SYNTHETIC AND ASYMMETRIC CATALYTIC STUDIES ON NEW DERIVATIVES OF THE COBALT SANDWICH COMPOUND, $(\eta^5\text{-Cp})Co(\eta^4\text{-}C_4Ph_4)$

by

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Submitted

in fulfillment of the requirements

of the degree of

Doctor of Philosophy

to the

Indian Institute of Technology, Delhi, India

April, 2012

Dedicated to

My Family, Friends

and

Teachers

CERTIFICATE

This is to certify that the thesis entitled "**Synthetic and Asymmetric Catalytic Studies on New Derivatives of the Cobalt Sandwich Compound, $(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$**", being submitted by Mr. Nem Singh 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. Nem Singh 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.

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Acknowledgements

I consider myself very lucky to have had as my supervisor **Prof. Anil J. Elias**, whose expertise, understanding, and patience, added considerably to my research experience. He is the one teacher who truly made a difference in my life. Every meeting with him was a learning experience, almost always yielding fruitful results. I thank him for this wonderful opportunity.

I express my gratitude to members of my student research committee, Prof. D. Bandyopadhyay, Prof. Ravi Shankar and Dr. J. Jacob for their help and suggestions. I also express my sincere thanks to Prof. A. Ramanan for discussions on crystallographic studies. I thank Prof. A. Ramanan and Prof. A. K. Ganguly-coordinators X-ray facility, for providing me an opportunity to learn and operate the single crystal X-ray diffractometer. I thank Dr. N. G. Ramesh for help in analyzing chiral compounds and for allowing me to use his HPLC initially when it was not there in our research lab. Thanks are due to Dr. S. Nagendran for his constant encouragement and inspiration.

I thank the present and previous heads of the Department of Chemistry for providing the necessary facilities. I express my gratitude to my seniors Dr. Senthil, and Dr. Behera for helping me in the initial stages of my stay at IIT Delhi. I thank my current labmates for providing a friendly atmosphere in the laboratory.

I thank my wife, Deepa for her unconditional support and encouragement. I thank my parents for their love, affection and constant encouragement.

Finally, I wish to thank UGC for giving me JRF and SRF. I also thank DST, CSIR and IIT Delhi for providing financial assistance in the research work.

Nem Singh

ABSTRACT

The thesis entitled “Synthetic and asymmetric catalytic studies on new derivatives of the cobalt sandwich compound, $(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$” presents the research work carried out on chiral and achiral cyclopentadiene derived monomeric and cyclobutadiene linked dimeric derivatives of the cobalt sandwich compound $(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$. The research work embodied in this thesis has been divided in to seven chapters.

Chapter 1 gives a general introduction to organometallic sandwich compounds. This is followed by an account of cobalt sandwich compounds in particular. A detailed literature survey of the synthesis, reactions and applications of $(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$ and related molecules is provided which also includes a brief description of some recent developments in the area of cyclophosphazene bound cobalt sandwich compounds. The chapter ends with scope of the present work carried out and reported in the thesis.

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

Chapter 3 describes the synthesis of cyclobutadiene linked dimeric analogues of $(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$ by the reaction of $\text{PhC}\equiv\text{CPh}$, $\text{PhC}\equiv\text{CC}\equiv\text{CPh}$ and $[\eta^5\text{-RCp}]\text{Co}(\text{PPh}_3)_2$ [R= H, C(O)OMe]. The diester derivative $\{[\eta^5\text{-MeOC(O)Cp}]\text{Co}(\eta^4\text{-C}_4\text{Ph}_3)\}_2$ was converted to achiral as well as chiral bis(oxazoline) derivative of the same. The chiral bis(oxazoline) was used to prepare novel palladacycles based on the dimeric cobalt sandwich compound. Structural studies on these palladacycles showed interesting $\text{C–H}\cdots\text{Pd}$ interactions which

has recently been described as anagostic interactions by Brookhart, Parkin and Green. This work also describes the application of palladacycles in the asymmetric aza-Claisen rearrangement of trichloroacetimidates to trichloroacetamides which is an elegant method for the synthesis of chiral allylic amines from prochiral allylic alcohols. The reactions, which were found to proceed at 70 °C, gave yields in the range of 65-87% and good ee's ranging from 83 to 96%.

