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New Phosphorus Based Polymer Systems

Introduction

During the past three years of this ONR contract, we have been exploring various preparative routes, utilizing Si-N-P and/or Si-C-P compounds as starting materials, to new types of phosphorus-based polymers of general compositions $[\text{RPN}]_n$ and $[\text{RPCR}_2]_n$. Much of this effort has involved the synthesis, reactivity, structure, and stereochemistry of new types of small molecule precursors to and/or models for these polymer systems. Many of these precursors are novel "low-coordinate" compounds in which phosphorus is sp^2 hybridized and π -bonded to either carbon or nitrogen. A more recent area of research, which represents somewhat of a broadening of our program beyond solely phosphorus-based polymers, involves the preparative chemistry of some novel Si-N-B and B-N-B compounds as possible precursors to boron-nitrogen polymers. Some of the more promising and significant results in these areas, which form the basis for the present proposal, are summarized in the following section.

Summary of Results

Precursors to $[\text{RPN}]_n$. We have concentrated our efforts in this area on the *bimolecular* condensation reactions of difunctional phosphines with N-silylated phosphoranimines. Generally, the reactions proceed with evolution of the expected amount of Me_3SiCl and formation of white solids having the approximate composition $[\text{RPN}]_n$. Elemental analyses of several samples gave nearly correct C:H:P ratios but residual chlorine contents of 2-5 % were also found. The ^1H and ^{13}C NMR spectra of the soluble materials consisted of broad resonances in the expected regions with complete absence of Me_3Si signals. Extremely broad peaks in the 0-20 ppm region of the ^{31}P NMR spectrum were seen for some samples while others gave no detectable signals even on concentrated solutions. Results of GPC analysis indicate peak molecular weights of these products in the range of 1,000-5,000. Taken together, the characterization data suggest that *the materials are linear or cyclic oligomers of moderate molecular weight with the approximate composition $[\text{RPN}]_n$.*

In an effort to better understand the factors controlling this process, we have carried out a study of several model "polymerization" reactions of N-silylphosphoranimines, $\text{Me}_3\text{SiN}=\text{PR}_2\text{X}$ [$\text{X} = \text{Cl}, \text{Br}, \text{OCH}_2\text{CF}_3$, $\text{N}(\text{SiMe}_3)_2$], with monofunctional phosphines, Ph_2PY ($\text{Y} = \text{Cl}, \text{OCH}_2\text{CF}_3$). These processes are considerably more complex than expected and, depending upon the nature of X and Y, can lead to simple condensation products or novel multi-phosphorus cations. In related work, a variety of new P^{III} and P^{V} compounds, $(\text{Me}_3\text{Si})_2\text{NP}(\text{R})\text{X}$ and $\text{Me}_3\text{SiN}=\text{P}(\text{R})\text{XY}$, have been prepared as possible precursors to $[\text{RPN}]_n$ via other types of condensation processes.

Chemistry of $\text{P}=\text{C}$ Compounds. Our recent studies of the synthesis and reactivity of "low-coordinate" $\text{P}=\text{C}$ systems have focused primarily on three systems: (1) the amino(methylene)phosphines, (2) the amino(methylene)phosphoranes, and (3) the 1-phosphadienes. In addition to being easily prepared, many of these compounds offer the unique opportunity for comparing the reactivity of the $\text{P}=\text{C}$ π bond in similarly-substituted P^{III} , P^{V} , and phosphadiene systems, respectively. Moreover, the facile cleavage reactions of the Si-N and P-N bonds in the $(\text{Me}_3\text{Si})_2\text{N-P}$ moieties serve to further extend the range of derivative chemistry of these "low-coordinate" phosphorus compounds.

Five major types of reactions of these $\text{P}=\text{C}$ π -bonded systems have been studied: (1) addition and cycloaddition to the $\text{P}=\text{C}$ bond, (2) complexation of transition metals to the phosphorus lone pair and/or the $\text{P}=\text{C}$ π bond, (3) oxidation of the two-coordinate P^{III} center to the three-coordinate P^{V} state, (4) nucleophilic substitution at the two-coordinate P^{III} center, and (5) cleavage of the Si-N bond(s) by protic reagents. Our recent studies have shown that (methylene)phosphines bearing the disilylamino group actually exhibit all of these reaction pathways. By contrast, the reactivity of the three-coordinate P^{V} analogues is less diverse and is limited primarily to 1,2-additions to the $\text{P}=\text{C}$ double bond. Interestingly, the $\text{P}=\text{N}$ double bond is found to be much less reactive. Alkyl lithium reagents and chlorophosphines, for example, add preferentially to the $\text{P}=\text{C}$ double bond. In some cases, cyclization resulting from Si-N bond cleavage accompanies the addition process.

The 1-phosphadienes also have a rich derivative chemistry which closely parallels that of the simple (methylene)phosphines. Addition of polar reagents (e.g., MeOH) to the P=C double bond and complexation of metals to phosphorus occur readily. On the other hand, in processes such as oxidation or addition of alkyl-lithium reagents, both the C=C and the P=C double bonds are found to participate, leading to novel 1,4-addition products and phosphacyclobutenes, respectively.

Chemistry of Si-C-P Compounds. Recently, we have prepared a large series of (silylmethyl)phosphines (i.e., Si-C-P systems) via nucleophilic substitution reactions of PCl_3 and PhPCl_2 . These compounds are of interest as possible condensation monomers for the synthesis of novel P-C backbone polymers, i.e., poly(phosphaalkenes). Preliminary thermolysis experiments indicate that elimination of Me_3SiX from some of these precursors is, in fact, possible, leading to oligomeric ($\text{MW} \approx 2,000$) products.

Boron-Nitrogen Polymer Precursors. Our objectives in this relatively new project are to design, prepare, and characterize a variety of small molecule precursors to be used for the synthesis of the first *high molecular weight, linear boron-nitrogen polymers, (RBNR)_n*. The major problem to overcome in this effort is the great tendency which B-N systems have for forming the extremely stable borazene ring system, $(\text{RBNR})_3$. Two different approaches, both involving diborylamines as condensation monomers, are being studied. Incorporation of the linear N-B-N-B unit along with other structural features should prevent these systems from condensing to the 6-membered borazene rings upon thermolysis.

In the first method, *acyclic diborylamines containing both the Si-N and the B-Cl groups* are the target compounds. A few such species have recently been prepared and characterized. In this case, a bulky t-Bu group on boron serves to stabilize the primary amine precursor and should also help to inhibit formation of the borazene thermolysis products. The second approach involves linking the nitrogen atoms of the N-B-N-B backbone through a trimethylene bridge by use of the 1,3,2-diazaboracyclohexane ring system. Several new mono- as well as disubstituted derivatives of this 6-membered ring have been prepared in our lab.

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(With support by ONR, 6-1-84 - 9-30-87)

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