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NEW INORGANIC POLYMER SYSTEMS

by

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Texas Christian University
Fort Worth, TX 76129

February 15, 1991

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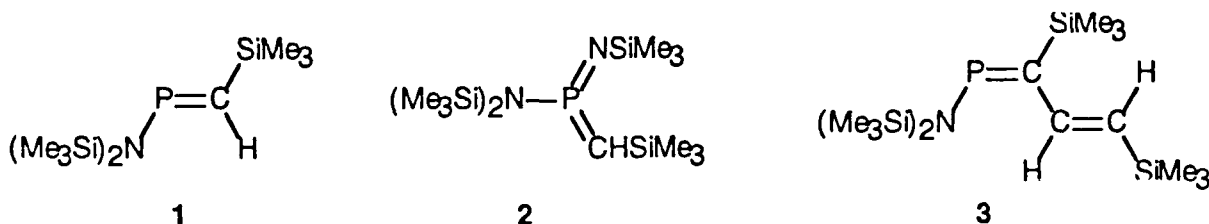
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Summary of Results

During the three year period of our current ONR contract, we have been exploring various preparative routes, utilizing Si-N-P, Si-C-P, and Si-N-B compounds as starting materials, to new types of phosphorus- and boron-based polymer systems including $[\text{RPN}]_n$, $[\text{RPCR}_2]_n$, and $[\text{RBNR}]_n$. 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. In the phosphorus area, these precursors are generally "low-coordinate" compounds in which phosphorus is π -bonded to either carbon or nitrogen. The most promising precursors to the B-N polymer system are diborylamines derived from the 1,3,2-diazaboracyclohexane ring.

Organophosphorus Chemistry. In the area of "low-coordinate" phosphorus compounds, our recent studies have focused primarily on three systems: the (methylene)phosphine **1**, the (methylene)phosphorane **2**, and the 1-phosphadiene **3**. In addition to being easily prepared, these compounds offer the unique opportunities for comparing the reactivity of the $\text{P}=\text{C}$ π bond in similarly substituted P^{III} , P^{V} , and P^{III} -diene systems. Moreover, the facile cleavage reactions of the Si-N and P-N bonds in the $(\text{Me}_3\text{Si})_2\text{N-P}$ moiety serve to further extend the range of derivative chemistry of these "low-coordinate" phosphorus compounds.

