# SYNTHESIS AND REACTIVITY OF SOME SILICON-NITROGEN-PHOSPHORUS SYSTEMS

by

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I want to thank my parents (Rui Li and Haiyi Shi ) and my wife (Yuan Tian) for their supports. When I feel weak, they light me the hopeful ways and brave me up. So I can keep pursuing my dream.

I would also like to thank friends and colleagues at the department of chemistry, Texas Christian University for their affection and support. Many thanks to the funding from Robert A. Welch Foundation and TCU research.

This acknowledgment will end with my favorite adage "You gain strength, courage and confidence by every experience in which you really stop to look fear in the face".

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# LITERATURE REVIEW

## INTRODUCTION

The synthesis and study of the phosphorus compounds containing silicon-nitrogen (Si-N) functional groups is an area of growing interest during last four decades since these types of compounds show a broad derivative chemistry and are synthetically useful.[1, 2] Many reactions could occur at the phosphorus atom in combination with facile cleavage of the Si-N bond, which make this type of compound useful precursors to some poly(phosphazenes)[3] as well as some low-coordinate phosphorus systems.

One of the most important inorganic polymers nowadays are poly(phosphazenes).[4-8] The properties of polyphosphazenes are determined by the side groups attached to phosphorus. A variety of substituents can be attached to the backbone phosphorus atom, so polyphosphazenes show a very broad spectrum of chemical and physical properties,[9,10] which make them useful for many applications.[11] Depending on the attachments, polyphosphazenes can be flexible at low temperatures, flame retardant, water soluble or repellent, stable at high temperatures, semiconductors[12] or insulators, and biologically active or inert.[13] Traditionally, polyphosphazenes are synthesized by two well-developed methods.

**Ring-opening polymerization.** In 1965, Allcock[14] and co-workers reported the first method to produce non-crosslinked, well-characterized polyphosphazenes via ring-opening polymerization (eq 1).

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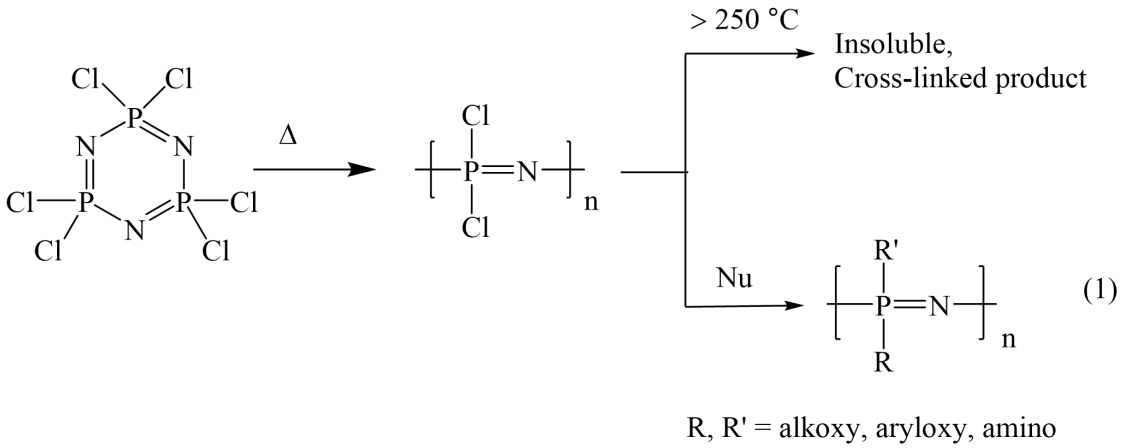


R, R' = alkoxy, aryloxy, amino

The ring-opening method is the most widely-used process. Many alkoxy-, aryloxy-, and partially alkyl/aryl substituted phosphazenes are synthesized by this method. During the heating step, the temperature must be carefully controlled since, when the trimer is heated above 250 °C, some undesirable, insoluble and cross-linked products will form.

**Condensation polymerization.** Condensation polymerization (eq 2) is one of the most successful ways to synthesize organic polymers, especially polyesters and polyamides.

$$n\,E{-}A{-}B{-}X \longrightarrow \left[A{-}B\right]_n + n\,EX \qquad (2)$$

This reaction could be extended to produce phosphazenes. The monomers in reaction (eq 2) should be thermally stable and should contain functional groups that lead to inert byproducts such as silyl ethers. Thus, certain types of *N*-silylphosphoranimines are good candidates for making new types of polyphosphazenes.

In 1980, the second general method for preparing polyphosphazenes was discovered and developed by Neilson and Wisian-Neilson.[15] They obtained the desired

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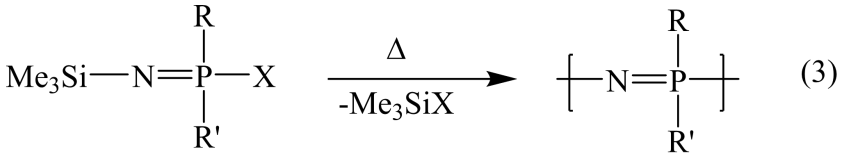
polyphosphazenes via the thermal condensation of *N*-silylphosphoranimine monomers (eq 3). This was the first successful synthesis of fully alkyl-substituted polyphosphazene. This process quantitatively yields polymers with high molecular weight ($M_w \approx 50{,}000$).




(3)

X = alkoxy, aryloxy R, R' = alkyl, aryl

The deprotonation-substitution reaction could occur on both polyphosphazenes and *N*-silylphosphoranimines. This has given a broad derivative chemistry to the N = P moiety.

The major advantage of the condensation approach over the ring-opening method is that it permits the introduction of the desired alkyl/aryl substituents at the small molecule stage prior to polymerization, thus bypassing the step of preparing the dichloro polymer[14] and avoiding the difficulties of its substitution reactions with organic nucleophiles (i.e., RMgX, RLi, etc.).

As discussed above, depending on the substituents attach to phosphorous center, polyphosphazenes could show broad chemical and physical properties. However, by introducing a spacer group into the polymer chain (**Figure 1**), commercially useful properties such as high glass transition temperature, conductivity,[12] etc. might also be possible, while the phosphazene itself keeps its positive properties such as thermal stability. In 1961, Herring[16] prepared the first linear polymer where a phenyl ring

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regularly alternates with the N=P bond. Years later, Lucht and his co-workers[17] did some related research on the electron donating properties of *p*-phenylene phosphine imides.

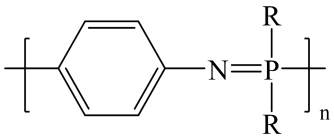

**Figure 1.** Poly(phenylene)phosphazene

In this thesis, two Si-N-P systems containing spacer groups shown in Figure **2** will be mainly discussed. They are both synthetically useful precursors to polyphosphazenes. The first one is (silylanilino)phosphine ($P^{III}$) (**I**) in which phosphorous is three coordinate and trivalent, and the second one is *N*-silylphosphoranimine ($P^{V}$) (**II**) in which phosphorous is four coordinate and pentavalent.

(I) (II)

**Figure 2.** Two types of Si-N-P systems

This literature review will cover the following 3 topics which are most relevant to the research in this thesis.

(1) Synthesis and reactivity of (silylamino)phosphines

(2) Chemistry of *N*-silylphosphoranimines

(3) Si-N-P systems containing spacer groups

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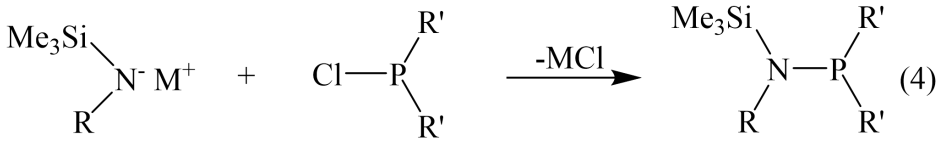
## SYNTHESIS AND REACTIVITY OF (SILYLAMINO) PHOSPHINES

### *Synthesis*

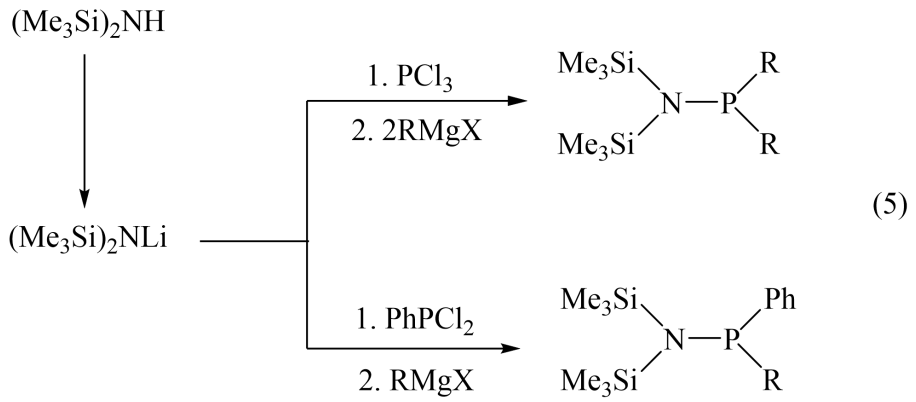
(Silylamino)phosphines were first synthesized in 1960's and 1970's[18] by reacting silyl amides with chlorophosphines (eq 4). In fact, some scientists are still using this method to prepare some (silylamino)diphenylphosphines because $Ph_2PCl$ is a cheap, readily available reagent. However, this method is not well suited for the preparation of dialkylchlorophosphines due to synthetic difficulty and handling large quantities of alkyl (chloro)phosphine reagents.



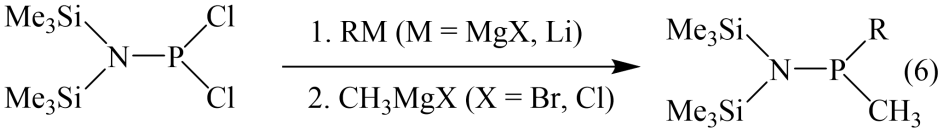

(4)

M = Li, Na  R = $SiMe_3$, alkyl  R' = Ph, Me, $CF_3$

Around the 1980's, a very versatile and convenient method, known as the Wilburn method, was discovered and developed by Neilson and Wilburn,[19] (named in the honor of Neilson's late co-worker, J. C. Wilburn). This is a very useful "one-pot" method to make both symmetrically substituted (silylamino)phosphines (eq 5) and unsymmetrically substituted (silylamino)phosphine derivatives (eq 6).[20]




(5)




(6)

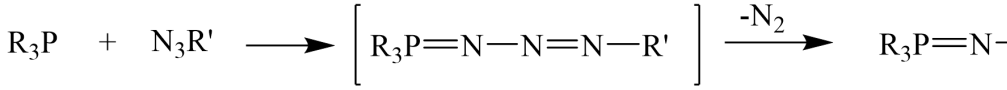
R = $CH_2SiMe_3$, *n*-Pr, *i*-Pr, *t*-Bu, $CH{=}CH_2$, $C_6H_4OCF{=}CF_2$

In summary, the Wilburn method is an easy, high-yield route to prepare almost any dialkyl and alkyl/phenyl substituted (silylamino)phosphine.

***Reactivity***

(Silylamino)phosphines are usually oxidized to *N*-silylphosphoranimines ($P^{III}$- $P^{V}$) to become precursors (containing Si-N=P linkage) of polyphophazenes. Two major reaction types will be reviewed in this thesis.

**Staudinger Reaction.** In the Staudinger reaction (eq 7), an azide will react with phosphines ($P^{III}$) to form phosphoranimines ($P^{V}$).

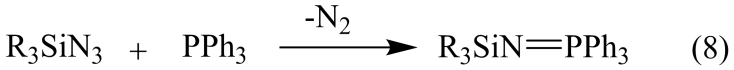



(7)

R, R' = alkyl, aryl

`

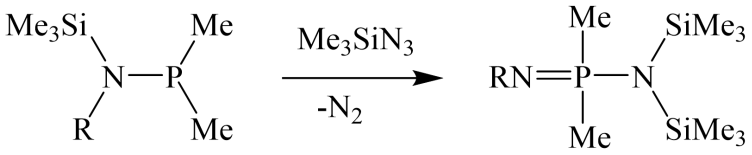
Staudinger Reaction was discovered and named after Herman Staudinger in 1919.[21] The major drawback of this method is that organic azides often have an explosive nature. However this problem can be overcome by using organosilicon azides. In 1962, the novel *N*-silylphosphoranimines were synthesized by West and Thayer[22] (eq 8). This opened a new way for the synthesis of *N*-silylphosphoranimines.




(8)

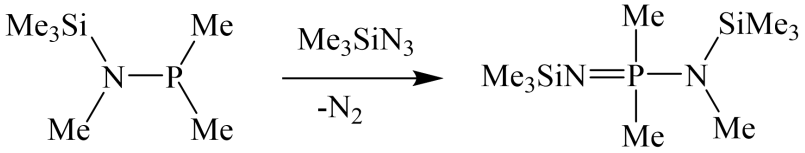
R = Ph, alkyl

With different substituents on the phosphorus atom, some new phosphoranimines were prepared by Neilson and co-workers[23] (eqs 9 & 10) with trimethylsilylazide and various phosphines.




(9)

R = *t*-Bu, $SiMe_3$, $SiMe_2$(*t*-Bu)




(10)

It was interesting to find that if R group on the amine is large enough, a [1-3]-silyl migration can occur (eq 9). Similar migrations were observed when the Staudinger reaction involved phosphines containing at least one alkoxy group (eq 11).[24]

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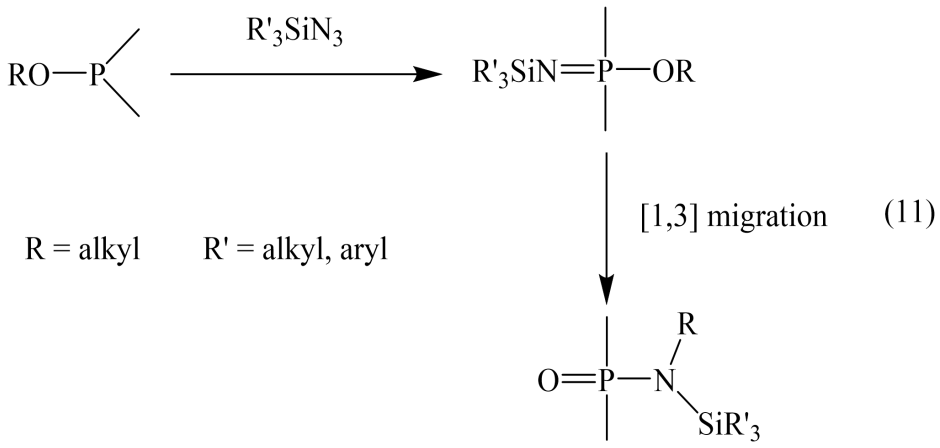
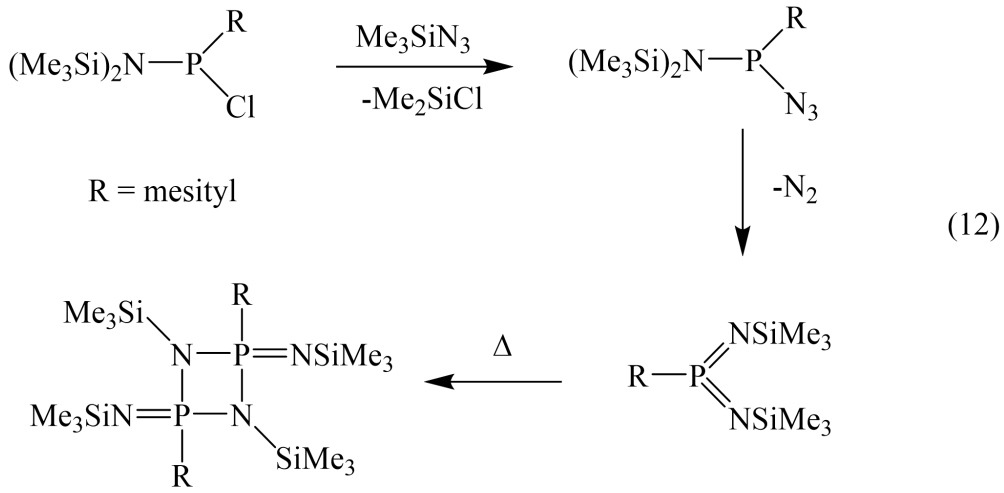
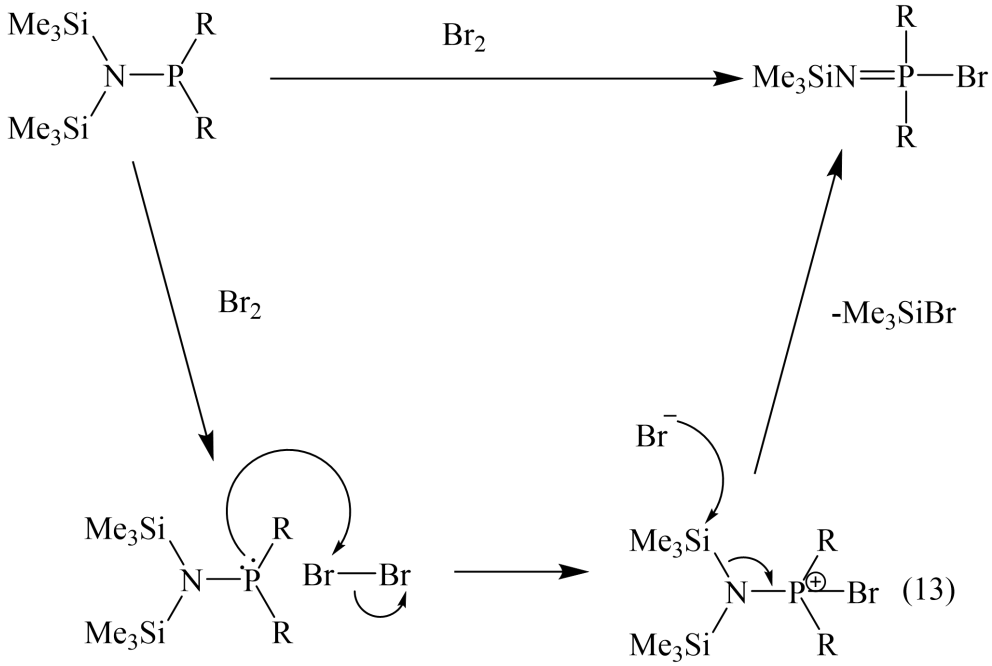



