	3.6.	Conclusions	125

	3.7.	Experimental section	126
CHAPTER	4	Synthesis, spectral and structural studies of porphyrins with sterically hindered cobalt sandwich compounds [η^5 -CpCo(η^4 -C ₄ Ph ₄)] units at the meso positions	143
	4.1.	Introduction	143
	4.2.	Results and discussion	145
	4.3.	Spectral Studies of compounds 35-50	152
	4.4.	Structural studies of compounds 35, 36, 38-42, 44, 46, 48 and 50	166
	4.5.	Electrochemical studies	182
	4.6.	Conclusions	187
	4.7.	Experimental section	188
CHAPTER	5	Synthesis and characterization of ferrocene and [η^5 - CpCo(η^4 -C ₄ Ph ₄)] substituted 2-pyridones	203
	5.1.	Introduction	203
	5.2.	Results and discussion	206
	5.3.	Spectral Studies of compound 51-57	209
	5.4.	Structural Studies of 55	213
	5.5.	Conclusions	216
	5.6.	Experimental Section	217
CHAPTER	6	Conclusions	224
REFERENCES			227