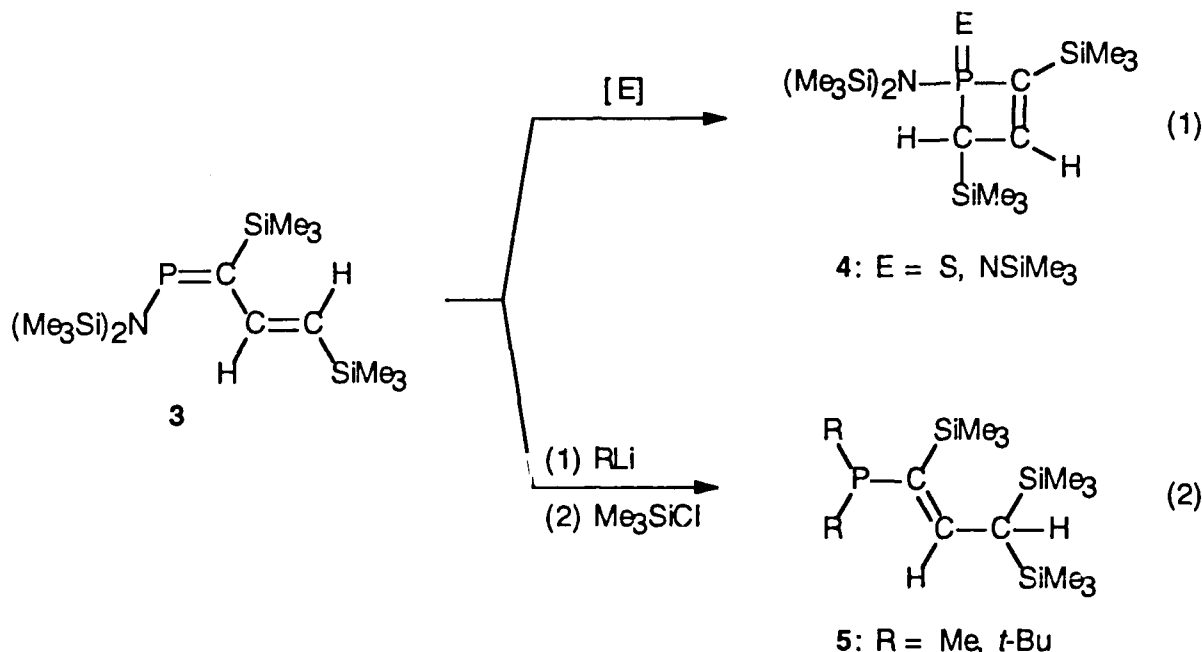


Five major types of reactions of these $\text{P}=\text{C}$ π -bonded systems have been studied: (1) addition and cycloaddition reactions of the $\text{P}=\text{C}$ bond, (2) complexation of transition metals to the phosphorus lone pair and/or the $\text{P}=\text{C}$ π bond, (3) oxidation of the two-coordinate 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. Indeed, our studies have shown that (methylene)phosphines bearing the disilylamino group (e.g., **1**) actually exhibit all of these reaction pathways.

By contrast, the reactivity of the three-coordinate P^{V} analogue **2** is less diverse and is limited primarily to simple 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 in this sense. 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.

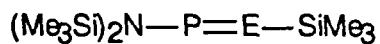
The 1-phosphadiene **3** also has a rich derivative chemistry which closely parallels that of the (methylene)phosphine **1**. Addition of polar reagents (e.g., MeOH)

to the P=C double bond and complexation of metals to phosphorus occur readily. On the other hand, in processes such as oxidation (eq 1) or addition of alkyllithium reagents (eq 2), both the C=C and the P=C double bonds are found to participate, leading to novel phosphacyclobutenes (4) and 1,4-addition products, respectively (5).

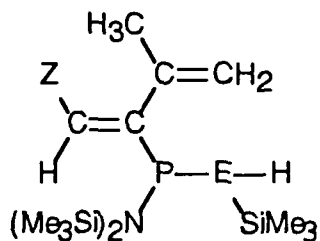


Some of our most recent and promising work has dealt with the electrophilic properties of the two-coordinate P^{III} center in the (methylene)phosphine **1** and its iminophosphine analogue, (Me₃Si)₂N-P=NSiMe₃ (**6**). In particular, we have been investigating the reactions of these compounds with a variety of unsaturated organic substrates including allenes, acetylenes, diketones, and acetylenic halides and alcohols. The results which are most relevant to this proposal generally involve the reactions with allenes (eq 3), leading to novel mono- (**7**) and diphosphorus- (**8**) substituted butadiene derivatives. The reactions of these two-coordinate phosphines with acetylenes (eqs 4 and 5) also give rise to high yields of novel products containing either the allenic (**9**) or the acetylenic (**10**) functional group attached to phosphorus. It is anticipated that many of these new compounds, especially the dienes **7** and **8**, will be very useful for the preparation of new "organic" polymers bearing reactive phosphorus functional groups as substituents on the polymer backbone.

A different area of organophosphorus chemistry that we have been exploring involves the synthesis and reactivity of various types of Si-C-P compounds that could be useful as condensation monomers for the preparation of poly(phosphaalkenes), [RPCR₂]_n. Specifically, we have prepared the (silylmethyl)phosphines **11** and the (1,3-disilylpropenyl)phosphines **12** via nucleophilic substitution reactions of phosphorus(III) halides with silylated organolithium reagents.

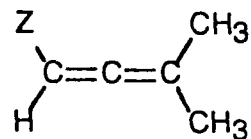


E = CH (1), N (6)

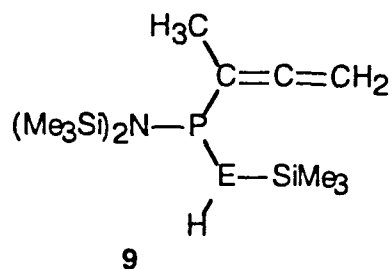
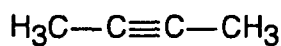


7: Z = H

8: Z = P(=O)(OR)₂

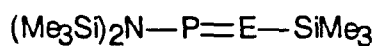


(3)

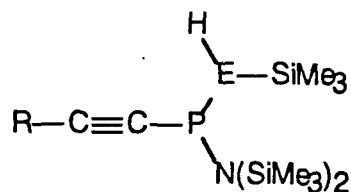


(4)

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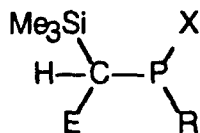


E = CH (1), N (6)



(5)

