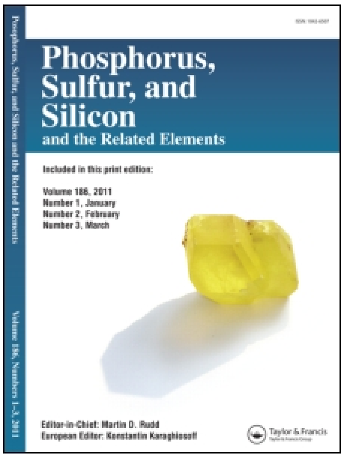

## Phosphorus, Sulfur, and Silicon and the Related Elements

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[a] Department of Chemistry, Box 32908, Texas Christian University, Fort Worth, TX

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# RING SYSTEMS DERIVED FROM N-SILYLPHOSPHORANIMINES

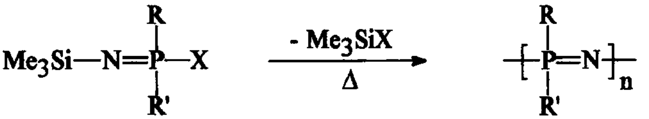
R. H. NEILSON,* K. AZIMI, C. E. DAVIS, R. HANI, D. L. JINKERSON, S. KARTHIKEYAN, J. JI, P. MUKERJEE, N. RETTA, and G. ZHANG

Department of Chemistry, Box 32908, Texas Christian University, Fort Worth, TX 76129.

**Abstract.** The N-silylphosphoranimines, $Me_3SiN{=}PR_2X$, undergo a variety of useful reactions such as condensation polymerization, Si-N bond cleavage, nucleophilic substitution at phosphorus, and deprotonation of pendent P-methyl groups. Several ring systems, including cyclic phosphazenes and novel B-N/P-N hybrid derivatives, are accessible from these Si-N-P reagents.

## INTRODUCTION

The title compounds, N-Silylphosphoranimines of the type $Me_3Si{=}NPR_2X$, are versatile, multifunctional reagents for the synthesis of many types of cyclic as well as linear P-N systems. For example, depending on the steric and electronic effects of the substituents (R) and leaving group (X), their condensation reactions (eq 1) produce cyclic and/or linear polyphosphazenes.[1]



$$Me_3Si{-}N{=}\overset{R}{\underset{R'}{P}}{-}X \xrightarrow[\Delta]{-\,Me_3SiX} \left[\overset{R}{\underset{R'}{P}}{=}N\right]_n \qquad (1)$$

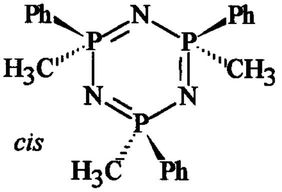
R, R' = alkyl, aryl, $CF_3$ $\qquad$ n = 3, 4, ..
X = Cl, Br, $OCH_2CF_3$, OPh

In addition to condensation polymerization, N-silylphosphoranimines[2] exhibit three other modes of reactivity: (1) silicon-nitrogen bond cleavage by reactive halides,[3] (2) deprotonation/substitution reactions at the pendent P-R groups,[4] and (3) nucleophilic substitution at the P-X site.[5] Employed separately, or in combination, these reactions can produce a wide variety of ring systems including several types of PN and BN/PN hybrid systems. Full details of the synthesis and characterization of these and related compounds will be reported elsewhere.

## RESULTS and DISCUSSION

**Cyclic Phosphazenes.** The nature of the products of the thermal condensation reactions of N-silylphosphoranimines (eq 1) is highly dependent on the type of leaving group present on phosphorus. Thus, while linear high polymers are obtained exclusively from thermolysis of the *trifluoroethoxy* and *phenoxy* derivatives, the P-*halogen* substituted systems (X = Br. Cl) usually give rise to cyclic phosphazenes. In this manner, a series of symmetrically substituted dialkyl phosphazenes, $[R_2P{=}N]_n$ (1: R = Me, Et, *n*-Pr, *n*-Bu, *n*-Hex), were prepared by heating the P-*bromo*phosphoranimines at ca. 150-180 °C for several hours. Generally, mixtures of cyclic trimers (n = 3), tetramers (n = 4), and pentamers (n = 5) are obtained with the trimers being the major products, especially when longer chain alkyl groups are present.

Other types of cyclic phosphazenes have also been recently prepared by variations of these condensation reactions of N-silylphosphoranimines. For example, the Si-N cleavage reaction of the P-$OCH_2CF_3$ precursor with $CF_3CH_2OH$ at room temperature afforded a mixture of cyclic phenyl/methyl phosphazenes from which the pure *cis* isomer (2) was obtained by crystallization. The *cis* configuration of this ring system was confirmed by an X-ray diffraction study. On the other hand, thermolysis of the P-*trifluoromethyl* substituted P-bromo precursors gave mixtures of cyclic trimers and polymers from which the pure trimers (3) were obtained by sublimation. Detailed NMR spectroscopic studies established the *trans* structure of these P-$CF_3$ derivatives.



