

**CHEMISTRY OF ALKENYL, ALKYNYL AND
CHIRAL OXAZOLINYL DERIVATIVES OF
CYCLOPHOSHAZENES**

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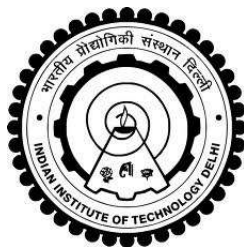
Submitted

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to the



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Dedicated

to

My Parents

CERTIFICATE

This is to certify that the thesis entitled “*Chemistry of alkenyl, alkynyl and chiral oxazolinyl derivatives of cyclophosphazenes*”, being submitted by Mr. **Dheeraj 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. **Dheeraj 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 “*Chemistry of alkenyl, alkynyl and chiral oxazolinyl derivatives of cyclophosphazenes.*” presents the results obtained from the research work carried out on the synthesis, characterization and exploration of the chemistry of alkene, alkyne, butadiyne and chiral oxazolinyl derivatives of cyclophosphazenes. The accompanied research work has been divided into the seven chapters.

Chapter 1 is a general introduction providing the background and literature required to follow up the actual experiments carried out and presented in the subsequent chapters. As the work described in this thesis is mainly focused on the cyclophosphazenes, salient features of cyclophosphazenes have been discussed with relevant background. The most widely studied among the perhalogenated cyclophosphazenes are trimeric chloro and fluorophosphazenes, whose stability, volatility and reactivity differs significantly. We have also discussed the reactions of cyclophosphazenes with various difunctional reagents with special emphasis on ansa vs spiro substitution. A brief literature on the use of cyclophosphazenes as scaffolds for building multi-site ligands is also described in this chapter. Alkynyl derived cyclophosphazenes are interesting structural motifs for synthesizing novel cyclophosphazene derived triazoles, organocobalt clusters, cobalt sandwich compounds, cobaltacyclopentadienes and have also shown their use in realizing multiphosphazenyl assemblies by cycloaddition reactions. Salient aspects of the literature known of such compounds is consolidated in this chapter. Reactions of cyclophosphazenes with various metal carbonyls are also discussed in detail.

The first chapter of this thesis include work on ring closing metathesis reactions with terminal alkene derived cyclophosphazenes, a brief literature on various types of olefin metathesis reactions, catalysts used and their applications in organic synthesis is reviewed in this chapter. As the work described in the thesis also encompass chemistry of various types of chiral oxazoline ligands, the literature on the chemistry of these compounds have also been covered in this chapter. 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 ring closing metathesis reactions of terminal alkene derived cyclic phosphazenes and thionylphosphazenes using Grubbs 1st generation catalyst. The primary objective was to recognize any selectivity in the nature of products formed (spiro, ansa and bino) if existing acyclic substituents on a cyclophosphazene scaffold are made to undergo ring formation and to identify the factors responsible for the formation of the same. Multiallyloxy derivatives of trimeric and tetrameric as well as thionylphosphazene has been found to exclusively form seven membered spirocyclic products upon ring closing metathesis. Interestingly, on replacing all the allyloxy groups on diphenyltetraallyloxy cyclophosphazene and S-phenyl thionylphosphazene by homoallyloxy units, a propensity to form intramolecular diansa and ansa-bisbino-ansa ring closed metathesis products was observed. Structural studies on the new spiro and ansa cycloalkene compounds indicated that the alkene double bonds in the spiro

derivatives are in the *cis* orientation while those on the ansa substituted derivatives are in the *trans* orientation. The eighteen membered geminal bisbino substituted dimeric compound $[\text{NPPh}_2]_2[\text{NP}(\text{OCH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{O})_2\text{PN}][\text{NPPh}_2]_2$, obtained as the major product in the ring closing metathesis of $[\text{NP}(\text{OCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2](\text{NPPh}_2)_2$ upon reaction with Grubbs 2nd generation catalyst was found to undergo a novel ring opening metathesis reaction converting partially to the nine membered spirocyclic compound $[\text{NPPh}_2]_2[\text{NP}(\text{OCH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{O})]$ as well as undergoing secondary metathesis reactions leading to a higher *E/Z* ratio.