If halophosphines are used in the Staudinger reaction, the reaction will proceed in a different manner (eq 12). Azidophosphines are first formed and then decompose to afford cyclic P-N compounds.[25]



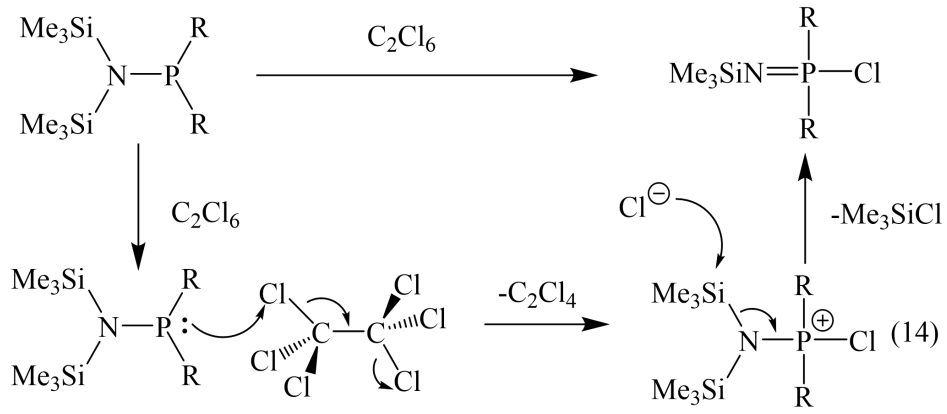

**Oxidation Reaction.** The second important reaction type to prepare *N*-silylphosphoranimines would involve elimination (usually halosilane) reactions. Many oxidizers (such as $Br_2$, $O_2$, $CCl_4$ and $C_2Cl_6$) could convert the (silylamino)phosphines into phosphazene precursors, i.e., *N*-silylphosphoranimines. This is illustrated by the bromination reaction (eq 13).




(13)

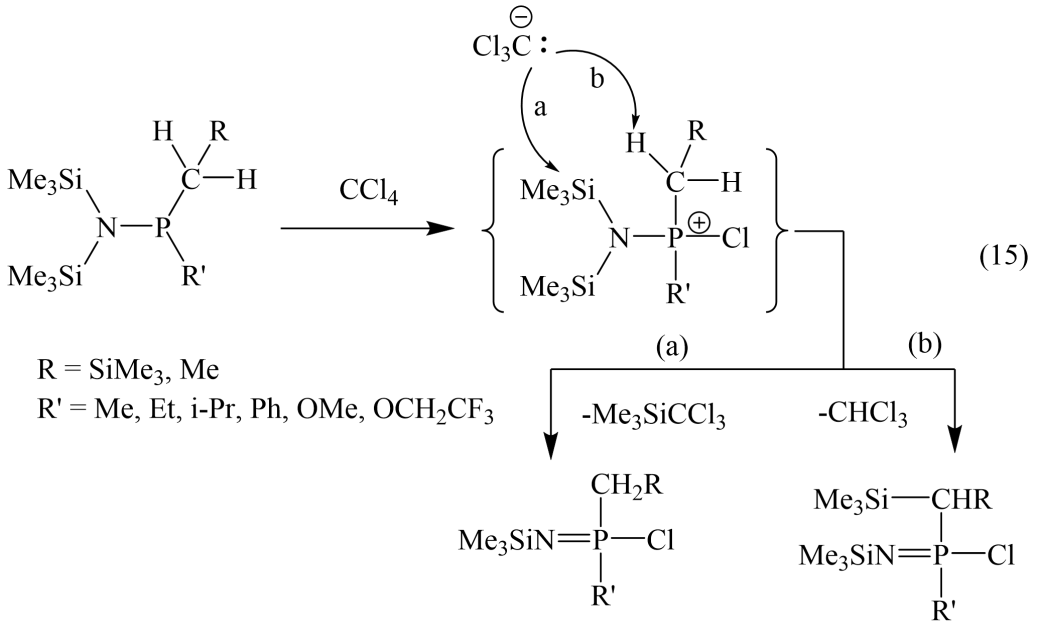
R = alkyl, aryl, alkoxy, aryloxy, dialkylamino, etc.

Halogenation reagents like $Br_2$ react with (silylamino)phosphines, eliminating $Me_3SiBr$ to give the desired *N*-silylphosphoranimine.[26] This process involves a nucleophilic attack by the phosphorus atom on the halogen moiety to form a phosphonium ion intermediate, which then undergoes a halosilane elimination to form the P-halogenated product. The products made from reaction (eq 13) are not thermally stable. Upon thermolysis, they often form cyclic phosphazenes. In a similar way, (silylamino)phosphines could react with hexachloroethane ($C_2Cl_6$) to give phosphoranimines (eq 14).[27]




R = alkyl, aryl, alkoxy, aryloxy, dialkylamino, etc.

The reactions of (silylamino)phosphines with $CCl_4$ (eq 15) are also reported and studied.[28] There are two attack targets from the $CCl_3^-$ anion in this reaction: (1) Attack at silicon (eq 15, path a) with a Si-N cleavage, (2) Abstraction of a proton from the carbon α to phosphorus (eq 15, path b) to yield chloroform and a C-silylated phosphoranimine. The second product is probably formed through a [1-3]-silyl shift from nitrogen to carbon in an ylide intermediate.




R = $SiMe_3$, Me
R' = Me, Et, i-Pr, Ph, OMe, $OCH_2CF_3$

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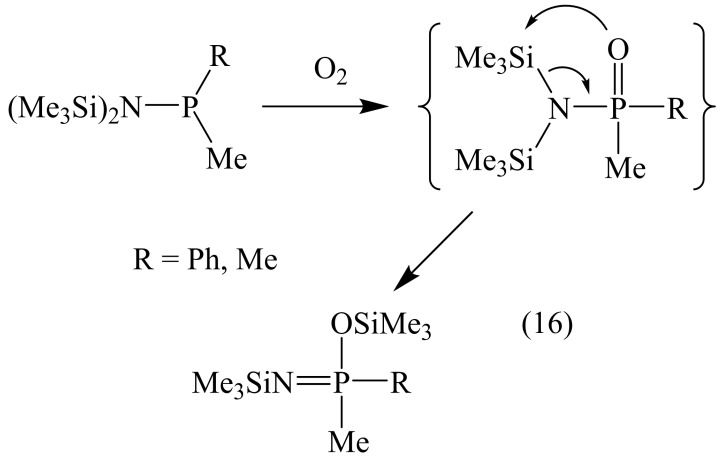
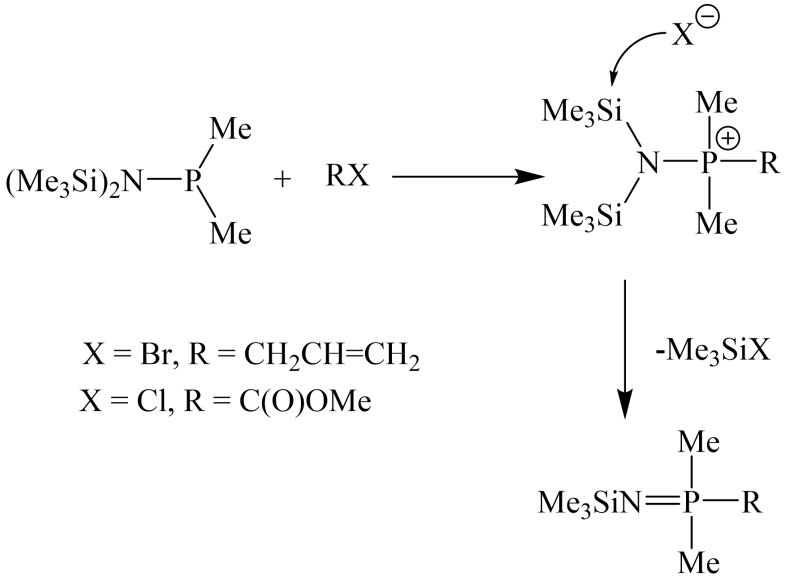
It is also reported that (silylamino)phosphines would react with $O_2$ to form *N*-silyl-*P*-siloxyphosphoranimines.[29] The oxygen could oxidize $P^{III}$ in phosphine to a phosphorus oxide intermediate. After that, a silyl migration occurs from nitrogen to oxygen (eq 16).




(16)

Neilson[30] and co-workers also reported that organic halides react with (silylamino)phosphines to form the phosphonium salt which then would readily undergo elimination of halosilane to give *N*-silylphosphoranimines.(eq 17).




(17)

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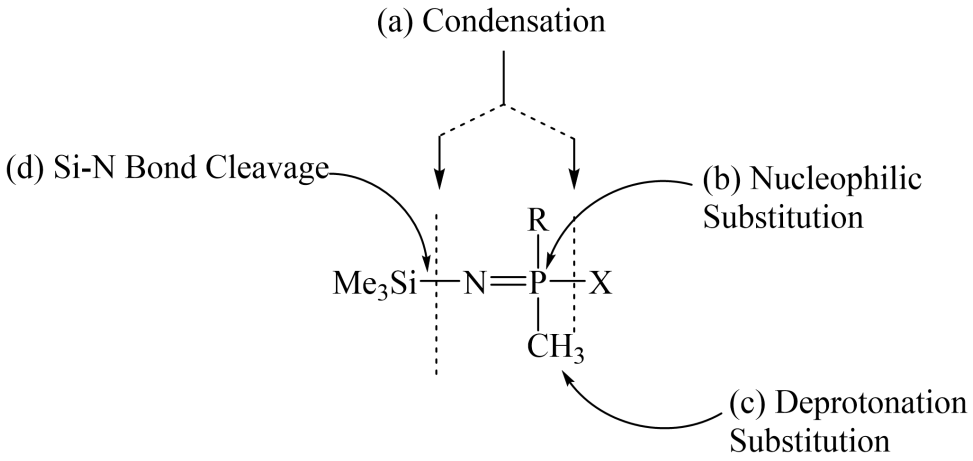
## CHEMISTRY OF *N*-SILYLPHOSPHORANIMINES

The *N*-silylphosphoranimines have a broad range of synthetic chemistry. Some of the derivatives are very useful precursors to polyphosphazenes. There are 4 major types of reactivity (**Scheme 1**).




**Scheme 1**. Reactive sites of *N*-silyphosphoranimines

**Condensation Polymerization**. The first evidence that phosphazenes could be synthesized by condensation polymerization including elimination of a silane (eq 18) was discovered by Wisian-Neilson and Neilson.[31] The expected products all underwent further fluorosilane elimination to give cyclic phosphazenes. Mass spectroscopy showed that there are trimers and tetramers in the final product.

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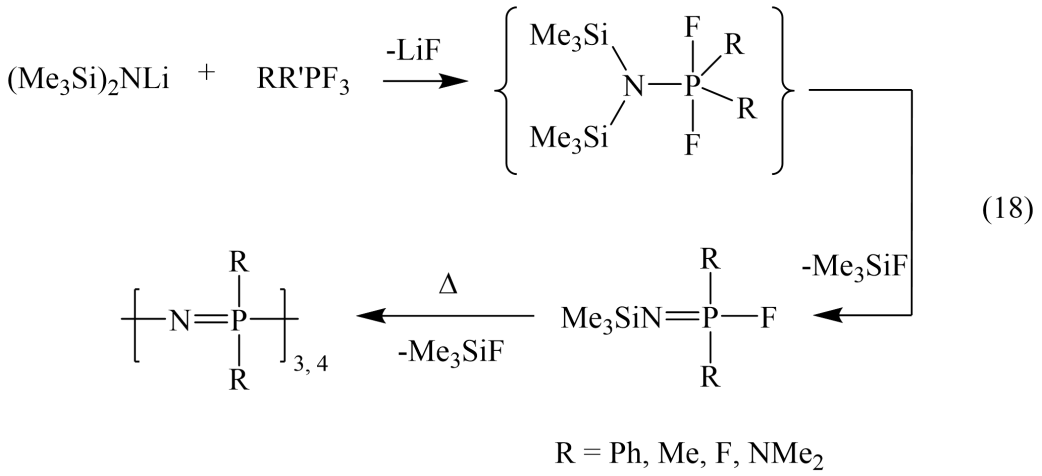
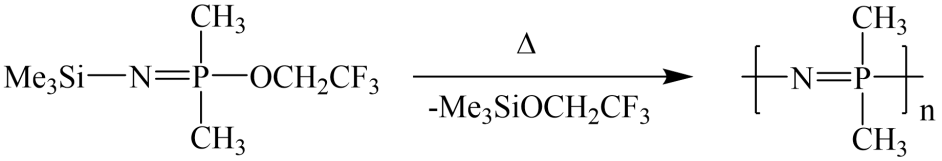



(18)

In 1980's, Wisian-Neilson and Neilson successfully synthesized the first fully substituted poly(alkyl/arylphosphazene) through the thermal condensation of an *N*-silyl-*P*-trifluorethoxyphosphoranimine (eq 19).[15] This method is smooth and quantitatively yields polymers with high molecular weights ($M_w \approx 50{,}000$).




(19)

The authors also stated that aryl (-OPh) substituted *N*-silylphosphoranimines can undergo condensation reaction to form polyphosphazenes.[15] Later on, Neilson and co-workers developed this condensation process as a general method for the preparation of polyphosphazene (eq 3).

**Nucleophilic Substitution at Phosphorus**. Many potential leaving groups (such as alkoxy, amino or aryloxy) could be added to the *N*-silylphosphoranimines through a nucleophilic substitution reaction for future use (eq 20).