Chapter 4 describes reactions carried out for identifying the intermediates in the formation of the dimeric cobalt sandwich compound and for understanding its mechanism of formation. On varying the stoichiometric ratio of the reactants of the three component reaction, two new cobalt sandwich compounds $[\eta^5\text{-MeOC(O)Cp}]\text{Co}[\eta^4\text{-C}_4\text{Ph}_3(\text{C}\equiv\text{CPh})]$ and $[\eta^5\text{-MeOC(O)Cp}]\text{Co}[\eta^4\text{-C}_4\text{-Ph}_2(\text{C}\equiv\text{CPh})_2]$ were found to form as viscous oily liquids. The identity of the mono alkyne compound was ascertained by oxidizing its alkyne moiety to yield a crystalline diketo compound $[(\eta^5\text{-(MeOC(O)Cp)Co}[\eta^4\text{-C}_4\text{Ph}_3(\text{C(O)-C(O)Ph})]$ whose crystal structure was determined. Further, the role of phenylethynyl derived monomeric sandwich compound as a precursor to the dimeric compound was established by synthesizing an unsymmetrical dimer, $\{\eta^5\text{-[MeOC(O)Cp]Co}(\eta^4\text{-C}_4\text{Ph}_3)\}[(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_3)]$ and a detailed mechanism for the formation of all compounds has been proposed.

Chapter 5 describes the synthesis of novel 1,2 and 1,3-difunctional derivatives of $(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$. The reaction of sodium salts of 1,2 and 1,3-dicarboalkoxycyclopentadienyls with $\text{CoCl(PPh}_3)_3$ and diphenylacetylene resulted in 1,2 and 1,3-cyclopentadienyl diester derived cobalt sandwich compounds $\{\eta^5\text{-[ROC(O)]}_2\text{C}_5\text{H}_3\}\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$ [R= Me, Et]. These diesters were converted to the dicarboxylic acids by refluxing with aq. KOH in ethanol. The diacyl chloride of the 1,2-

diacid yielded a novel bis metallocenyl acenequinone having both iron and cobalt sandwich units in the same compound. The 1,3-dicarboxylic acid was converted to a novel cyclopentadienyl 1,3-bis(oxazoline) derived bidentate chiral ligand [η^5-1,3-(4-*i*Pr-2-Ox)$_2$C$_5$H$_3$]Co(η^4-C$_4$Ph$_4$) (Ox = oxazolinyl). A chiral palladium complex has been synthesized using this 1,3-bis(oxazoline) ligand. This palladium complex has been found to be quite efficient in bringing about the aza-Claisen rearrangement of trichloroacetimidates at ambient temperature with good yields and high enantioselectivity. The 1,2 and 1,3-diesters have also been used for the synthesis of novel 1,2 and 1,3-difunctional derivatives of (η^5-Cp)Co(η^4-C$_4$Ph$_4$) with functional groups such as CH$_2$OH, CH$_2$OC(O)Me, CH$_2$N$_3$, CH$_2$SPh, CHO, C≡CH and CH=NPh.

Chapter 6 describes the synthesis and reactions of the first examples of butadiyne derived fluorophosphazene N$_3$P$_3$F$_5$(C≡CC≡CPh) and N$_3$P$_3$F$_4$(C≡CC≡CPh)$_2$ which were synthesized by the reaction of PhC≡CC≡C-Li with N$_3$P$_3$F$_6$. A reaction of N$_3$P$_3$F$_5$(C≡CC≡CPh) with Cp(CO)$_2$Mo≡Mo(CO)$_2$Cp yielded a novel dimolybdenum cluster Cp(CO)$_2$(Mo$_2$C$_2$)(P$_3$N$_3$F$_5$)(C≡CPh)(CO)$_2$Cp. Interestingly, only the alkyne moiety adjacent to the fluorophosphazene ring was found to react forming the Mo$_2$C$_2$ cluster. Reaction of N$_3$P$_3$F$_5$(C≡CC≡CPh), PhC≡CPh and [η^5-MeOC(O)Cp]Co(PPh$_3$)$_2$ resulted in the formation of a novel cyclobutadiene linked dimeric cobalt sandwich {[η^5-MeOC(O)Cp]Co[η^4-(C$_4$Ph$_2$P$_3$N$_3$F$_5$)]}{[η^5-MeOC(O)Cp]Co(η^4-C$_4$Ph$_3$)} having a P$_3$N$_3$F$_5$ unit bound to one of the cyclobutadiene rings.

Chapter 7 gives the overall conclusions of the entire work carried out in the present study.

TABLE OF CONTENTS