

# Investigation of Synthesis Inefficiency and Handling Problems in Chlorophosphazene Chemistry

PhD Research Project of Zin-Min Tun

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Phosphazene polymers are classically synthesized by the ring-opening polymerization (ROP) of  $[\text{PCl}_2\text{N}]_3$ , followed by the functionalization of  $[\text{PCl}_2\text{N}]_n$  with desired side groups. Despite their versatile properties, phosphazene polymers are not widely used because of the inefficiency in the synthesis through the ROP process and difficulties in handling the  $[\text{PCl}_2\text{N}]_n$ . The overall goal of this research is to study the acid-base chemistry of  $[\text{PCl}_2\text{N}]_3$  with the end result of finding cheaper and more efficient synthetic routes to chlorophosphazenes.

The reactions of  $[\text{PCl}_2\text{N}]_3$  with  $\text{MX}_m$  ( $M = \text{Group 13}$ ,  $X = \text{Halides}$ ) under strict anaerobic conditions gave adducts  $[\text{PCl}_2\text{N}]_3 \cdot \text{MX}_m$ , which were found to be fluxional in solution. Dynamic NMR studies were done to investigate their fluxional behavior, and thermodynamic parameters obtained suggest an intramolecular exchange process. In the presence of stoichiometric quantity of water or  $\text{HX}$ , the reactions of  $[\text{PCl}_2\text{N}]_3$  with  $\text{MX}_m$  gave adducts  $[\text{PCl}_2\text{N}]_3 \cdot \text{HMX}_{m+1}$  ( $\text{HMX}_{m+1} = \text{HAlCl}_4, \text{HAlBr}_4, \text{HGaCl}_4, \text{HSbCl}_6$ ) instead. Because  $[\text{PCl}_2\text{N}]_3$  is a poor base and it takes a very strong acid to protonate it, acid strength of  $\text{HMX}_{m+1}$  species became a subject of interest. A qualitative acid strength scale based on IR  $\nu\text{NH}$  frequency showed that these  $\text{HMX}_{m+1}$  species are superacids.  $[\text{PCl}_2\text{N}]_3 \cdot \text{MX}_m$  and  $[\text{PCl}_2\text{N}]_3 \cdot \text{HMX}_{m+1}$  adducts were characterized by X-ray crystallography, mass spectrometry, and multi-nuclear and variable-temperature NMR studies.

On the basis of our work on the reactions of Lewis acids with  $[\text{PCl}_2\text{N}]_3$ , we suspect that at least some of the complications in chlorophosphazene chemistry may arise from a strong acid or a superacid that is generated from the interaction of Lewis-acid  $\text{PCl}_5$  with  $\text{HCl}$ .  $\text{PCl}_5$  is a reagent, catalyst or initiator in all syntheses of  $[\text{PCl}_2\text{N}]_n$ , and  $\text{HCl}$  is generated as a by-product during some syntheses of chlorophosphazenes or from hydrolysis of P-Cl bonds. We isolated the first reported  $\text{HPCl}_6$  species as complexes of 12-crown-4 and 18-crown-6. Currently, we are investigating the interactions of  $\text{HPCl}_6$  with various chlorophosphazenes.