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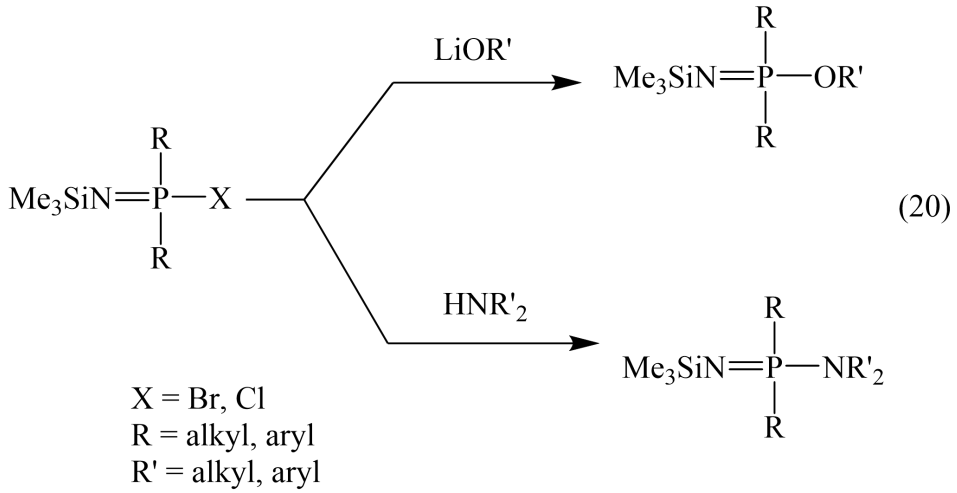
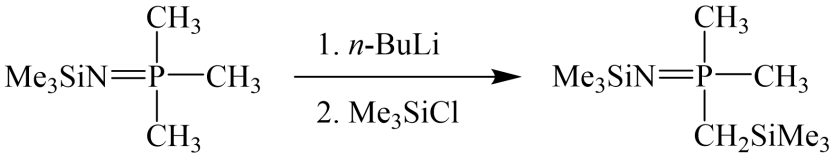



(20)

**Deprotonation-Substitution at the *P*-CH$_3$ Group**. It was first reported by Schmidbaur[32] that the methyl group on a P atom could be deprotonated by *n*-BuLi and then substituted by $Me_3SiCl$ (eq 21) under certain conditions.




(21)

There were literature reports[33] reporting that *P*-methyl groups on polyphosphazenes could be deprotonated then reacted with an electrophile. However, Neilson and coworkers[34-37] also found that, under mild conditions, the methyl group in a variety of phosphazene precursors could be deprotonated by *n*-BuLi to yield a carbanion intermediate (eq 22). Then, the carbanion intermediate in THF reacted with different kinds of alkyl, silyl halides or chlorophosphines to give the desired *N*-silylphosphoranimines. The carbanion also reacted with bromine to afford the bromo-methyl derivatives.

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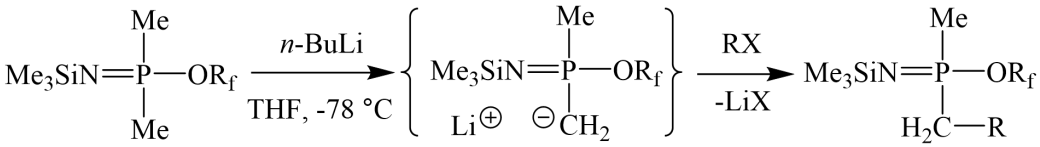
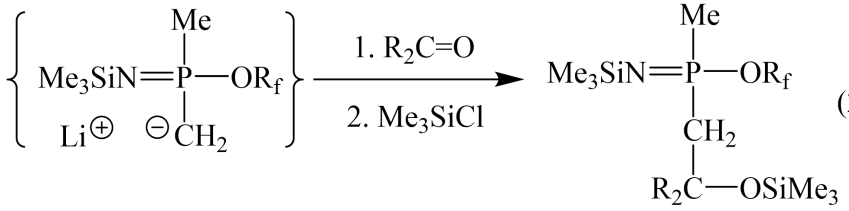



(22)

$R_f = CH_2CF_3$
R = Me, $CH_2Ph$, $CH_2CH{=}CH_2$, $PPh_2$, $P(NMe_2)_2$

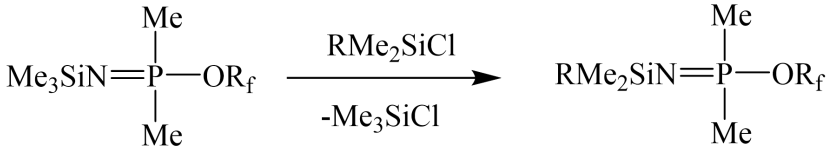
The carbanion intermediate[34-37] could also react with other electrophiles including carbonyl compounds. In this reaction, the carbanion intermediate anion will be quenched with $Me_3SiCl$ to afford the *C*-siloxy derivatives (eq 23).




(23)

$R_f = CH_2CF_3$
$R_2C(O)$ = MeC(O)Me, PhC(O)Me, PhC(O)H, MeC(O)CH=$CH_2$

**Si-N bond Cleavage Reactions.** The Si-N bond in phosphoranimines is easy to break under a nucleophilic attack due to the high polarity of the bond. A good example of this type of reactivity is the trans-silylation process (eq 24).[38]




(24)

$R_f = CH_2CF_3$
R = Ph, $CH{=}CH_2$, $CH_2Cl$, $CH_2(CH_2)_2C{\equiv}N$

Bis/tris(phosphoranimino)phosphines could be synthesized by reacting phosphoranimine with di/trichlorophosphines (eq 25).[39]

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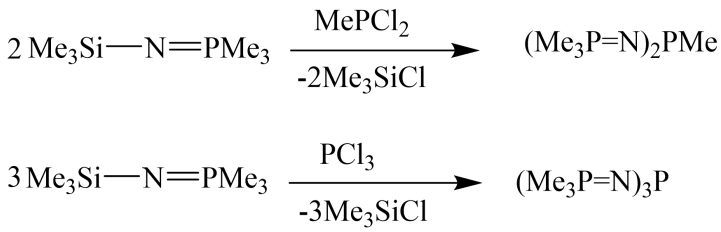
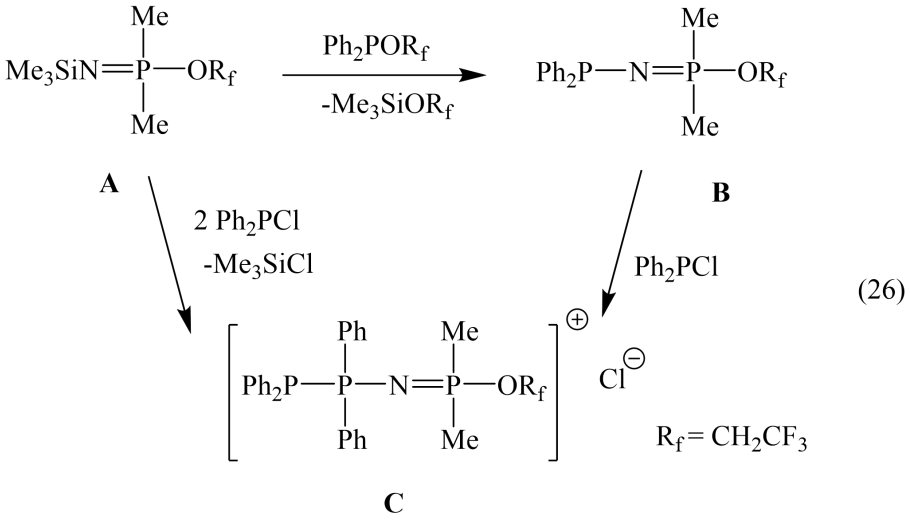


(25)

The Si-N bond in phosphoranimines such as **A** (eq 26) could also be broken in reactions with diphenyl(trifluoroethoxy)phosphines. This phosphine reacts with **A** to yield a novel P3-N-P5 derivative **B**, which then will react with another molecule of chlorodiphenylphosphine to afford the phosphonium salt **C** (eq 26).



(26)

## Si-N-P SYSTEMS CONTAINING SPACER GROUPS

It was reported that the glass transition temperature ($T_g$) of a polymer system could be increased when the rigidity of the polymer backbone is increased.[40] In other words, incorporation of a rigid spacer group (such as a phenyl ring) into the phosphazene back-bone should lead to polymers with higher $T_g$ values. Wang[41] also suggested that incorporation of a spacer group into the polymer back-bone could increase the

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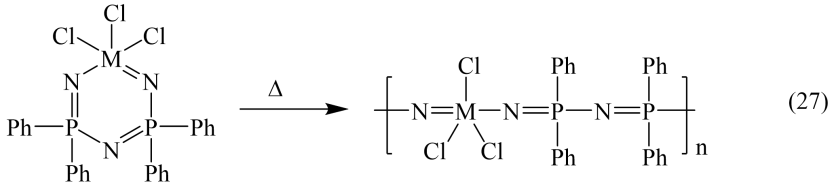
conductivity of the system while maintaining key properties such as high thermal stability. Therefore the synthesis of poly(phenylene)phosphazene seems a promising project.

(1) **Polymers with Spacer Groups from Ring-Opening Polymerization (ROP)**.

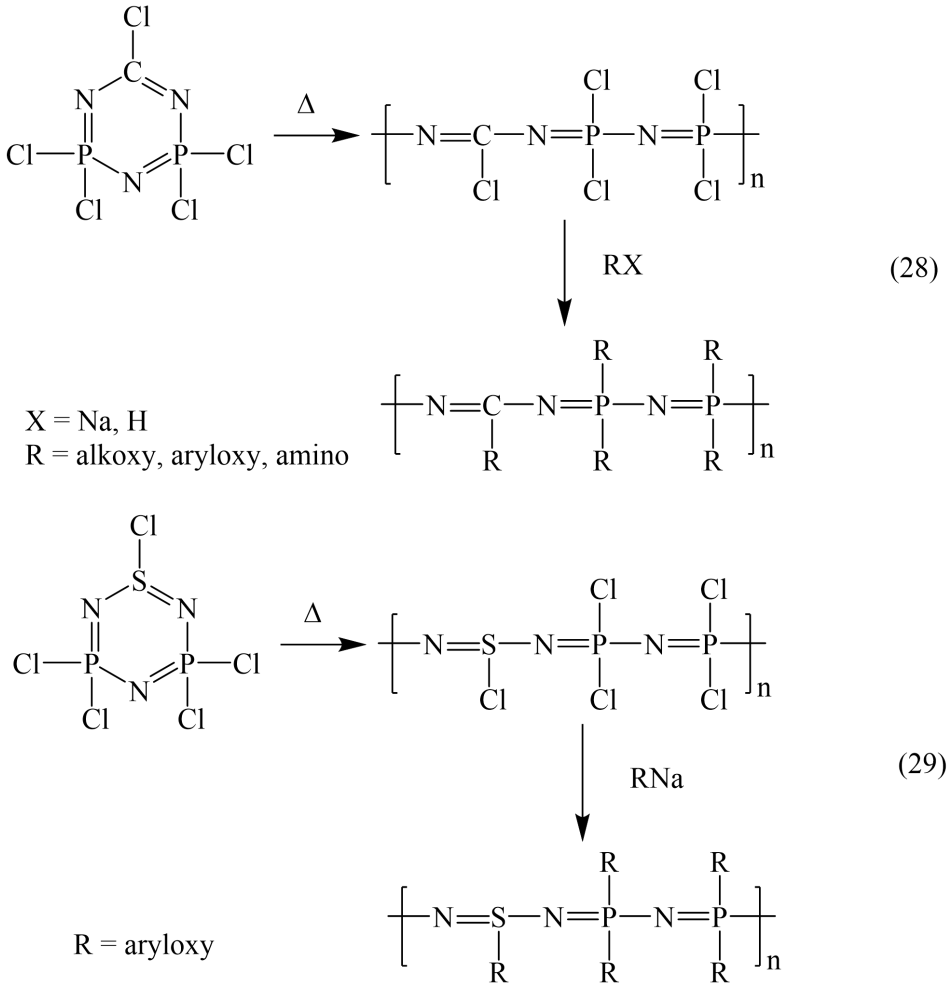
Scientists are looking for new and better materials for electronic and ceramic applications. In order to accomplish this, some polymers with a spacer atom/group have been prepared. In 1989, Roesky[42] discovered the synthesis of stable polyphosphazenes that included transition metals in the polymer chain (eq 27).




M = Mo, W

(27)

Allcock and co-workers made some polyphosphazenes with either carbon (polycarbophosphazenes) (eq 28) or sulfur (polythiophosphazenes) (eq 29)[43] with spacer groups in the back-bone by ROP. Since mobility of the polymer chain is lowered by replacing the P atom with a C atom, the glass transition temperatures ($T_g$) of the polycarbophosphazenes are found to be much higher than the analogous polyphosphazenes. The $T_g$ values of the thiophosphazenes are between most of the analogous phosphazenes and carbophosphazenes (20-110℃).




(28)

(29)

Manners also prepared some poly (chlorothionyphosphazenes)[44] with higher oxidation states of sulfur ($S^{VI}$) by the ROP method followed by nucleophilic substitution at the phosphorus center to replace the halogen. Unlike the C-Cl, P-Cl or S (Ⅳ)-Cl bonds, the S(Ⅵ)-Cl bond in poly(thionylphosphazenes) is quite stable and cannot be replaced by normal nucleophilic substitution. However, the S(Ⅵ)-Cl bonds do undergo dehydrohalogenation reactions to give the amino substituted poly(thionylphosphazenes) as shown below (eq 30).