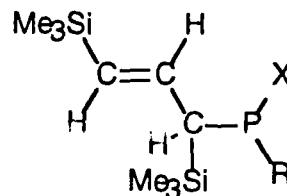
10: R = Ph, SiMe₃



11: E = H, SiMe₃

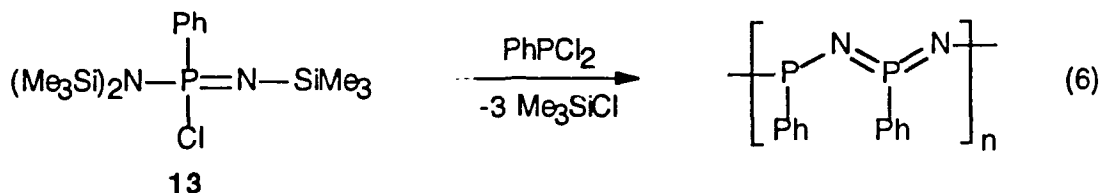
R = X, Ph, *t*-Bu

X = Cl, OCH₂CF₃, NMe₂

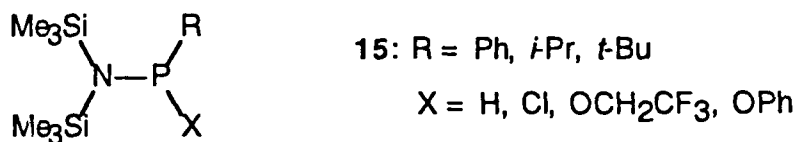
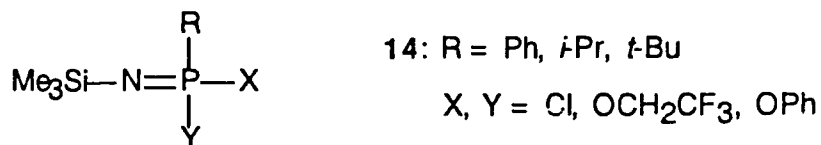


12: R, X = Cl, Ph, NMe₂

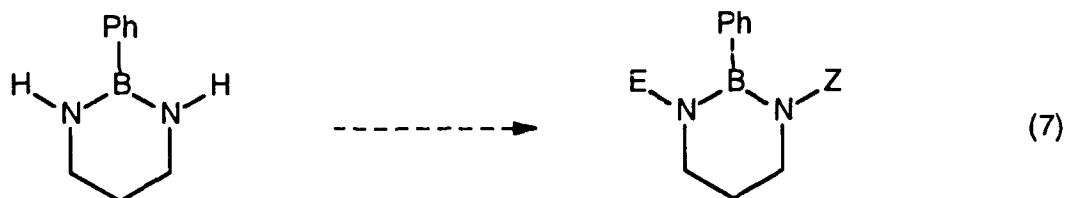
Phosphorus-Nitrogen Chemistry. About six years ago we observed that the bimolecular condensation reactions (eq 6) of difunctional phosphines (e.g., PhPCl_2) with certain N-silylated phosphoranimines (e.g., **13**) afforded yellow solid products that were tentatively identified as the first examples of a new class of inorganic polymers, the poly(phosphanitrides), $[\text{RPN}]_n$. At that time, several impure samples of $[\text{PhPN}]_n$ were found to have molecular weights in the 1,000 - 5,000 range.



Subsequently, we proposed some new synthetic approaches to these poly(phosphanitrides) based on the condensation reactions of single precursors containing the requisite $\text{P}^{\text{III}}\text{-N-P}^{\text{V}}$ linkages. While the desired precursors have not yet been prepared, we have recently synthesized a series of difunctional N-silylphosphoranimines **14** that will be important starting materials in our renewed efforts to obtain the poly(phosphanitrides). Other new compounds prepared in our laboratory that should be useful in this context include the unsymmetrically substituted (silylamino)phosphines **15**.



Boron-Nitrogen Chemistry. Our primary objective in this area is to prepare and characterize the first *high molecular weight, linear, boron-nitrogen polymers*, $[\text{RBNR}]_n$. The major problem to overcome in this endeavor is the very great tendency that B-N systems have for forming the extremely stable cyclic trimer, the borazene ring system, $[\text{RBNR}]_3$. Our primary approach to solving this problem involves the "skeletal stabilization" of the B-N-B-N backbone through the trimethylene bridge of the 1,3,2-diazaboracyclohexane ring system. Thus, we have prepared a large series of silyl and boryl derivatives (**16**) of this ring by relatively straightforward deprotonation/substitution reactions (eq 7). More recently, a few analogues with a *t*-Bu group rather than phenyl on boron have also been synthesized.



