

**ORGANOCOBALT CHEMISTRY OF CYCLIC PHOSPHORUS
NITROGEN COMPOUNDS**

by

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Department of Chemistry

Submitted

in fulfillment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

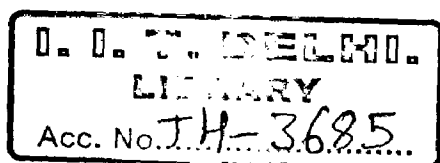
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organic compounds



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Dedicated to
My Beloved Parents, Prof. Anil J. Elias
and
Teachers

CERTIFICATE

This is to certify that the thesis entitled “**Organocobalt Chemistry of Cyclic Phosphorus Nitrogen Compounds**”, being submitted by Mr. **M. Senthil Kumar** 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. M. Senthil Kumar 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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ABSTRACT

The thesis entitled “Organocobalt Chemistry of Cyclic Phosphorus Nitrogen Compounds” presents the research work carried out on the synthesis, characterization and exploration of the chemistry of novel fluorophosphazene derived cobalt based sandwich compounds and metallacycles. The research work embodied in this thesis has been divided in to seven chapters.

The $[\eta^5\text{-cyclopentadienyl}][\eta^4\text{-tetraphenylcylobutadiene}]$ cobalt is a metal-sandwich system which has turned out to be a potential competitor to ferrocene in many aspects. Closely related to such sandwich compounds are PPh_3 stabilized cobaltamettallacycles. The first part of **Chapter 1** describes salient aspects of the chemistry of metallocenes and metallacycles with emphasis on the cobalt based metal sandwich compounds and metallacycles available in the literature.

Among inorganic heterocycles, perhalogenated cyclic phosphazenes occupy a very prominent place as the precursors for polyphosphazenes, whose property can be tuned by changing the substituents on the phosphorus sites. The second part of **Chapter 1** provides the relevant literature background on cyclophosphazenes in general and fluorinated cyclophosphazenes in particular. This chapter ends with a description on the scope of the work carried out and presented in the thesis.

Chapter 2 describes the general experimental procedures adopted in 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 of this thesis deals with the reaction of (β -phenylethynyl) pentafluorocyclotriphosphazene, $\text{F}_5\text{P}_3\text{N}_3\text{C}\equiv\text{CPh}$ with *in situ* generated $\eta^5\text{-(MeOC(O)C}_5\text{H}_4\text{)Co(PPh}_3\text{)}_2$ which resulted in the formation of two novel

fluorophosphazene derived cobaltocyclopentadienyl metallacycles $[(\eta^5\text{-carbomethoxycyclopentadienyl}) (\text{triphenylphosphine})\text{-}2,5\text{-bis(pentafluorocyclotriphosphazenyl)}\text{-}3,4\text{-diphenylcobaltacyclopentadiene}]$ and $[(\eta^5\text{-carbomethoxycyclopentadienyl}) (\text{triphenylphosphine})\text{-}2,4\text{-bis(pentafluorocyclotriphosphazenyl)}\text{-}3,5\text{-diphenylcobaltacyclopentadiene}]$ stabilized with triphenylphosphine, and one cyclobutadienyl cobalt sandwich compound having two fluorophosphazenyl groups *trans* to each other on the cyclobutadiene ring. This work also describes a novel synthetic route for making aryl bridged fluorinated cyclophosphazenes by the reaction of the metallacycles with substituted acetylenes.

Chapter 4 describes the reaction of $[\eta^5\text{-MeOC(O)C}_5\text{H}_4]\text{Co(COD)}$, $\text{PhC}\equiv\text{CP}_3\text{N}_3\text{F}_5$ and phenylacetylene in the presence or absence 1,5-cyclooctadiene which resulted in the formation of mono fluorophosphazene derived $[\eta^5\text{-cyclopentadienyl}][\eta^4\text{-}1,3\text{-cyclohexadiene}]$ cobalt complex, along with the sandwich compound $[\eta^5\text{-carbomethoxycyclopentadienyl}][\eta^4\text{-}1,3\text{-bis(pentafluorocyclotriphosphazenyl)}\text{-}2,4\text{-diphenylcyclobutadiene}]$ cobalt and acetylene trimerized products. This work also explores the reactions of $[\eta^5\text{-MeOC(O)C}_5\text{H}_4]\text{Co(COD)}$ and $\text{PhC}\equiv\text{CP}_3\text{N}_3\text{F}_5$ in the presence of dicyclopentadiene as well as indene which resulted in the formation of bis(fluorophosphazene) derived cobalt cyclohexadiene complexes. The formation of mono and bis fluorophosphazene derived cobalt cyclohexadiene complexes provides experimental evidence for a metallacyclopentadiene pathway for cobalt based cyclohexadiene formation from CpCo(COD) reactions.

Chapter 5 has been divided in to two parts. Part A describes the synthesis of a new *gem*-diphenyltrifluorophosphazene derived alkyne and its reactions with *in situ* generated $\text{RCpCo(PPh}_3)_2$, which resulted in the unprecedented formation of a novel spirocyclic phosphazacyclopentadiene bound to a CpCo unit, in addition to *gem*-

diphenyltrifluorophosphazene derived metallacyclic compounds and CpCo stabilized cyclobutadiene complex having two phosphazene units in the alternate carbon atoms.

Part B of this chapter describes the reactions of the same alkyne with RCpCo(COD) in the presence and absence of external alkene, which resulted in the formation of *gem*-diphenyltrifluorophosphazene derived CpCo stabilized 1,3-cyclohexadiene complexes. The formation of CpCo stabilized 1,3-cyclohexadiene complexes further confirms the existence metallacyclopentadiene as the intermediate for the formation of cobalt based (1,3-cyclohexadiene) complex.

Chapter 6 deals with the reactions of a model compound, $[\eta^5\text{-carboxycyclopentadiene}][\eta^4\text{-tetraphenylcyclobutadiene}]$ cobalt with various alkyl and aryl tin oxides. The reaction of $[\eta^5\text{-carboxycyclopentadiene}][\eta^4\text{-tetraphenylcyclobutadiene}]$ cobalt with $(\text{Ph}_3\text{Sn})_2\text{O}$ resulted in the formation of monomeric compound $\text{Ph}_3\text{SnOC}(\text{O})\text{C}_5\text{H}_4\text{CoC}_4\text{Ph}_4$. The reaction of $[\eta^5\text{-carboxycyclopentadiene}][\eta^4\text{-tetraphenylcyclobutadiene}]$ cobalt with $[(n\text{Bu})_2\text{SnO}]_n$ and $(\text{Ph}_2\text{SnO})_n$ in refluxing toluene resulted in the formation of dimeric compounds $n\text{Bu}_2\text{Sn}[\text{OC}(\text{O})\text{C}_5\text{H}_4\text{CoC}_4\text{Ph}_4]_2$ and $\text{Ph}_2\text{Sn}[\text{OC}(\text{O})\text{C}_5\text{H}_4\text{CoC}_4\text{Ph}_4]_2$.

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

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