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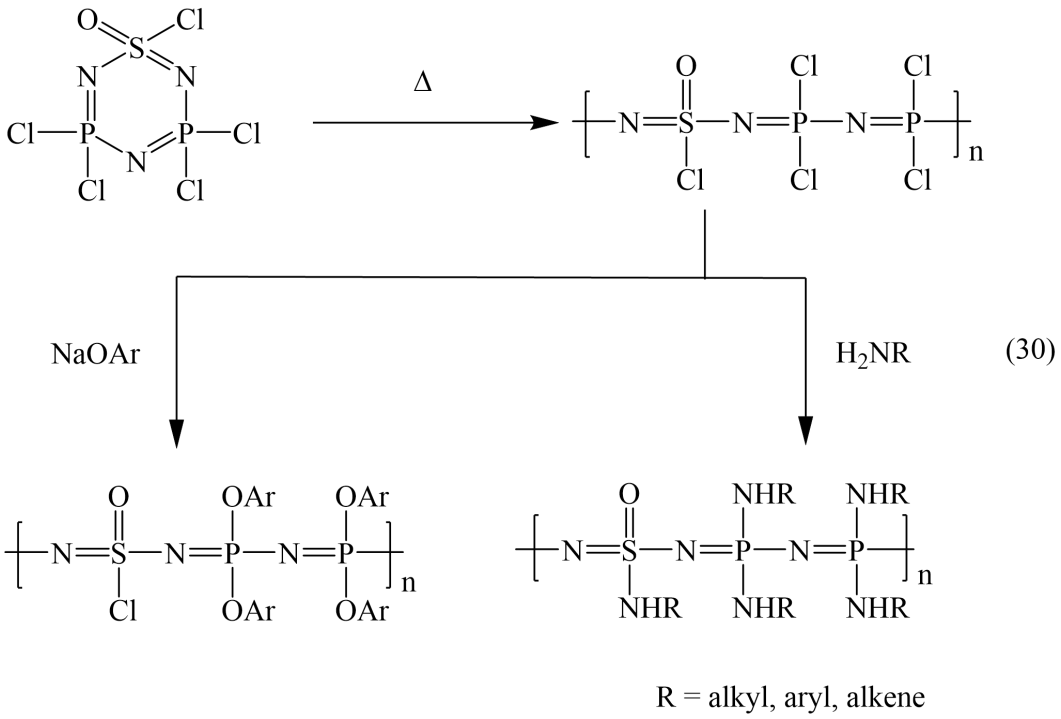


(30)

(2) **Polymers from Condensation Methods**

It is preferred to use the condensation method for making polyphosphazenes with spacer groups because the Si-N-P precursors can be fully alkyl/aryl substituted during the process. It is reported that when an *N*-silylphosphoranimine is reacted with an *N*-silylsufonamidate,[45] a monomeric thionylphosphazene is formed. Then the monomer will afford the poly(thionylphosphazene) via thermal condensation (eq 31). However, the monomer can also be protonated and then polymerized to poly (thionylphosphazene) at a lower temperature.[46]

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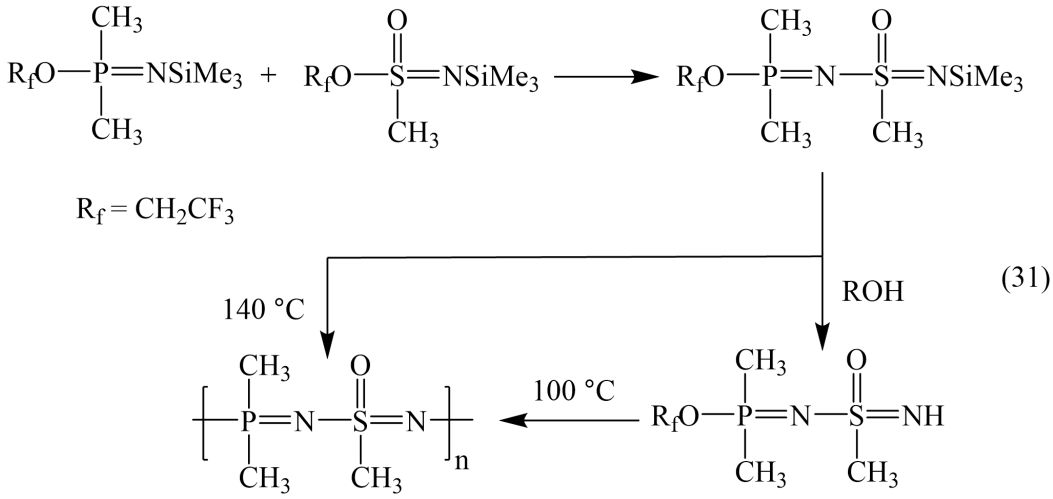
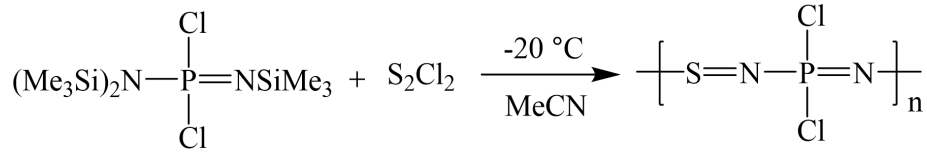


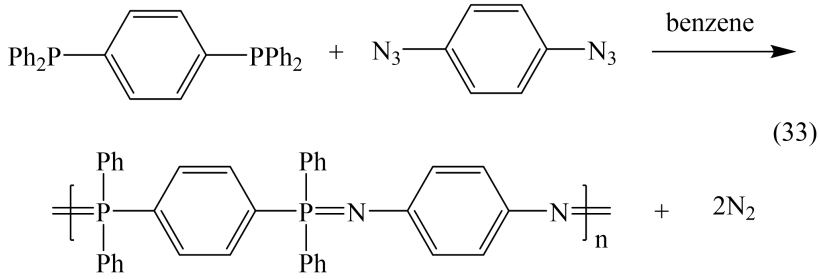

(31)

Poly(thiazylphosphazenes), hybrids of poly (sulfur nitride) and polyphosphazenes, were also reported in 1996 (eq 32).[47]




(32)

The Staudinger reaction can be used to prepare phosphazenes with spacer groups. Herring[48] reported the synthesis of a polymeric product with phosphorus, nitrogen and benzene rings in the backbone. A diazide and a diphosphine react to give a polyphosphazene analog as below (eq 33).




(33)

Some other polymers were prepared in the same manner (eq 34).[49] Their molecular weights are in the range 1,800-3,600 with $T_g$ values ranging from 100-300 °C.

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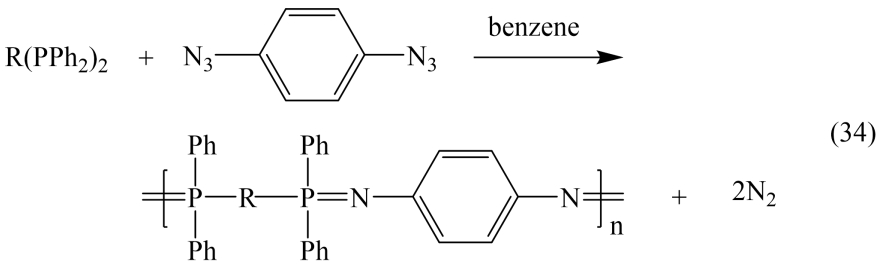
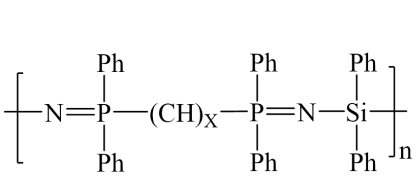


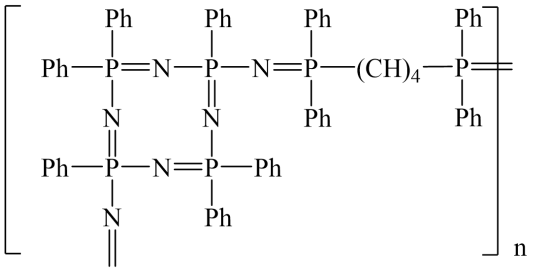

(34)

$R = (CH_2)_2, (CH_2)_3, (CH_2)_4, (CH_2)_5, C_6H_4$

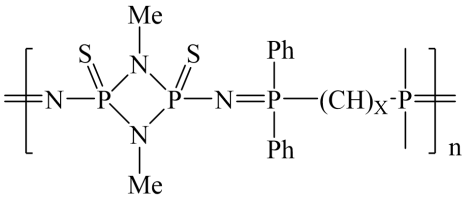
There are four more types of precursors with spacer groups that have been used with diazides to synthesize related polymers: (1) silanes[50] (2) phosphazenes[51] (3) dithiodiazadiphosphetidines[52] and (4) decaborane.[53]



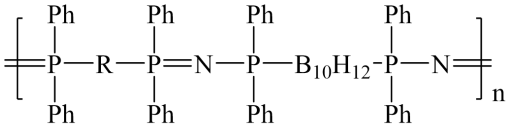

Silane




Phosphazene

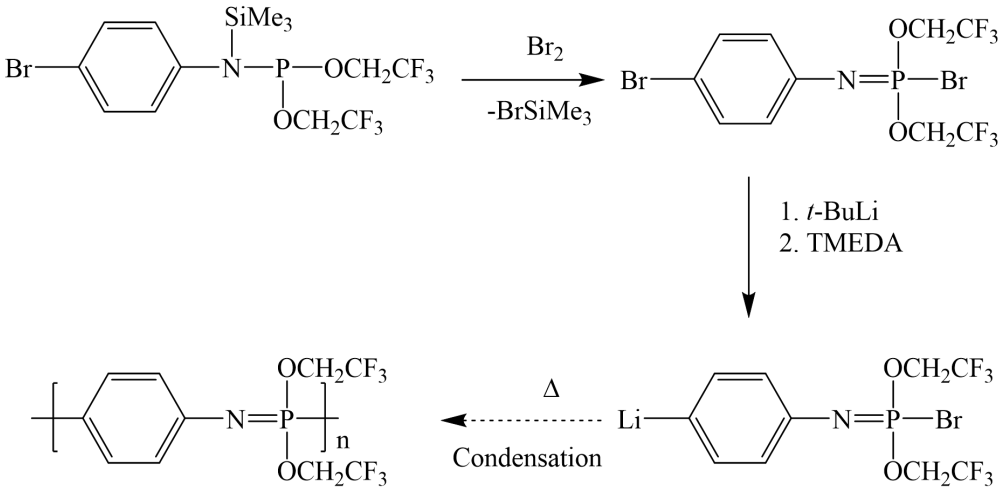



Dithiodiazadiphosphetidine



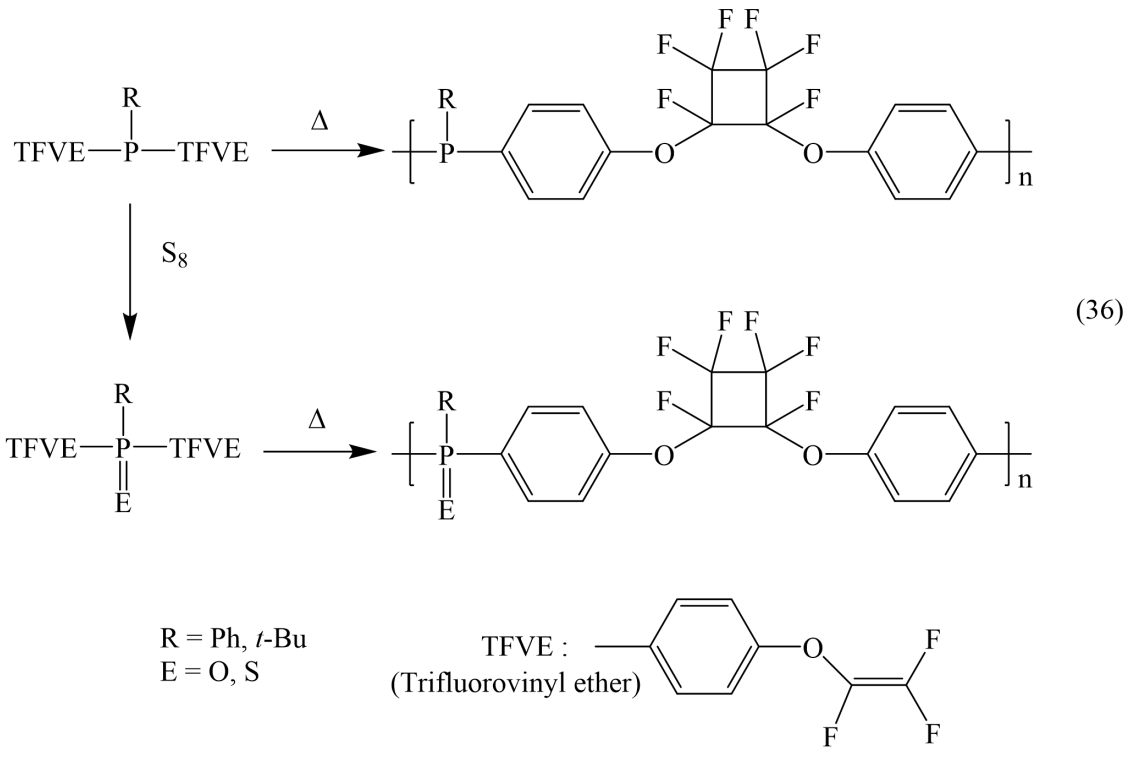

Decaborane

Some preliminary results reported by Wang[54] indicated that poly(phenylenephosphazenes) could be prepared by a condensation reaction (eq 35) using $Br_2$ as an oxidizing reagent.




(35)

In 1998, Ji and Neilson[55] reported some interesting perfluorocyclobutane (PFCB) phosphorus polymers with spacer groups in the back-bone by thermal condensation reactions (36).




(36)

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## CONCLUSIONS

Polyphosphazenes and their precursors have attracted more and more attention from scientists due to their variety of chemical and physical properties. They can be candidates for many applications. This is mainly because many substituents could be added to the P center, which give them good synthetic versatility. The attachments on P center can be introduced at either the polymer stage or the monomer stage.

Among many polyphosphazenes with different side groups, it is interesting to look into poly(phenylene)phosphazene in which a spacer group appears in the polymer back-bone. This thesis will present the synthesis and reactivity of various types of precursors to poly(phenylene)phosphazenes including (silylanilino)phosphines and *N*-silylphos-phoranimines.

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# SECTION ONE

## SYNTHESIS OF (SILYLANILINO)PHOSPHINES AND THEIR PRECURSORS

### 1. Introduction

As we mentioned earlier, compounds containing Si-N-P bonds play an important role in synthetic chemistry. Some of them are useful precursors to polyphosphazenes. A wide variety of oxidation and substitution reactions at phosphorus atoms combined with facile Si-N bond cleavage often leads to intermolecular silyl group rearrangement or elimination of small-molecule silane byproducts. In this section, we will discuss the synthesis of a series of (silylanilino)phosphines. These novel phosphines are similar to traditional (silylamino)phosphines, but with a bulky group (phenyl group) connected to the nitrogen atom. These starting materials could potentially be used as precursors to poly(phenylene)phosphazenes. The literature review presented some methods to prepare (silylamino)phosphines, however the best route to synthesize such phosphines at present appears to be the "Wilburn" method. The synthesis and characterization of these (silylanilino)phosphines will be presented in this section.

### 2. Results and Discussion

**Synthesis of Silylaniline Starting Materials (A-F).** The silylaniline starting materials (**A-F**) were prepared (eq 1) in good yields from *p*-bromoaniline. When

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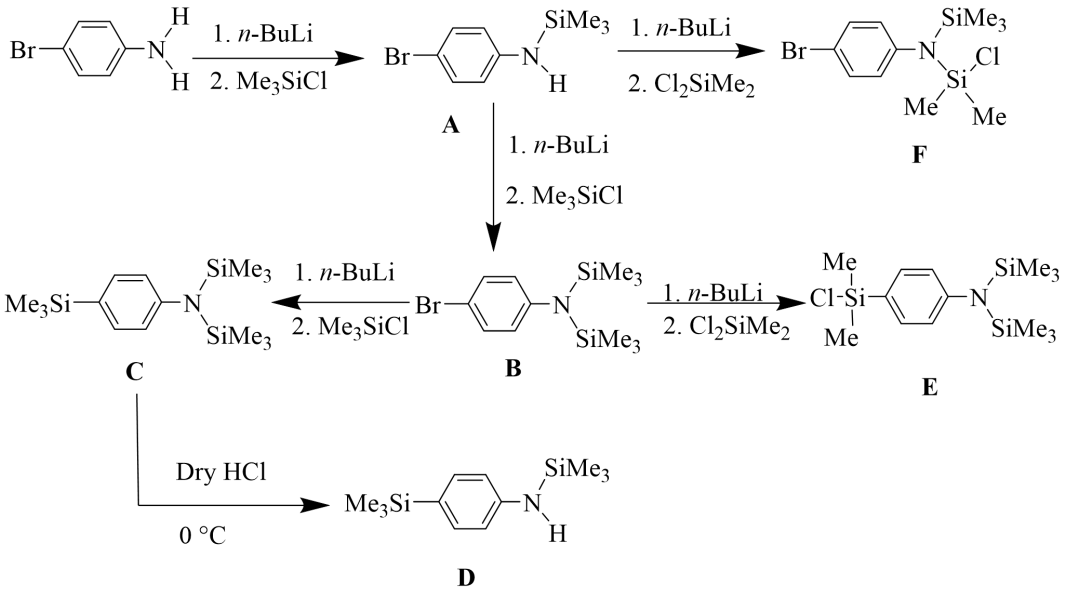
*p*-bromoaniline was reacted with one equivalent of *n*-BuLi, followed by trimethylchlorosilane, the *N*-monosilylated compound **A** was formed. Compound **A**, on reacting with one equivalent of *n*-BuLi, followed by addition of the trimethylsilyl group, afforded the *N*-disilylated compound **B**. Treatment of compound **A** with *n*-BuLi and dichlorodimethylsilane gave the N-Si-Cl derivative **F.** Compound **C** was formed by the metal-halogen exchange reaction of **B** with *n*-BuLi, followed by a substitution reaction with trimethylchlorosilane. The aryl-Si-Cl substituted derivative **E** was formed by reacting compound **B** with one equivalent of the *n*-BuLi, followed by addition of the chlorodimethylsilyl group. Compound **D** was formed by the N-Si bond cleavage reaction of compound **C** with dry HCl.




