

**CHLORO AND AMINO SUBSTITUTED CYCLOCARBAPHOSPHAZENES:
REAGENTS FOR ORGANIC TRANSFORMATIONS AND PRECURSORS FOR
NOVEL LIGANDS**

by

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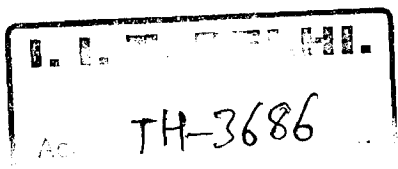
Ligands

Ligands - Organic synthesis

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Dedicated
to my
Beloved Parents and Teachers

CERTIFICATE

This is to certify that the thesis entitled "**CHLORO AND AMINO SUBSTITUTED CYCLOCARBAPHOSPHAZENES: REAGENTS FOR ORGANIC TRANSFORMATIONS AND PRECURSORS FOR NOVEL LIGANDS**", being submitted by Mr. Nabakrushna Behera 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. Nabakrushna Behera 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, "Chloro and amino substituted cyclocarbaphosphazenes: Reagents for organic transformations and precursors for novel ligands" presents the research work carried out on the synthesis and applications of chloro and amino substituted cyclocarbaphosphazene and their novel derivatives. The research work embodied in this thesis has been divided in to seven chapters.

Cyclocarbaphosphazenes are bridging heterocycles between organic *s*-triazines and inorganic cyclophosphazenes as they contain both P–N and C–N moieties as part of their ring framework. **Chapter 1** brings out the literature information pertaining to the work carried out in this study. Various objectives of the present investigation are spelt out at the end of this chapter. A detailed account of the synthetic, structural, application and spectroscopic aspects of cyclocarbaphosphazenes along with a brief introduction of inorganic heterocycles is provided. Details of various types of reactions shown by cyclocarbaphosphazenes as well as their uses are also discussed in this chapter. This chapter ends with a description on the scope of the work carried out and presented in the thesis.

Chapter 2 describes the details of the preparation and purification of starting materials, various solvents used and their methods of purification as well as different techniques employed for isolation and characterization of compounds. Also details of the sources for obtaining various spectral and analytical data on the compounds synthesized in this study are provided.

Chapter 3 deals with the use of tetrachlorocyclocarbaphosphazene, $(\text{Cl}_2\text{PN})(\text{ClCN})_2$ as a reagent for oxidation of alcohols to corresponding carbonyl compounds as well as for conversion of alcohols to alkyl chlorides. While both the P–Cl and C–Cl bonds

of the cyclodibiphosphazene can in principle bring about the reaction, we observe an increased preference for the C-Cl bonds over the P-Cl bonds in the oxidation of the alcohols.

Chapter 4 contains the reactions of dilithiated diols with 3, 5- bis (N, N-dimethylamino)-1, 1-dichlorodibiphosphazene to afford the first examples of lariat ether type cyclodibiphosphazene derivatives. Complexation studies of a suitable ligand with various metal ions have been discussed. The chapter also describes the reaction of the tetrasodium salt of pentaerythritol with the bis(N,N-dimethylamino)dichlorodibiphosphazene and bis(morpholino)dichlorodibiphosphazenes resulting in the first examples of pentaerythritoxy bridged carbiphosphazenes.

Chapter 5 presents the synthesis, characterization and complexation studies of azacrown derived cyclodibiphosphazenes. Complexation studies of some of the compounds with Na(I) and Ag(I) ions have been carried out by conductance measurements. The studies indicate 1:1 complex formation between the metal ions and azacrown derived cyclodibiphosphazenes. A comparative study on the stability and reactivity of tetraazacrown derived cyclodibiphosphazene with analogous tetrapyrazolyl derived cyclodibiphosphazene has also been carried out.

Chapter 6 provides details of the synthesis and characterization of cyclodibiphosphazenes having Schiff-base units and acetylenic units as substituents. The stability of the above carbiphosphazene based Schiff bases and their complexation ability with Cu(II) ions are discussed in this chapter. The crystal structure of one of the acetylenic derivatives has also been discussed.

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

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