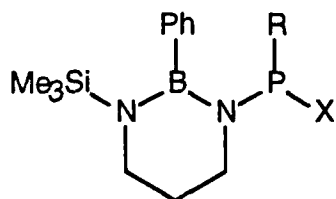
16: E = H, SiMe₃, SiMe₂H, SiMe₂(*t*-Bu),

B(Ph)NMe₂, B(NMe₂)₂

Z = E, B(Ph)OCH₂CF₃

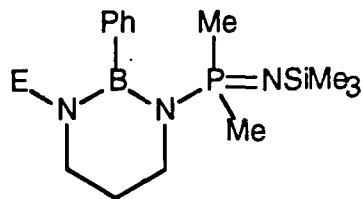
The fact that several of these diborylamines [e.g., E = B(Ph)NMe₂, B(NMe₂)₂] are thermally stable, distillable liquids is good evidence that the skeletal stabilization concept is effective, since the simple acyclic diborylamines are unstable with respect to borazene formation. On heating for several days at higher temperatures (ca. 200°C), some of these compounds do undergo partial condensation polymerization to give oligomers of 1,000 - 5,000 molecular weight via elimination of Me₂NH. The molecular structure of the symmetrical bis(amino) derivative [E = Z = B(NMe₂)₂] has been determined by single crystal X-ray diffraction. This compound, with its linear backbone of six B-N monomer units, may be viewed as a simple model for the corresponding high polymer.

In other related work, we have been investigating the feasibility of preparing phosphorus derivatives of the diazaboracyclohexane ring system. Treatment of the N-lithio derivative of the N-silyl- or N-boryl-B-phenyl starting materials with appropriate phosphorus halides has afforded both phosphorus-(III) and -(V) derivatives **17** and **18**, respectively.



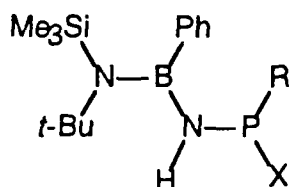
17: R = Ph, *t*-Bu

X = Cl, OCH₂CF₃, NMe₂



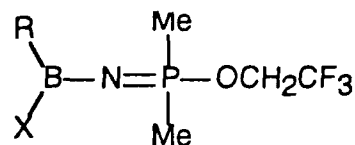
18: E = SiMe₃, B(NMe₂)₂

Although most of our efforts in the B-N area have been with the above ring systems, we have also prepared several new *acyclic* compounds of two types: (1) compounds **19** with the B-N-P-N linkage functionalized by an N-silyl group on one end and a potential leaving group on phosphorus at the other end; and (2) N-borylphosphoranimines **20** obtained from the Si-N cleavage reaction of the N-silylphosphoranimine with chloroboranes. The latter compounds are important as models for structure and reactivity studies of the -NR-RB-N=PR₂- repeating unit in the proposed poly(borazene/phosphazenes).



19: R = Ph, *t*-Bu

X = Cl, OCH₂CF₃, NMe₂



20: R = Ph, NMe₂

X = NMe₂, OCH₂CF₃

Recent Publications

Shaw, Y. S.; DuBois, D. A.; Neilson, R. H. "Boron-Nitrogen Polymer Precursors" *ACS Symposium Series* 1988, 360, 385.

Thoma, R. J.; Prieto, C. A.; Neilson, R. H. "Synthesis and NMR Characterization of New Amino(methylene)phosphines" *Inorg. Chem.* 1988, 27, 784.

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Shaw, Y. S.; DuBois, D. A.; Watson, W. H.; Neilson, R. H. "Boron-Nitrogen Polymer Precursors. Synthesis, Structure, and Stereochemistry of N-Boryl Derivatives of the 1,3,2-Diazaboracyclohexane Ring System" *Inorg. Chem.* 1988, 27, 974.

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Davis, C. E.; Hani, R.; Jinkerson, D. J.; Mukherjee, P.; Scheide, G. M.; Wood, C. E.; Neilson, R. H. "Synthesis and Reactivity of New Phosphorus-Nitrogen and Phosphorus-Nitrogen-Boron Condensation Monomers" *Phosphorus, Sulfur, and Silicon* 1990, 51/52, 161.

Shaw, S. Y.; Neilson, R. H. "Synthesis and Characterization of (Trifluoroethoxy)boranes" *Inorg. Chem.* 1991, 30, 148.