The compounds **A-F** are air/moisture sensitive, colorless to light yellow colored, distillable liquids. On standing, compound **A** usually crystallizes to a low-melting yellow

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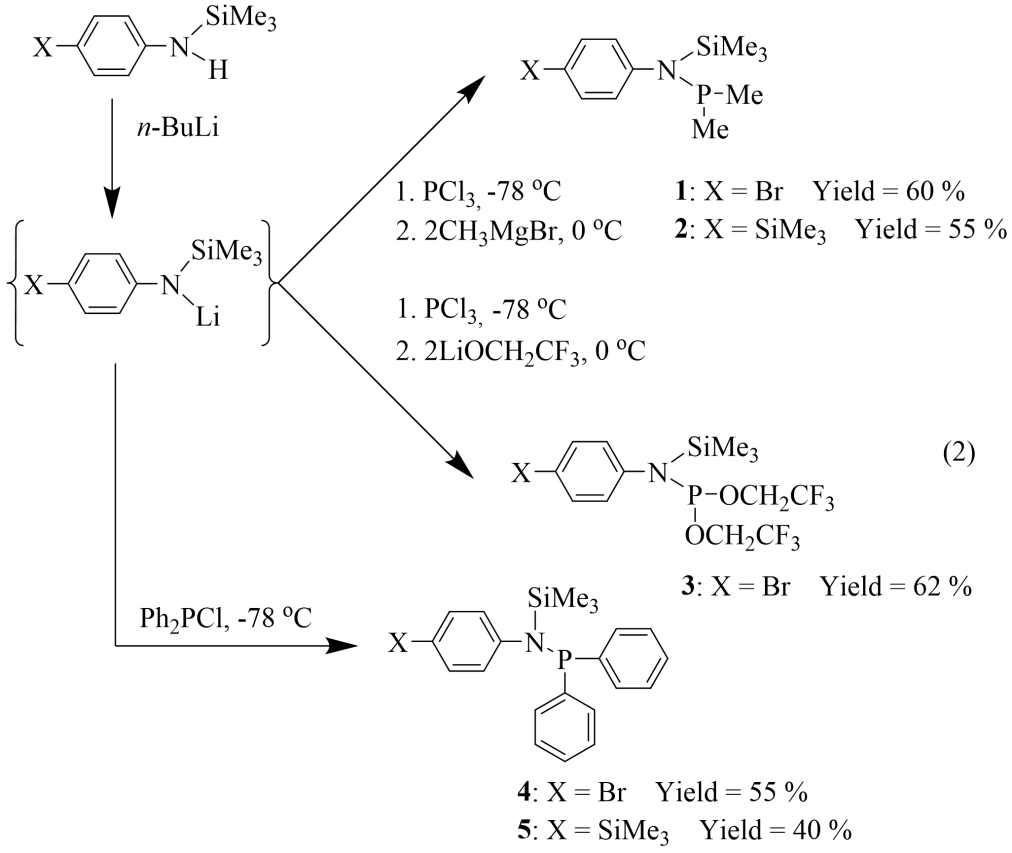
to brown solid. Compounds **A-F** were characterized by $^{1}H$, $^{13}C$ NMR spectroscopy (Tables 1-6). Some $^{13}C$ assignments of phenyl carbons are based on similar data reported by Wang[54] and Devulapalli.[56]

**Synthesis of (silylanilino)phosphines.** Some novel (silylanilino)phosphines were prepared in a standard "Wilburn" procedure (eq 2, 3).[19] In a typical deprotonation-substitution process, the N-H group was deprotonated by *n*-BuLi with subsequent addition of a chlorophosphine reagent, followed by treatment with various organolithium or Grignard reagents to afford the new (silylanilino)phosphines **1-9**.



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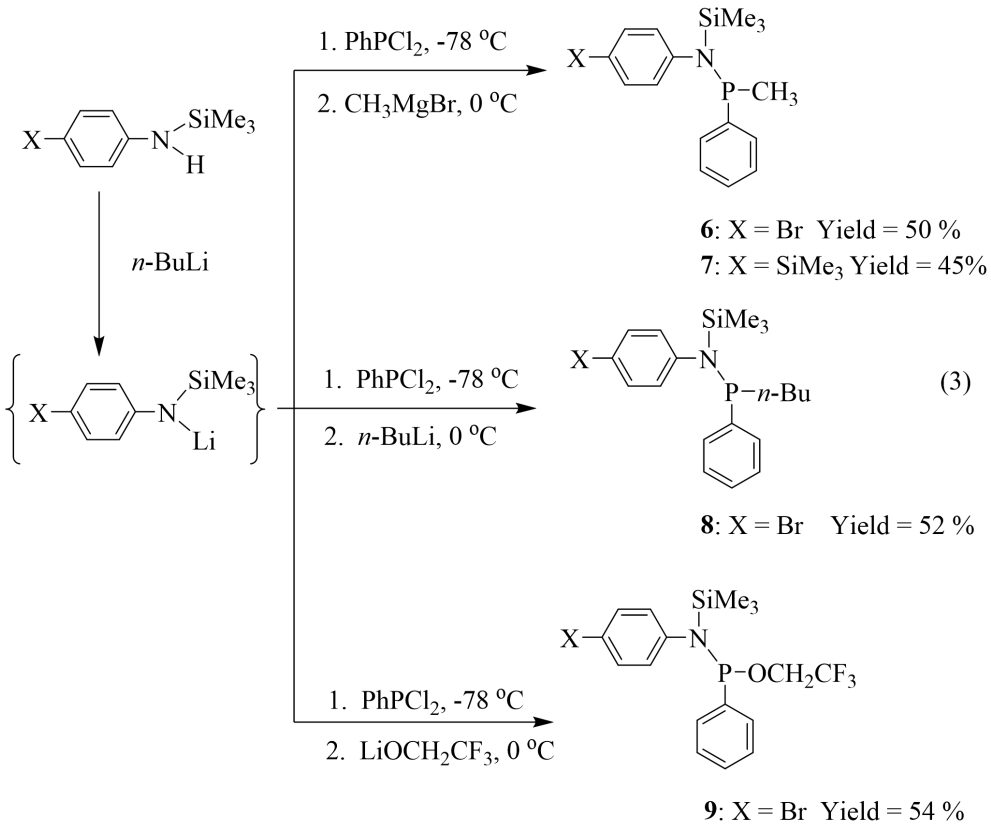
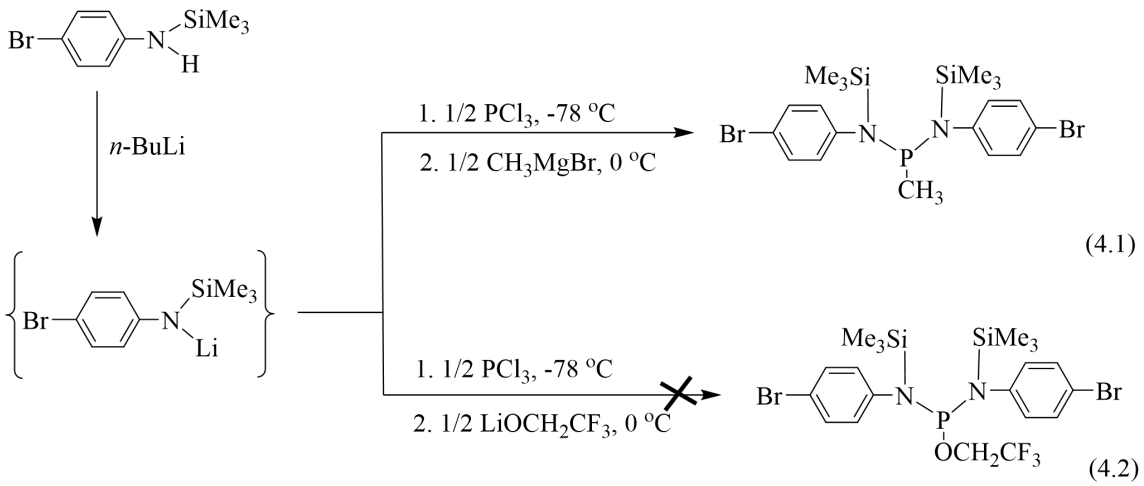



(3)

Compounds **1-3, 6-9** are colorless to pale yellow and air/moisture-sensitive liquids. They were all purified by long path vacuum distillation (fractional distillation). These phosphines were characterized by $^{1}H$, $^{13}C$, $^{31}P$ NMR spectroscopy (Tables 7-15). The diphenyl phosphine derivatives **4** and **5** solidified quickly after distillation or during the distillation process to form white wax-like solids.

According to Devulapalli[56] an interesting phosphine could be prepared with different stoichiometry of reagents (eq 4.1). However, in our work, when $LiOCH_2CF_3$ was used instead of $CH_3MgBr$, the reaction did not occur (eq 4.2). One possible reason is that the larger group $OCH_2CF_3$ will not do the nucleophilic attack on the crowded chlorophosphine intermediate.




## 3. Experimental section

**Materials and General Precursors.** All reagents were obtained from commercial sources and used without further purification: $PCl_3$, $PhPCl_2$, $Ph_2PCl$, *p*-bromoaniline, $Me_3SiCl$, *n*-BuLi (3.0 M in ether), etc. $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Varian 300 or Bruker-400 spectrometers using $CDCl_3$ as the solvent. All reactions and other manipulations were carried out under dry nitrogen or under vacuum unless otherwise specified.

**Preparation of Silylaniline Reagent A.** A 3-neck, 3000 mL, round-bottom flask, equipped with a mechanical stirrer, $N_2$ inlet, rubber septum and an addition funnel, was charged with $Et_2O$ (1500 mL) and $BrC_6H_4NH_2$ (172.03 g, 1 mol). The mixture was cooled to 0 °C and *n*-BuLi (430 mL, 1.075 mol) was added slowly via addition funnel. The reaction mixture was allowed to warm to room temperature and was stirred for one hour. The mixture was again cooled to 0 °C and $Me_3SiCl$ (126.5 mL, 1 mol) was added dropwise. The mixture was allowed to warm to room temperature and was stirred for five

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hours. Ether was removed under reduced pressure and hexane (600 mL) was added to precipitate the salt. The salt (LiCl) was removed by filtration and the filtrate was collected. The solvents were removed under reduced pressure and the product was distilled at 66-70 °C (0.1 mm Hg) as a pale yellow liquid, that turns to a solid on standing at room temperature. The yield was 80 %.

**Preparation of Silylaniline Reagent B.** A 3-neck 2000 mL, round-bottom flask, equipped with a mechanical stirrer, $N_2$ inlet, a rubber septum, and an addition funnel, was charged with $Et_2O$ (600 mL) and compound **A** (73.2 g, 300 mmol). The mixture was cooled to 0 °C and *n*-BuLi (120 mL, 300 mmol) was added slowly. The mixture was allowed to warm to room temperature and was stirred for one hour. Ether was removed under reduced pressure and hexane (1000 mL) was added. The mixture was again cooled to 0 °C and $Me_3SiCl$ (350 mmol) was added dropwise. The mixture was then refluxed for 8 hours, and the salt was allowed to settle and the supernatant solution was removed by cannula. The solvent was removed under reduced pressure and the product was distilled at 67-70 °C (0.1 mm Hg) as a colorless to pale yellow colored liquid. The yield was 80 %.

**Preparation of Silylaniline Reagent C.** The aniline analog **C** was prepared in a similar way as compound **A**, except that compound **B** was used instead of $BrC_6H_4NH_2$. The product was distilled at 55-65 °C (0.1 mm Hg) as a colorless liquid. The compound was stored under $N_2$ atmosphere. The yield was 73 %.

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**Preparation of Silylaniline Reagent D.** A 3-neck 1000 mL, round-bottom flask, equipped with a mechanical stirrer, $N_2$ inlet, a rubber septum, and an additional funnel, was charged with $Et_2O$ (600 mL) and compound **C** (62 g, 200 mmol). The mixture was cooled to 0 °C and HCl (150 mL, 150 mmol, 1.0 M solution in ether) was added dropwise. After completion of the addition, the mixture was stirred at 0 °C for about four hours. Ether was removed under reduced pressure and hexane (200 mL) was added to precipitate the salt. The salt was removed by filtration and the product was distilled at 65-71 °C (0. 1 mm Hg) as a colorless to pale yellow colored liquid. The yield was 60 %.

**Preparation of Silylaniline Reagent E.** The analog **E** was prepared from compound **B** in the same manner as that for reagent **C** except that $Me_2SiCl_2$ was used instead of $Me_3SiCl$. Yield was 35 %.

**Preparation of Silylaniline Reagent F.** The analog **F** was prepared from compound **A** in the same manner as that for reagent **B** except $Me_2SiCl_2$ was used instead of $Me_3SiCl$. Yield was 50 %.

**Preparation of Phosphines 1–3.** A 3-neck, 500 mL, round-bottom flask, equipped with a mechanical stirrer, $N_2$ inlet, rubber septum, and an addition funnel, was charged with $Et_2O$ (350 mL) and compound **A** (34.38 g, 140 mmol). The mixture was cooled to 0 °C and *n*-BuLi (60 mL, 150 mmol) was added slowly. The mixture was allowed to warm to room temperature and was stirred for one hour to form the lithiated silylaniline intermediate. The mixture was again cooled to 0 °C, while stirring. Simultaneously,

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another 3-neck, 1000 mL, round-bottom flask, equipped with a mechanical stirrer, $N_2$ inlet, a rubber septum, and an addition funnel, was charged with $Et_2O$ (300 mL) and $PCl_3$ (19.22 g, 140 mmol). The mixture was cooled to -78 °C and the lithiated silylaniline (prepared above), which was at 0 °C, was added slowly from an addition funnel. The mixture was then allowed to warm to 0 °C and was stirred for one hour, before $CH_3MgBr$ (100 mL, 280 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for four hours. Ether was removed under reduced pressure and hexane (300 mL) was added to precipitate the salt. The salt was removed by filtration and hexane was removed under reduced pressure. The product was distilled at 89-92 °C (0.1 mm Hg) to yield phosphine **1**. Yield was 60 %. For the preparation of phosphine **2**, silylaniline reagent **D** was used instead of silylaniline reagent **A**. Similarly, for the synthesis of phosphine **3**, silylaniline reagent **A** was used, and freshly made $LiOCH_2CF_3$, was used instead of $CH_3MgBr$.

**Preparation of Phosphine 4 and 5.** A 3-neck, 500 mL, round-bottom flask, equipped with a mechanical stirrer, $N_2$ inlet, rubber septum, and an addition funnel, was charged with $Et_2O$ (250 mL) and compound **A** (27.7 g, 113.50 mmol). The mixture was cooled to 0 °C and *n*-BuLi (48 mL, 118 mmol) was added slowly. The mixture was allowed to warm to room temperature and was stirred for one hour to form the lithiated silylaniline intermediate. The mixture was cooled to -78 °C and $Ph_2PCl$ (24.93 g, 113.50 mmol) was added dropwise. The reaction mixture was allowed to warm to room

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temperature and was stirred for four hours. Ether was removed under reduced pressure and hexane (300 mL) was added to precipitate the salt. The salt was removed by filtration and hexane was removed under reduced pressure. The product was distilled at 175-180 °C (0.1 mm Hg) to yield phosphine **4**. Yield was 63 %. Normally **4** is a wax-like solid, but it dissolves readily in chloroform-*d*. For the preparation of phosphine **5**, silylaniline reagent **D** was used instead of silylaniline reagent **A**.