Chapter 4 describes the synthesis, characterization and complexation studies of chiral multidentate oxazoline ligands based on the cyclophosphazene cores. Various ester derivatives of cyclophosphazenes ($\text{P}_3\text{N}_3\text{Cl}_6$, *gem*- $\text{Ph}_2\text{P}_3\text{N}_3\text{Cl}_4$ and *gem*- $\text{Ph}_4\text{P}_3\text{N}_3\text{Cl}_2$) were synthesized by the reactions of their P-Cl bonds with methyl-3-hydroxy benzoate/methyl-4-hydroxy benzoate/dimethyl 5-hydroxyisophthalate in the presence of Cs_2CO_3 in the molar ratio 1:1:2. These ester derivatives of cyclophosphazenes were converted to the corresponding carboxylic acid derivatives by using base promoted hydrolysis with $\text{KO}(\text{t-Bu})$ at room temperature. Acid derivatives on treatment with oxalyl chloride followed by reaction with chiral 2-amino alcohols, trimethylamine and mesyl chloride were converted to the various chiral oxazoline derivatives of the cyclophosphazenes. Using this approach, we have prepared C_2 symmetric chiral bisoxazoline derivatives of cyclophosphazenes, C_3 symmetric hexaoxazoline derivatives of cyclophosphazene and ligands having chiral multiphebox units substituted on the phosphazene scaffold. Preliminary complexation studies with $\text{Pd}(\text{OAc})_2$ and $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$ indicate that monomeric chiral palladium complexes are isolable especially if oxazoline ring is

substituted at the para position of the phenyl group attached to the phosphazene ring through P-O bonds.

Chapter 5 begins with the synthesis of ferrocenylbutadiyne substituted fluorinated cyclophosphazenes. The reactions of lithiated ferrocenylbutadiyne with hexafluorocyclotriphosphazene was found to proceed at -78 °C with the formation of mono ferrocenylbutadiyne and germinal bis(ferrocenylbutadiyne) derived fluorophosphazenes. Compounds having both dialkyne and alkyne units attached to same phosphorus atom of a fluorophosphazene ring were also synthesized starting from the monosubstituted compounds $P_3N_3F_5C\equiv C-C\equiv CR$ ($R = Ph, Fc$). The second part of this chapter deals with the reduction reactions of alkyne/butadiyne derived cyclophosphazenes using Pd/C. Alkyne and butadiyne derivatives of fluorophosphazenes (mono, geminal disubstituted and geminal alkynyl butadiynyl substituted) were reduced using Pd/C to give tethered alkyl derivatives of the cyclophosphazenes, which were otherwise difficult to synthesize. We have also shown the partial reduction of the ethynyl ferrocene derived cyclophosphazene, $P_3N_3F_5(C\equiv CFc)$ to alkene derived cyclophosphazene $P_3N_3F_5(CH=CHFc)$ in good yields using the Lindlar catalyst. An attempted hydrogenation of chlorinated phosphazene, $[FcC\equiv C(Cl)PN](PNCl_2)_2$ using Pd/C as catalyst resulted in the compound $[(FcCH_2CH_2)(OCH_3)PN](PNCl_2)_2$ having methoxy substitution on the alkyl substituted phosphorus atom.

Chapter 6 describes the reactions of alkyne and butadiyne derived fluorinated cyclophosphazenes with diiron and dimolybdenum carbonyls. Reaction of (β -phenylethynyl)pentafluorocyclotriphosphazene, $P_3N_3F_5C\equiv CPh$, with $Fe_2(CO)_9$ in

refluxing hexane resulted in a range of products based on five membered cyclopentadienone and ferracyclopentadiene rings bound to $\text{Fe}(\text{CO})_3$ moieties along with an unusual compound, where a (2, 5-diphosphazeryl)cyclopentadienone ring was bound to $\text{Fe}(\text{CO})_2(\text{P}_3\text{N}_3\text{F}_5)\text{C}=\text{C}(\text{Ph})$ unit, where Fe was η^5 bonded to the cyclopentadienone ring and the alkene carbon that is α to the $\text{P}_3\text{N}_3\text{F}_5$ unit is σ bonded to the Fe atom. Similar reaction tried in presence of an activator, trimethylamine N-oxide resulted only in compounds having cyclopentadienone ring bound to the $\text{Fe}(\text{CO})_3$ moiety. In contrast to the $\text{Fe}_2(\text{CO})_9$ reaction, reaction of alkyne derived pentafluorocyclotriphosphazenes, $\text{P}_3\text{N}_3\text{F}_5\text{C}\equiv\text{CR}$ [$\text{R} = \text{Ph}, \text{Fe}(\text{C}_5\text{H}_5)_2$] with the molybdenum complex $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ in refluxing toluene resulted in simple tetrahedral clusters. The reaction of $\text{N}_3\text{P}_3\text{F}_5(\text{C}\equiv\text{C}-\text{C}\equiv\text{CFc})$ with *in situ* generated $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ indicated the preferential formation of a tetrahedral Mo_2C_2 clusters with the alkyne unit closer to the $\text{P}_3\text{N}_3\text{F}_5$ ring selectively. The new iron and molybdenum complexes and clusters compounds showed interesting differences in their structural and spectral properties and these have been compared.

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

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