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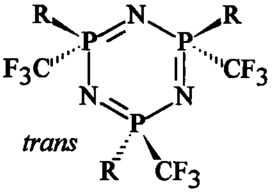
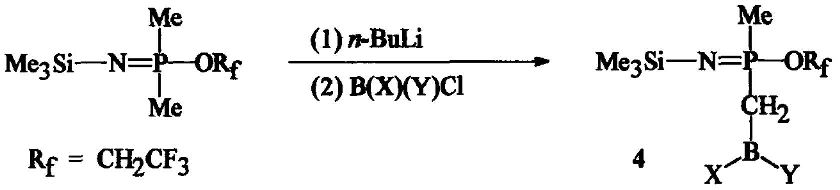
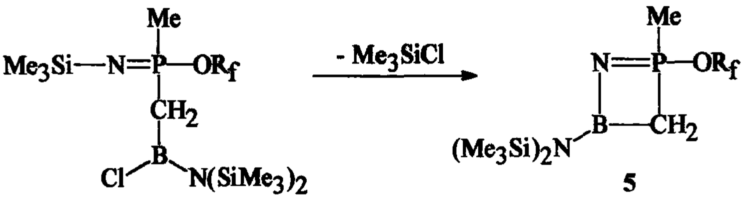


3: R = Ph, *n*-Pr

**Boron-Nitrogen-Phosphorus Systems.** By employing some of the other modes of reactivity of N-silylphosphoranimines, a very wide variety of new derivatives, including several novel P-N/B-N hybrid systems, have been prepared. For example, deprotonation of the P-$CH_3$ group, followed by addition of appropriate chloroboranes afforded the P-C-B products 4 (eq 2). Depending on the nature of the other substituents on boron, these compounds then underwent cyclization (eq 3) or transamination (eq 4) reactions to give new ring systems **5** and **6**, respectively.



(2)



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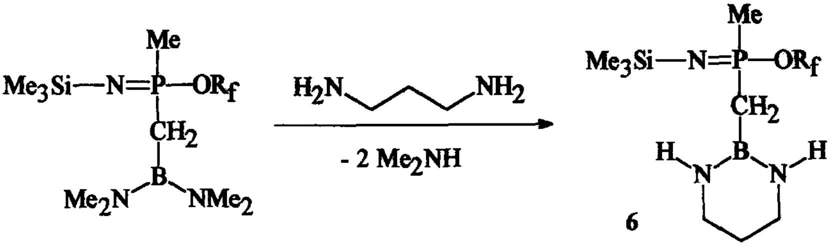
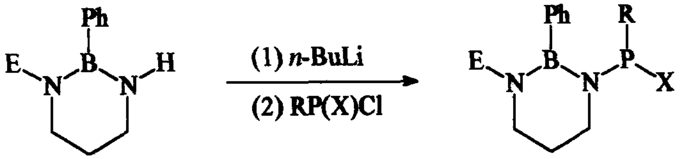


(4)

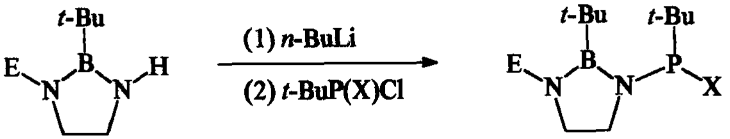
In a different approach, reactions involving nucleophilic substitution at phosphorus by anions derived from diazaboracycloalkanes[6] can also be used to prepare novel B-N ring systems that contain exocyclic N-P linkages. A few examples that have been recently prepared include phosphine (i.e., $P^{III}$) derivatives of both the 6-membered $BN_2C_3$ (**7**, eq 5) and the 5-membered $BN_2C_2$ (**8**, eq 6).



(5)

E = H, $SiMe_3$

**7**: R = Ph, *t*-Bu
X = $NMe_2$, $OCH_2CF_3$

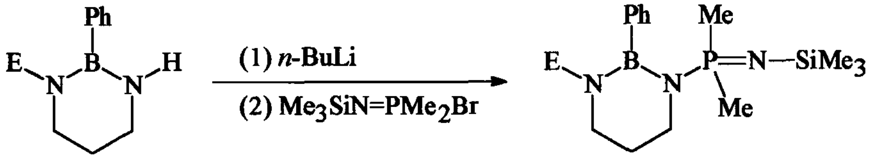


(6)

E = H, $SiMe_3$

**8**: X = Cl, $NMe_2$, $OCH_2CF_3$

We have also employed a similar procedure to prepare some interesting new phosphoranimine (i.e., $P^V$) derivatives **9** of the 6-membered $BN_2C_3$ rings (eq 7). In spite of the rather long chain of main group elements (e.g., Si-N=P-N-B-N-B-N) which some of these compounds contain, they are still stable, distillable liquids.



(7)

**9**: E = H, $SiMe_3$, $B(NMe_2)_2$

Compounds of types **6** - **9** and several related derivatives have been fully characterized by NMR spectroscopy and elemental analysis. The possibility of extending the chain of B-N and P-N bonds in many of these "skeletally stabilized" systems, with the ultimate goal of preparing polymeric analogs, is under active investigation in our laboratory.

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