**Preparation of Phosphines 6-9.** A 3-neck, 500 mL, round-bottom flask, equipped with a mechanical stirrer, $N_2$ inlet, rubber septum, and an addition funnel, was charged with $Et_2O$ (200 mL) and compound **A** (24.40 g, 100 mmol). The mixture was cooled to 0 °C and *n*-BuLi (42 mL, 105 mmol) was added drop-wise. The mixture was allowed to warm to room temperature and was stirred for one hour to form the lithiated silylaniline intermediate. The mixture was cooled to -78 °C and $PhPCl_2$ (17.90 g, 100 mmol) was added dropwise. The mixture was allowed to warm to room temperature and was stirred for three hours. Then it was cooled to 0 °C and $CH_3MgBr$ (33.33 mL, 100 mmol) was added slowly. The reaction mixture was allowed to warm to room temperature and was stirred for three hours. Ether was removed under reduced pressure and hexane (200 mL) was added to precipitate the salt. Salt was removed by filtration and hexane was removed under reduced pressure. The product was distilled at 130-134 °C (0.1 mm Hg) to yield phosphine **6**. Yield was 58 %. Compounds **7-9** were prepared in a similar manner.

**Table 1.** NMR Spectroscopic Data for Compound **A**

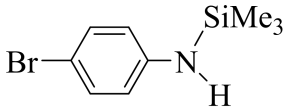
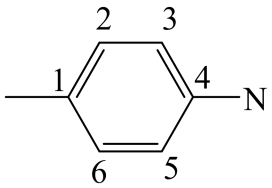
| | | $^{1}$H | $^{13}$C |
|---|---|---|---|
| **Compound** | **Signal** | δ | δ |
|  **A** | $NSiMe_3$ | 0.06(s) | 0.08(s) |
| | N*H* | 3.25(s) | |
| | $NC_6H_4$ | 6.3-7.1(m) | |
|  | $C_1$ | | 113.50(s) |
| | $C_{2,6}$ | | 120.34(s) |
| | $C_{3,5}$ | | 132.46(s) |
| | $C_4$ | | 148.45(s) |

**Table 2.** NMR Spectroscopic Data for Compound **B**

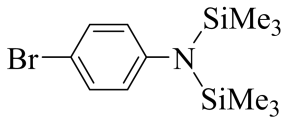
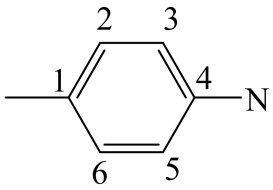
| | | $^{1}H$ | $^{13}C$ |
|---|---|---|---|
| **Compound** | **Signal** | **δ** | **δ** |
|  **B** | $N(SiMe_3)_2$ | 0.10(s) | 0.12(s) |
| | $NC_6H_4$ | 6.5-7.3(m) | |
|  | $C_1$ | | 109.32(s) |
| | $C_{2,6}$ | | 116.77(s) |
| | $C_{3,5}$ | | 132.56(s) |
| | $C_4$ | | 147.68(s) |

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**Table 3.** NMR Spectroscopic Data for Compound **C**

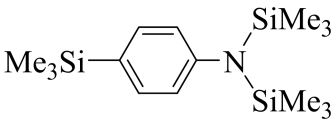
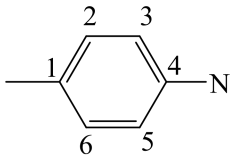
| | | $^{1}H$ | $^{13}C$ |
|---|---|---|---|
| **Compound** | **Signal** | δ | δ |
|  **C** | $N(SiMe_3)_2$ | 0.139(s) | 0.00(s) |
| | $CSiMe_3$ | 0.319(s) | 2.92(s) |
| | $NC_6H_4$ | 6.9-7.4(m) | |
|  | | | |
| | | $C_1$ | 116.40(s) |
| | | $C_{2,6}$ | 130.77(s) |
| | | $C_{3,5}$ | 134.35(s) |
| | | $C_4$ | 149.38(s) |

**Table 4.** NMR Spectroscopic Data for Compound **D**

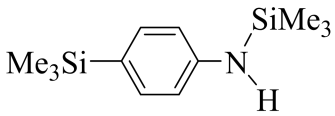
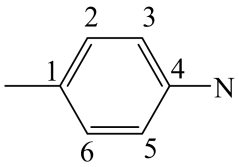
| Compound | Signal | $^1$H δ | $^{13}$C δ |
|---|---|---|---|
|  **D** | $NSiMe_3$ | 0.047(s) | 0.016(s) |
| | $CSiMe_3$ | 0.06(s) | 0.16(s) |
| | N*H* | 3.781(s) | |
| | $NC_6H_4$ | 6.7-7.4(m) | |
|  | | | |
| | $C_1$ | | 114.67(s) |
| | $C_{2,6}$ | | 127.15(s) |
| | $C_{3,5}$ | | 134.45(s) |
| | $C_4$ | | 148.57(s) |

**Table 5.** NMR Spectroscopic Data for Compound **E**

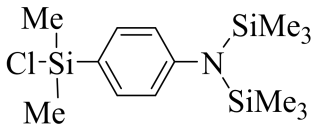
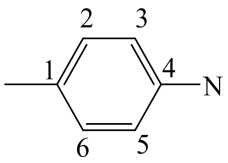
| Compound | Signal | $^1$H δ | $^{13}$C δ |
|---|---|---|---|
|  **E** | $N(SiMe_3)_2$ | 0.12(s) | -0.65(s) |
| | $CSiMe_2Cl$ | 0.72(s) | 2.20(s) |
| | $NC_6H_4$ | 6.9-7.5(m) | |
|  | $C_1$ | | 123.56(s) |
| | $C_{2,6}$ | | 130.45(s) |
| | $C_{3,5}$ | | 133.53(s) |
| | $C_4$ | | 150.52(s) |

**Table 6.** NMR Spectroscopic Data for Compound **F**

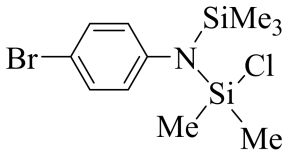
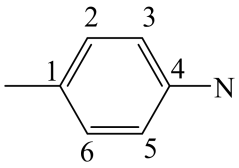
| | | $^{1}H$ | $^{13}C$ |
|---|---|---|---|
| **Compound** | **Signal** | **δ** | **δ** |
|  **F** | $NSiMe_3$ | 0.15(s) | 1.62(s) |
| | $NSiMe_2Cl$ | 0.40(s) | 4.32(s) |
| | $NC_6H_4$ | 6.8-7.3(m) | |
|  | $C_1$ | | 116.68(s) |
| | $C_{2,6}$ | | 131.47(s) |
| | $C_{3,5}$ | | 132.02(s) |
| | $C_4$ | | 144.93(s) |

**Table 7.** NMR Spectroscopic Data for Compound **1**

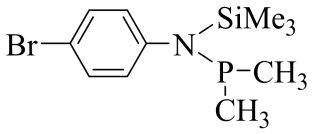
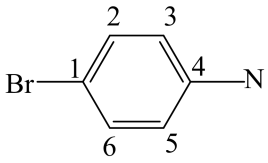
| | | $^{1}H$ | | $^{13}C$ | | $^{31}P$ |
|---|---|---|---|---|---|---|
| **Compound** | **Signal** | **δ** | **$J_{PH}$** | **δ** | **$J_{PC}$** | **δ** |
|  | $SiMe_3$ | 0.11(s) | | 0.08(s) | | |
| | $PCH_3$ | 0.92(d) | 6.2 | 17.05(d) | 16.1 | 15.62(s) |
| **1** | $NC_6H_4$ | 6.6-7.4(m) | | | | |
|  | $C_1$ | | | 118.29(s) | | |
| | $C_{2,6}$ | | | 131.22(s) | | |
| | $C_{3,5}$ | | | 132.83(s) | | |
| | $C_4$ | | | 141.11(s) | | |

**Table 8.** NMR Spectroscopic Data for Compound **2**

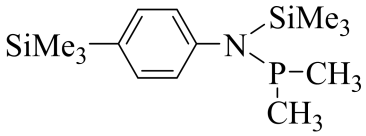
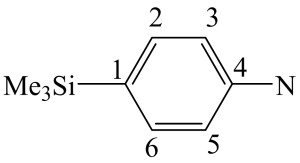
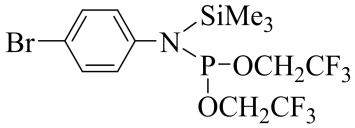
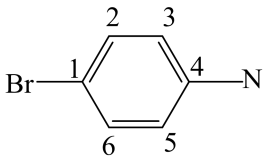
| Compound | Signal | $^1$H δ | $^1$H $J_{PH}$ | $^{13}$C δ | $^{13}$C $J_{PC}$ | $^{31}$P δ |
|---|---|---|---|---|---|---|
|  **2** | NSi*Me*$_3$ | 0.06(s) | | 0.10(s) | | |
| | CSi*Me*$_3$ | 0.19(s) | | 1.04(s) | | |
| | P*C*H$_3$ | 0.82(d) | 4.3 | 19.99(d) | 11.5 | 16.30(s) |
| | N*C*$_6$H$_4$ | 6.6-7.3(m) | | | | |
|  | C$_1$ | | | 115.56(s) | | |
| | C$_{2,6}$ | | | 127.62(s) | | |
| | C$_{3,5}$ | | | 135.55(s) | | |
| | C$_4$ | | | 149.10(s) | | |

**Table 9.** NMR Spectroscopic Data for Compound **3**

| Compound | Signal | $^1$H δ | $^1$H $J_{PH}$ | $^{13}$C δ | $^{13}$C $J_{PC}$ | $^{31}$P δ |
|---|---|---|---|---|---|---|
|  **3** | NSi*Me*$_3$ | 0.218(d) | 1.6 | 0.65(d) | 7.5 | |
| | *POCH*$_2$CF$_3$ | 3.9-4.1(m) | | 61.52(dq) | 20.2 | 146.50(s) |
| | | | | | 35* | |
| | OCH$_2$*CF*$_3$ | | | 122.19(dq) | 6.0 | |
| | | | | | 261* | |
| | N*C*$_6$*H*$_4$ | 6.8-7.4(m) | | | | |
|  | | | | | | |
| | C$_1$ | | | 119.81(s) | | |
| | C$_{2,6}$ | | | 131.76(s) | | |
| | C$_{3,5}$ | | | 132.39(s) | | |
| | C$_4$ | | | 138.31(s) | | |

*$J_{FC}$ value

**Table 10.** NMR Spectroscopic Data for Compound **4**

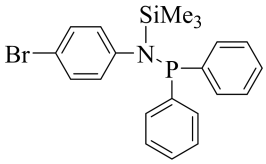
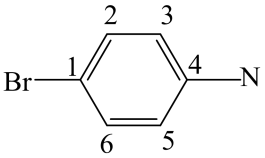
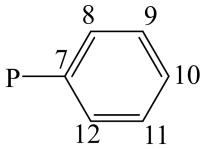
| Compound | Signal | $^1$H δ | $^1$H $J_{PH}$ | $^{13}$C δ | $^{13}$C $J_{PC}$ | $^{31}$P δ |
|---|---|---|---|---|---|---|
|  **4** | NSi*Me*$_3$ | 0.01(s) | | 0.02(s) | | |
| | *PNC*$_6$*H*$_4$ | 6.4-7.3(m) | | | | 51.53(s) |
|  | | | | | | |
| | | | C*$_1$* | 128.71(s) | | |
| | | | C*$_{2,6}$* | 130.28(s) | | |
| | | | C*$_{3,5}$* | 132.12(s) | | |
| | | | C*$_4$* | 133.51(s) | | |
| | P*C*$_6$*H*$_5$ | 6.9-7.0(m) | | | | |
|  | | | | | | |
| | | | C*$_7$* | 140.38(d) | 18.2 | |
| | | | C*$_{8,12}$* | 146.88(d) | 5.6 | |
| | | | C*$_{9,11}$* | 132.12(s) | | |
| | | | C*$_{10}$* | 128.94(s) | | |

**Table 11.** NMR Spectroscopic Data for Compound **5**

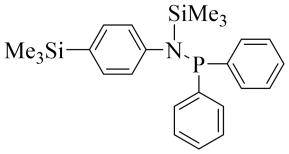
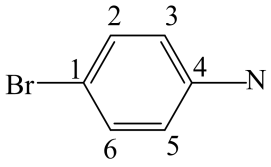
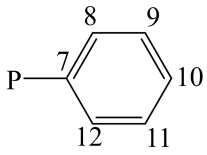
| | | $^{1}H$ | | $^{13}C$ | | $^{31}P$ |
|---|---|---|---|---|---|---|
| **Compound** | **Signal** | **δ** | **$J_{PH}$** | **δ** | **$J_{PC}$** | **δ** |
|  **5** | $NSiMe_3$ | 0.07(s) | | 0.00(s) | | |
| | CSiMe3 | 0.32(s) | | 2.48(d) | 8.1 | |
| | $PNC_6H_4$ | 6.5-7.4(m) | | | | 51.25(s) |
|  | $C_1$ | | | 128.79(s) | | |
| | $C_{2,6}$ | | | 130.30(s) | | |
| | $C_{3,5}$ | | | 134.13(s) | | |
| | $C_4$ | | | 140.61(s) | | |
| $PC_6H_5$ | | 7.2-7.3(m) | | | | |
|  | $C_7$ | | | 128.71(d) | 24.1 | |
| | $C_{8,12}$ | | | 140.50(d) | 6.2 | |
| | $C_{9,11}$ | | | 129.40(s) | | |
| | $C_{10}$ | | | 133.68(s) | | |

**Table 12.** NMR Spectroscopic Data for Compound **6**

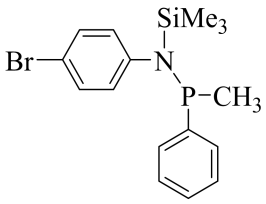
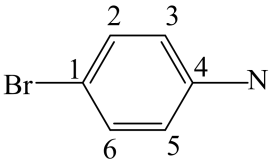
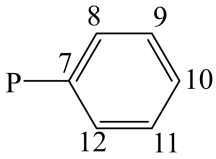
| Compound | Signal | $^1$H δ | $^1$H $J_{PH}$ | $^{13}$C δ | $^{13}$C $J_{PC}$ | $^{31}$P δ |
|---|---|---|---|---|---|---|
|  **6** | $NSiMe_3$ | 0.03(s) | | 1.25(s) | | |
| | $PCH_3$ | 1.1(d) | 7.5 | 12.20(d) | 15.9 | 28.12(s) |
| | $NC_6H_4$ | 6.2-7.0(m) | | | | |
|  | $C_1$ | | | 116.58(s) | | |
| | $C_{2,6}$ | | | 131.47(s) | | |
| | $C_{3,5}$ | | | 132.26(s) | | |
| | $C_4$ | | | 141.03(s) | | |
| | $PC_6H_5$ | 7.0-7.2(m) | | | | |
|  | $C_7$ | | | 128.68(d) | 20.0 | |
| | $C_{8,12}$ | | | 131.22(d) | 4.8 | |
| | $C_{9,11}$ | | | 128.30(s) | | |
| | $C_{10}$ | | | 118.17(s) | | |

**Table 13.** NMR Spectroscopic Data for Compound **7**

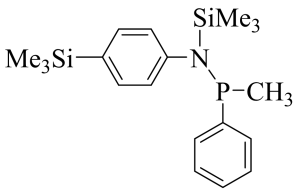
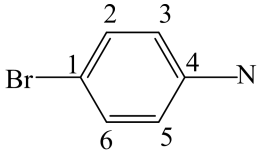
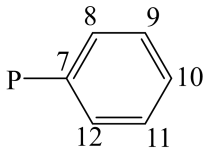
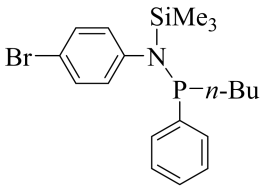
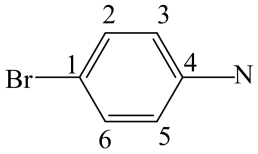
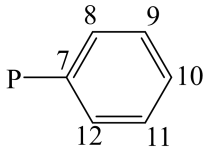
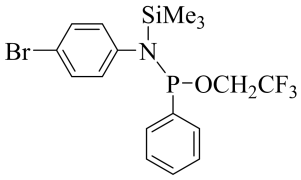
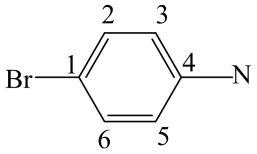
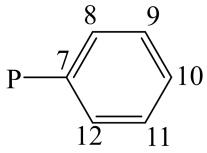
| Compound | Signal | $^1$H δ | $^1$H $J_{PH}$ | $^{13}$C δ | $^{13}$C $J_{PC}$ | $^{31}$P δ |
|---|---|---|---|---|---|---|
|  **7** | $NSiMe_3$ | 0.03(s) | | 0.00(s) | | |
| | $CSiMe_3$ | 0.02(s) | | 2.21(d) | 7.6 | |
| | $PCH_3$ | 1.09(d) | 7.3 | 13.33(d) | 15.6 | 28.38(s) |
| | $NC_6H_4$ | 6.3-7.0(m) | | | | |
| |  | | | | | |
| | | | $C_1$ | 117.92(s) | | |
| | | | $C_{2,6}$ | 133.28(s) | | |
| | | | $C_{3,5}$ | 135.26(s) | | |
| | | | $C_4$ | 140.15(s) | | |
| | $PC_6H_5$ | 7.0-7.1(m) | | | | |
| |  | | | | | |
| | | | $C_7$ | 127.44(d) | 19.2 | |
| | | | $C_{8,12}$ | 132.45(d) | 4.8 | |
| | | | $C_{9,11}$ | 129.83(s) | | |
| | | | $C_{10}$ | 136.22(s) | | |

**Table 14.** NMR Spectroscopic Data for Compound **8**

| Compound | Signal | $^1$H δ | $^1$H $J_{PH}$ | $^{13}$C δ | $^{13}$C $J_{PC}$ | $^{31}$P δ |
|---|---|---|---|---|---|---|
|  **8** | $NSiMe_3$ | 0.14(s) | | 0.02(s) | | |
| | $CH_2CH_2\mathit{CH_3}$ | 0.60(t) | 6.0* | 14.90(s) | | |
| | $CH_2\mathit{CH_2}CH_3$ | 1.2-1.3 (m) | | 23.80(d) | 14.2 | |
| | $PCH_2\mathit{CH_2}$ | 1.2-1.3(m) | | 25.13(d) | 13.6 | |
| | $P\mathit{CH_2}$ | 1.5-1.6(m) | | 28.06(d) | 13.4 | 35.02(s) |
| | $NC_6H_4$ | 6.3-7.0(m) | | | | |
|  | $C_1$ | | | 116.52(s) | | |
| | $C_{2,6}$ | | | 129.68(s) | | |
| | $C_{3,5}$ | | | 130.38(s) | | |
| | $C_4$ | | | 141.08(s) | | |
| | $PC_6H_5$ | 7.0-7.2(m) | | | | |
|  | $C_7$ | | | 133.98(d) | 18.6 | |
| | $C_{8,12}$ | | | 130.39(d) | 4.4 | |
| | $C_{9,11}$ | | | 129.47(s) | | |
| | $C_{10}$ | | | 128.68(s) | | |

*$J_{HH}$ value

**Table 15.** NMR Spectroscopic Data for Compound **9**

| | | $^1$H | | $^{13}$C | | $^{31}$P |
|---|---|---|---|---|---|---|
| **Compound** | **Signal** | **δ** | **$J_{PH}$** | **δ** | **$J_{PC}$** | **δ** |
|  | $NSiMe_3$ | 0.01(s) | | 0.03(s) | | |
| | $POCH_2CF3$ | 3.9-4.1(m) | | 64.10(dq) | 24.0 | 124.08 |
| | | | | | 56.2* | |
| **9** | $OCH_2CF_3$ | | | 117.28(dq) | 9.2 | |
| | | | | | 240* | |
| | $NC_6H_4$ | 6.2-7.0(m) | | | | |
|  | | | | | | |
| | | | $C_1$ | 117.29(s) | | |
| | | | $C_{2,6}$ | 130.20(s) | | |
| | | | $C_{3,5}$ | 129.56(s) | | |
| | | | $C_4$ | 140.05(s) | | |
| | $PC_6H_5$ | 7.0-7.1(m) | | | | |
|  | | | | | | |
| | | | $C_7$ | 128.12(d) | 20.0 | |
| | | | $C_{8,12}$ | 139.98(d) | 8.6 | |
| | | | $C_{9,11}$ | 126.55(s) | | |
| *$J_{FC}$ value | | | $C_{10}$ | 128.73(s) | | |

`

## SECTION TWO

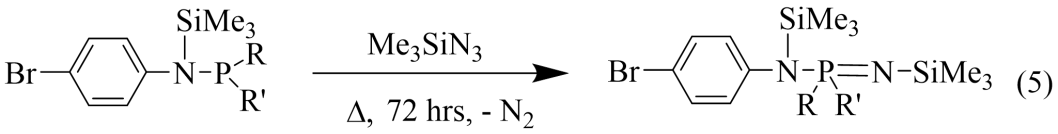
## REACTIVITY OF (SILYLANILINO)PHOSPHINES

### 1. Introduction

In order for the (silylanilino)phosphines, as prepared in **Section 1**, to be used as precursors to poly(phosphazenes), the P atom in these compounds must be oxidized to the $P^V$ oxidation state. The unique chemistry of the Si-N-P linkage plays an important role in this oxidation process. The Staudinger reaction[23] has been previously reported already for preparing *N*-silylphosphoranimines from (silylamino)phosphines. We also used the oxidative bromination reaction to test the reactivity of (silylanilino)phosphines. For the bromination product, we investigated the deprotonation-substitution reaction at the *P*-methyl group. The reactivity studies of these compounds may provide extensive information related to the preparation poly(phosphazenes) in future studies.

### 2. Results and Discussion

**Staudinger Reaction of (Silylanilino)phosphines**. The Staudinger reaction is one of the oldest methods for the synthesis of *N*-Silylphosphoranimines. In this work, when the (silylanilino)phosphines (**1** and **9)** were refluxed for 48 hours with an excess of trimethylsilylazide, in the absence of solvent, the desired phosphoranimines (**10** and **11**) were formed (eq 5).



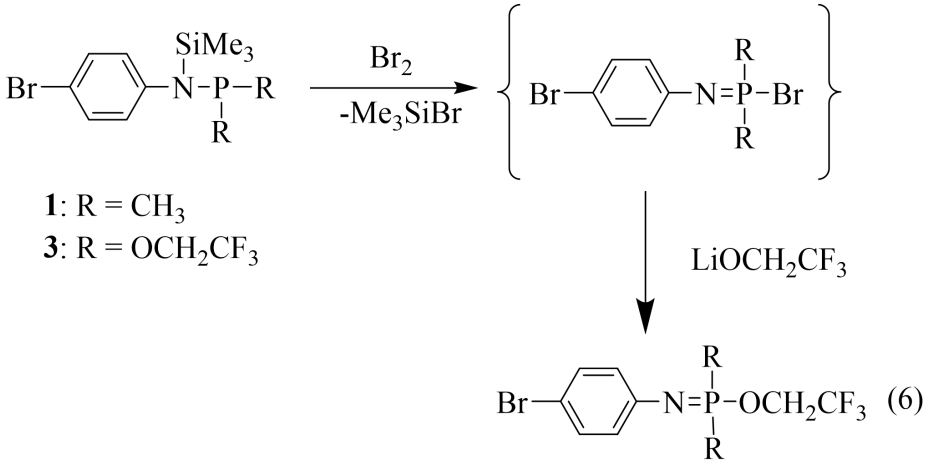

(5)

**1**: R = R' = $CH_3$ **10**: R = R' = $CH_3$ Yield = 40 %

**9**: R = $OCH_2CH_3$, R' = Ph **11**: R = $OCH_2CH_3$, R' = Ph Yield = 37 %

Compounds **10** and **11** are air/moisture sensitive and were purified by long path vacuum distillation. These phosphoranimines were characterized by $^{1}H$, $^{31}P$ and $^{13}C$ NMR spectroscopy (Tables 16 and 17).

**Oxidative Bromination Reaction**. We used the same method as described by Neilson and Wisian-Neilson (eq 6)[28] for (silylamino)phosphines to synthesize the new phosphoranimines **12** and **13**. The Si-N bond is easily cleaved by nucleophilic attack of the bromide anion. In this process, bromination at phosphorus occurs with trimethylsilyl bromide elimination to give the P-bromophosphoranimine intermediate. Nucleophilic substitution with $LiOCH_2CF_3$ then afforded the desired phosphoranimines (**12** and **13**).




(6)

**1**: R = $CH_3$

**3**: R = $OCH_2CF_3$

**12**: R = $CH_3$ Yield = 60 %

**13**: R = $OCH_2CF_3$ Yield = 40%

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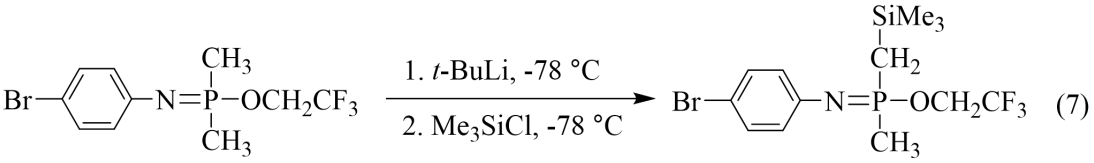
These compounds are air/moisture sensitive colorless liquids. They were characterized by $^{1}H$, $^{13}C$, $^{31}P$ NMR spectroscopy (Table 18 and 19).

**Deprotonation-Substitution at the *P*-Methyl Group of *N*-Silylphosphoranimines.** According to the literature,[36] the *P*-methyl group on *N*-silylphosphoranimine could undergo deprotonation-substitution reaction with *t*-BuLi as the deprotonating reagent. The reason of picking *t*-BuLi rather than *n*-BuLi here is that the bulky nucleophile (*t*-$Bu^{-}$) is less likely to attack the phosphorus center and therefore substitution at the P center should not be favored. The phosphoranimine **12** was treated with *t*-BuLi at -78°C to deprotonate a hydrogen from the *P*-methyl group, followed by addition of TMSCl at that temperature. The reaction was then warmed to room temperature to give the product **14** (eq 7).




(7)

**12** **14**

Compound **14** is a colorless, air/moisture sensitive liquid that was purified by long-path vacuum distillation. It was characterized by $^{1}H$, $^{13}C$, and $^{31}P$ NMR spectroscopy (Table 20). As distilled, the product contains small amounts of an unidentified impurity but the intense peaks near 0 ppm (both for $^{1}H$ and $^{13}C$) show that the $Me_3Si$ group was incorporated into the structure. Additional work is required to improve the purity and characterization of **14** and related compounds.

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## 3. Experimental section.

**Materials and general procedures.** All reagents were obtained from commercial sources and used without further purification. $^{1}H$, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded on Varian XL-300 or Bruker-400 spectrometers using $CDCl_3$ as the solvent. All reactions and other manipulations were carried out under dry nitrogen or under vacuum unless otherwise specified.

**Staudinger Reaction of (Silylanilino)phosphine 10-11.** A one-necked round-bottom flask, equipped with a magnetic stir bar, $N_2$ inlet, and a reflux condenser was charged with compound **1** (14.1 g, 46.35 mmol) and $Me_3SiN_3$ (21.36 g, 185.40 mmol). The mixture was heated at 100 °C for 48 hours. Vacuum distillation of the crude mixture gave the *N*-silylphosphoranimine **10** at 130-135 °C (0.1 mm Hg). Yield was 35 %. The products were stored under $N_2$ atmosphere. Compound **11** was prepared in the same way using compound **9** as starting material.

**Preparation of Phosphoranimine 12-13 by Oxidative Bromination Reaction.** A three-neck 1000 mL round-bottom flask, equipped with a mechanical stirrer, a rubber septum, $N_2$ inlet, and an addition funnel, was charged with compound **1** (31.7 g, 104.2 mmol) and benzene (250 mL). The mixture was cooled to 0 °C and $Br_2$ (17.9 g, 112 mmol), dissolved in benzene (30 mL), was added slowly. The reaction mixture was stirred at room temperature for 90 minutes. Solvents and $Me_3SiBr$ were removed under reduced pressure and then, $CH_2Cl_2$ (30 mL) and $Et_2O$ (100 mL) were added to form a

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solution. A separate 3-neck, 500 mL round bottom flask, equipped with a mechanical stirrer, $N_2$ inlet, rubber septum and an additional funnel, was charged with $CF_3CH_2OH$ (12.5 g, 125 mmol) and $Et_2O$ (200 mL). The mixture was cooled to 0 °C and *n*-BuLi (50 mL, 125 mmol) was added dropwise. The mixture was allowed to warm to room temperature and was stirred for one hour to form a solution of $LiOCH_2CF_3$. The flask containing the intermediate solution was cooled to 0 °C, to which the solution of $LiOCH_2CF_3$ was added slowly. After the addition, the reaction mixture was allowed to warm to room temperature and stirred for 4 hours. Solvents were removed under reduced pressure and hexane (500 mL) was added to precipitate the salt (LiBr). The salt was removed by filtration and hexane was removed under reduced pressure. Distillation at 120-125 °C (0.1 mm Hg) gave compound **12** as a pale yellow liquid. Yield was 60 %. Compound **13** was prepared in the same way except using compound **3** as starting material.

**Deprotonation-Substitution Reaction of *N*-silylphosphoranimines 12**. A 3-neck, 100 mL, round-bottom flask, equipped with a magnetic stirring bar, an $N_2$ inlet, a rubber septum, and an addition funnel, was charged with $Et_2O$ (40 mL) and compound **12** (1.02 g, 0.003 mol). The reaction flask was cooled to -78 °C. Next, *t*-BuLi (1.2 mL, 0.003 mol) was slowly added. After the addition, the solution was stirred for about 30 minutes and $Me_3SiCl$ (0.4 mL, 0.003 mol) was then added. The solution was stirred for another 30 minutes and then the flask was allowed to warm to room temperature and was stirred for

about four hours. The solution turned cloudy. The solvents were removed under reduced pressure, and hexane (~80 mL) was added to precipitate the salt. The salt was removed by filtration and the filtrate was collected. Distillation at 130-140 °C (0.25 mm Hg) to yield compound **14** as a colorless liquid. Yield was 25 %.

**Table 16.** NMR Spectroscopic Data for Compound **10**

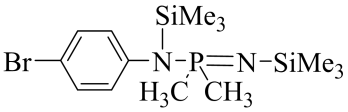
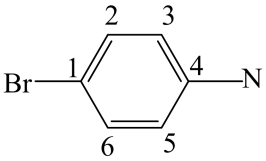
| Compound | Signal | $^1$H δ | $^1$H $J_{PH}$ | $^{13}$C δ | $^{13}$C $J_{PC}$ | $^{31}$P δ |
|---|---|---|---|---|---|---|
|  **10** | $NSiMe_3$ | 0.00(s) | | 0.02(s) | | |
| | $P{=}NSiMe_3$ | 0.10(s) | | 1.22(d) | 3.0 | |
| | $PCH_3$ | 1.16(d) | 11.8 | 16.8(d) | 60.6 | 16.98 |
| | $NC_6H_4$ | 6.8-7.4(m) | | | | |
|  | $C_1$ | | | 90.40(s) | | |
| | $C_{2,6}$ | | | 126.54(s) | | |
| | $C_{3,5}$ | | | 129.90(s) | | |
| | $C_4$ | | | 140.29(s) | | |

**Table 17.** NMR Spectroscopic Data for Compound **11**

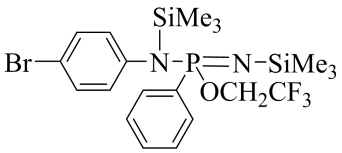
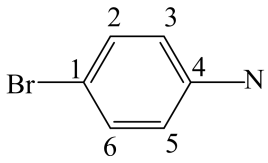
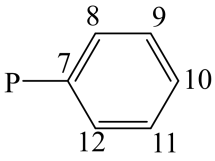
| Compound | Signal | $^1$H δ | $^1$H $J_{PH}$ | $^{13}$C δ | $^{13}$C $J_{PC}$ | $^{31}$P δ |
|---|---|---|---|---|---|---|
|  **11** | $NSiMe_3$ | 0.01(s) | | 0.02(s) | | |
| | $P{=}NSiMe_3$ | 0.26(s) | | 0.92(d) | 2.8 | |
| | $POCH_2CF3$ | 4.2-4.4(m) | | 60.23(dq) | 30.2 | 6.95(s) |
| | | | | | 76.8* | |
| | $OCH_2CF_3$ | | | 125.69(dq) | 12.8 | |
| | | | | | 220* | |
| | $NC_6H_4$ | 6.4-7.2(m) | | | | |
|  | | | $C_1$ | 117.28(s) | | |
| | | | $C_{2,6}$ | 131.76(s) | | |
| | | | $C_{3,5}$ | 130.85(s) | | |
| | | | $C_4$ | 142.39(s) | | |
| | $PC_6H_5$ | 7.5-7.8(m) | | | | |
|  | | | $C_7$ | 123.67(d) | 8.0 | |
| | | | $C_{8,12}$ | 127.13(s) | | |
| *$J_{FC}$ value | | | $C_{9,11}$ | 130.40(s) | | |
| | | | $C_{10}$ | 129.68(s) | | |

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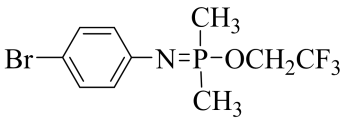
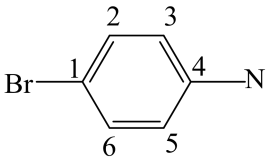
**Table 18.** NMR Spectroscopic Data for Compound **12**

| | | $^1$H | | $^{13}$C | | $^{31}$P |
|---|---|---|---|---|---|---|
| **Compound** | **Signal** | **δ** | **$J_{PH}$** | **δ** | **$J_{PC}$** | **δ** |
| | P*CH*$_3$ | 1.73(d) | 12.0 | 14.25(d) | 98.0 | 38.34(s) |
|  | O*CH*$_2$CF$_3$ | 4.2-4.3(m) | | 60.3(dq) | 4.6 | |
| | | | | | 34.0* | |
| **12** | OCH$_2$*CF*$_3$ | | | 124.26(dq) | 5.0 | |
| | | | | | 260* | |
| | N*C*$_6$*H*$_4$ | 6.6-7.6(m) | | | | |
|  | | | | | | |
| | | | C*$_1$ | 111.43(s) | | |
| | | | C$_{2,6}$ | 130.79(s) | | |
| | | | C$_{3,5}$ | 124.35(d) | 8.0 | |
| | | | C*$_4$ | 146.29(d) | 12.0 | |

*$J_{FC}$ value

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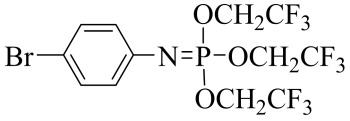
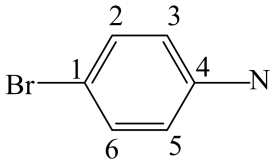
**Table 19.** NMR Spectroscopic Data for Compound **13**

| | | $^1$H | | $^{13}$C | | $^{31}$P |
|---|---|---|---|---|---|---|
| **Compound** | **Signal** | **δ** | **$J_{PH}$** | **δ** | **$J_{PC}$** | **δ** |
|  **13** | PO*CH*$_2$CF$_3$ | 4.3-4.4(m) | | 63.23(dq) | 12 | -17.90(s) |
| | | | | | 28.8* | |
| | OCH$_2$*CF$_3$* | | | 119.50(dq) | 15.8 | |
| | | | | | 254* | |
| | N*C$_6$H$_4$* | 6.7-7.6(m) | | | | |
|  | | | | | | |
| | | | C*$_1$* | 109.58(s) | | |
| | | | C$_{2,6}$ | 134.46(s) | | |
| | | | C$_{3,5}$ | 131.17(d) | 8.2 | |
| | | | C*$_4$* | 143.28(d) | 15.0 | |

*$J_{FC}$ value

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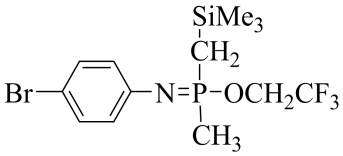
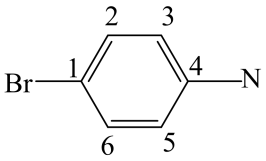
**Table 20.** NMR Spectroscopic Data for Compound **14**

| | | $^1$H | | $^{13}$C | | $^{31}$P |
|---|---|---|---|---|---|---|
| **Compound** | **Signal** | **δ** | **$J_{PH}$** | **δ** | **$J_{PC}$** | **δ** |
|  **14** | $SiMe_3$ | 0.00(s) | | 0.05(s) | | |
| | $OCH_2CF_3$ | 3.7-4.2(m) | | 62.3(dq) | 5.0 | |
| | | | | | 40.2* | |
| | $OCH_2CF_3$ | | | 125.66(dq) | 9.6 | |
| | | | | | 235* | |
| | $PCH_2$ | 1.22(d) | 8.0 | 16.54(d) | 60.2 | |
| | $PCH_3$ | 1.56(d) | 4.2 | 22.68(d) | 54.6 | 35.30(s) |
| | $NC_6H_4$ | 6.6-7.6(m) | | | | |
|  | $C_1$ | | | 114.23(s) | | |
| | $C_{2,6}$ | | | 131.68(s) | | |
| | $C_{3,5}$ | | | 134.80(d) | 6.6 | |
| | $C_4$ | | | 143.16(d) | 13.2 | |

*$J_{FC}$ value

**Table 21.** Physical and Analytical Data for Compounds **A-F** and **1-14**

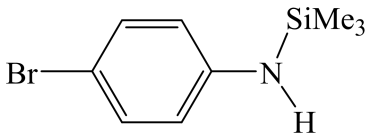
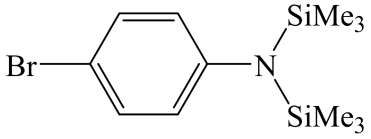
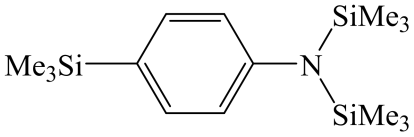
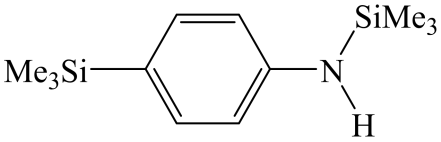
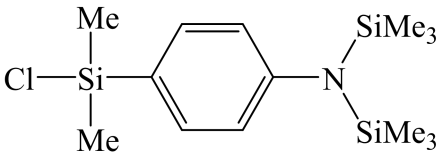
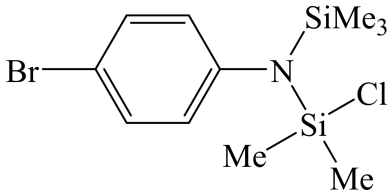
| Compound | % Yield | Bp, ℃ (mmHg) |
|---|---|---|
|  **A** | 85 | 60-67 (0.1) |
|  **B** | 80 | 67-70 (0.1) |
|  **C** | 73 | 55-65 (0.1) |
|  **D** | 60 | 65-71 (0.1) |
|  **E** | 35 | 85-90 (0.1) |
|  **F** | 50 | 120-125 (0.1) |

**Table 21.** Physical and Analytical Data for Compounds **A-F** and **1-14** (continued)

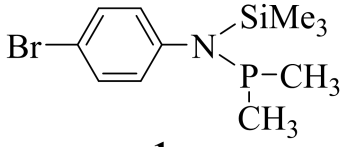
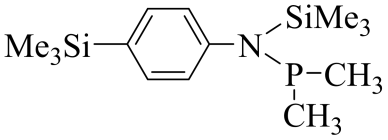
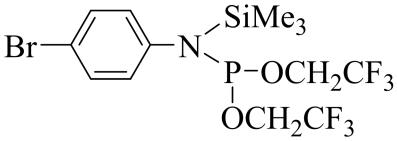
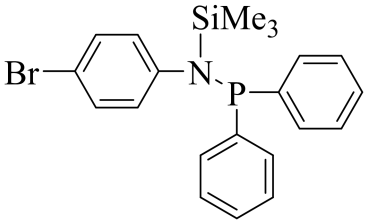
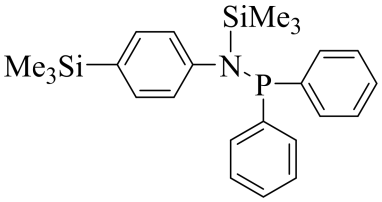
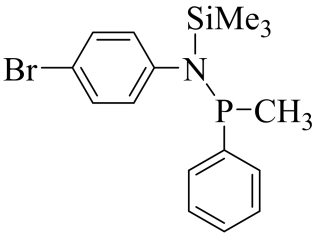
| Compound | % Yield | Bp, ℃ (mmHg) |
|---|---|---|
|  **1** | 60 | 89-92 (0.1) |
|  **2** | 50 | 89-92 (0.1) |
|  **3** | 60 | 82-87 (0.1) |
|  **4** | 63 | 170-178 (0.1) |
|  **5** | 55 | 175-180 (0.1) |
|  **6** | 58 | 130-134 (0.1) |

**Table 21.** Physical and Analytical Data for Compounds **A-F** and **1-14** (continued)

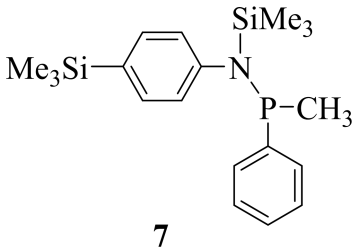
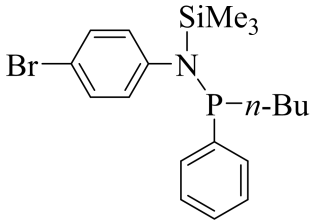
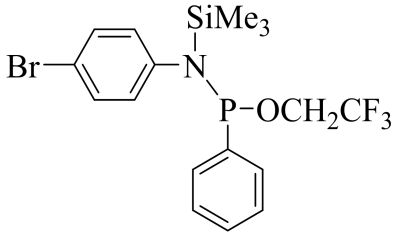
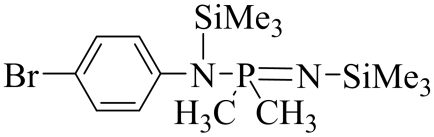
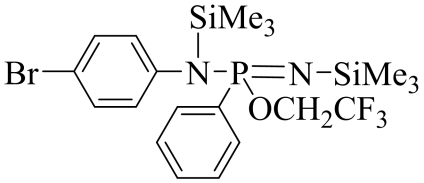
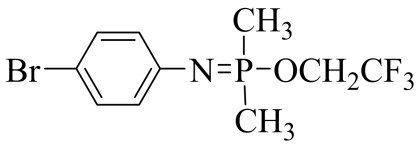
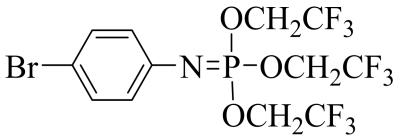
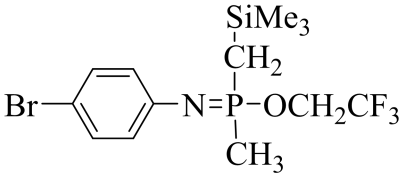
| Compound | % Yield | Bp, ℃ (mmHg) |
|---|---|---|
|  **7** | 54 | 140-144 (0.1) |
|  **8** | 45 | 145-155 (0.1) |
|  **9** | 40 | 155-160 (0.1) |
|  **10** | 30 | 130-136 (0.1) |
|  **11** | 45 | 120-130 (0.1) |

**Table 21.** Physical and Analytical Data for Compounds **A-F** and **1-14** (continued)

| Compound | % Yield | Bp, ℃ (mmHg) |
|---|---|---|
|  **12** | 40 | 120-125 (0.1) |
|  **13** | 64 | 95-100 (0.1) |
|  **14** | 25 | 130-135 (0.1) |

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## CONCLUDING REMARKS

Poly(phosphazenes) have a wide range of applications depending on the substituents at phosphorus. Phosphorus compounds containing a Si-N bond are very useful precursors to poly(phosphazenes). It is also of fundamental interest to study related polymers with spacer groups within the P-N polymer back-bone. In this research, some Si-N-P containing phosphines with spacer groups on the back-bone have been synthesized by a one-pot method. These phosphines could undergo oxidation reaction with $Me_3SiN_3$ (Staudinger Reaction), or bromination reaction to yield phosphoranimines. These phosphoranimines containing leaving groups such as $–OCH_2CF_3$ and $–SiMe_3$ are potential precursors to poly(phosphazenes) by the thermal condensation method. The *P*-Methyl group on phosphoranimines underwent deprotonation-substitution reactions. This deprotonation-substitution reaction on alkyl groups at the monomer stage has produced an opportunity for incorporating a wide spectrum of functional groups (electrophiles) onto the polymers. The chemistry and properties of these precursors to inorganic polymers are worthy of more study.

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# Vita

Boran Shi was born in Beijing, China on November 13, 1985. He is the child of Haiyi Shi and Rui Li. He received a Bachelor of Engineering degree with a major in Polymer Science and Materials from East China University of Science and Technology, Shanghai, China in 2008.

After graduating from college, Boran Shi entered Texas Christian University in August, 2008 under the direction of Dr. Robert H. Neilson and performed research in inorganic synthetic chemistry.

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# Abstract

## SYNTHESIS AND REACTIVITY OF SOME SILICON-NITROGEN-PHOSPHORUS SYSTEMS

by Boran Shi, MS, 2016

Department of Chemistry and Biochemistry

Texas Christian University

Thesis advisor: Robert H. Neilson, Professor of Chemistry

In recent years, an important branch of polymer chemistry has been the area of polyphosphazenes. Depending on the substituents on the P center, polyphosphazenes exhibit a wide variety of chemical and physical properties and are potential candidates for many applications in chemistry and biology. These polyphosphazenes are often synthesized from organophosphorus compounds like *N*-silyl-phosphoranimines by a condensation polymerization method.

In this research, we report the synthesis of some new (silylanilino)phosphines by the Wilburn method and the synthesis of *N*-silylphosphoranimines by oxidative bromination and the Staudinger reaction, respectively. These compounds with Si-N-P bond are synthetically useful precursors to poly(phosphazenes). The deprotonation-substitution reaction on *P*-methyl group of phosporanimines was also studied. All the products are

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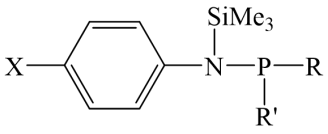
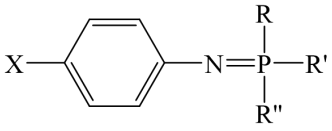
fully characterized by $^{1}H$, $^{13}C$, and $^{31}P$ NMR spectroscopy.



(Silylanilino)phosphines



*N*-silylphosphoranimine
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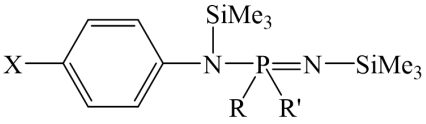
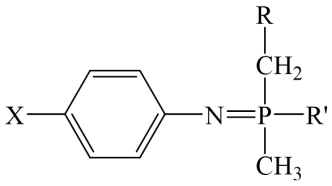
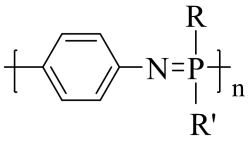


*N*-silylphosphoranimine
by Staudinger reaction



Derivatives of
*N*-silylphosphoranimine

These (silylanilino)phosphines and their derivatives are being studied as precursors to traditional poly(phosphazenes) and novel poly(phenylenephosphazenes).



Poly(phenylenephosphazene)