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Poly(alkyl/arylphosphazenes) and Their Precursors

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I. Introduction

In recent years one of the most exciting and rapidly expanding branches of materials science/chemistry has been the area of inorganic and organometallic polymers.[1] The synthesis and development of several such systems has indeed been productive and prospects for the future of the field appear to be very bright. For example, while the silicone polymers[2] (Si–O backbone) have been of widespread commercial importance for many years, more recent studies of polysilanes[3] (Si–Si backbone) and polysilazanes[4] (Si–N backbone) as ceramic precursors have greatly stimulated the growth of main group element chemistry. In a similar vein, the discovery[5] of the electrical conductivity of poly(sulfur nitride), $(SN)_n$, has spurred the search for numerous other conducting polymeric materials.[6]

From a synthetic viewpoint, the polyphosphazenes,[7,8] $(R_2P{=}N)_n$, with a backbone of alternating phosphorus and nitrogen atoms and two substituents at each phosphorus, are the most versatile class of inorganic polymers. Because a tremendous variety of substituents can be attached to the backbone phosphorus atoms, these polymers exhibit a very broad spectrum of chemical and physical properties which make them suitable for many applications.[9] Depending on the substituents, polyphosphazenes can be flame retardant, flexible at low temperatures, water soluble or repellent, resistant to harsh chemicals and UV radiation, stable at high temperatures, semiconductors[10] or insulators, and biologically active[11] or inert. Some polyphosphazenes are currently being produced commercially[12] and the development of markets for P–N based polymers will surely continue.

For the purposes of this review, polyphosphazenes are conveniently divided into two major classes—those in which the side groups are attached to phosphorus via oxygen (P–OR) or nitrogen ($P–NR_2$) linkages and those in which *the substituents are attached directly to phosphorus through phosphorus–carbon bonds*, i.e., the poly(alkyl/arylphosphazenes). Since several excellent reviews[8,13,14] of the former type of phosphazenes are available, we will concentrate here on the poly(alkyl/arylphosphazenes), a relatively new class of phosphazenes that have not been previously reviewed. Specifically, this review will cover the synthesis, characteristic properties, and chemical reactivity of the title compounds and will also survey the relevant preparative chemistry of their silicon–nitrogen–phosphorus precursors.

II. Synthetic Routes to Polyphosphazenes

In order to place the chemistry of poly(alkyl/arylphosphazenes) in the proper perspective, we will begin with an outline (Table I) of the four major methods that are used for the synthesis of polyphosphazenes. The overall scope and present limitations of each of these methods will then be described in more detail in the following sections.

These synthetic methods differ from each other in two important respects. First, they involve fundamentally different chemistry—methods A and B are based on a *ring-opening* polymerization of hexachlorocyclotriphosphazene and its derivatives, followed by substitution reactions; method C is a direct *condensation* polymerization of N-silylphosphoranimine[7] "monomers"; and method D involves derivative chemistry of the preformed poly(alkyl/arylphosphazenes) obtained via route C. Second, and more importantly, *the methods differ in terms of the type of polyphosphazene products which they afford.* The four methods are very much complementary to each other since each one is best suited to the synthesis of a dif-

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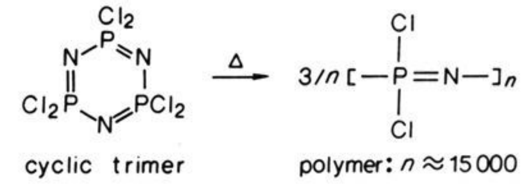
ferent subclass of phosphazene materials. It is this variety of synthetic methods and the great diversity of polymeric products that make the polyphosphazenes unique in the realm of synthetic macromolecules.

A. Substitution Reactions of Poly(dichlorophosphazene), $[Cl_2PN]_n$

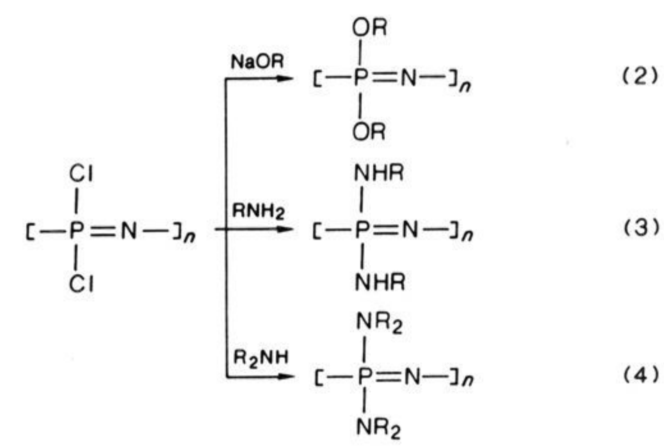
The best studied and most widely used method for preparing polyphosphazenes is the ring-opening/substitution route developed by Allcock and co-workers.[8] The major breakthrough in the field was their discovery that, under carefully controlled conditions, the cyclic trimer can be thermally ring opened to yield high molecular weight, soluble (and, therefore, not cross-linked) poly(dichlorophosphazene) (eq 1).



(1)

Since its initial discovery, this ring-opening reaction has been studied extensively and is currently thought to occur via a cationic chain growth mechanism,[8,15] initiated by cleavage of the polar $P^{\delta+}–Cl^{\delta-}$ bond. A variety of catalysts, notably Lewis acids such as BCl_3, have been found both for the solution polymerization[16] as well as the normally practiced[12] bulk process. Although it is very moisture sensitive and, thus, easily cross-linked, the dilute solution properties of $[Cl_2PN]_n$ have been carefully measured.[17] A typical uncatalyzed, bulk polymerization run at 250 °C yields very high molecular weight polymer with a broad molecular weight distribution (e.g., $M_w \approx 2 \times 10^6$ and $M_w/M_n \approx 10$), while the catalyzed process (in solution or neat) generally gives somewhat lower molecular weight products having narrower molecular weight distributions.[9,16] The ring-opening polymerization of the analogous *fluoro* trimer, $[F_2PN]_3$, also occurs, but only at much higher temperatures (ca. 350 °C).[18] Moreover, the synthetic utility of poly(difluorophosphazene), $[F_2PN]_n$, is severely limited by its insolubility in all but fluorinated organic solvents. It should also be mentioned that there is another route to poly(dichlorophosphazene) which has been recently reported. This method involves the condensation polymerization of the monomeric phosphoranimine, $Cl_2P(=O)N=PCl_3$, which occurs with elimination of phosphoryl chloride, $P(O)Cl_3$.[19] Details of this new process and/or its potential for commercialization have not yet appeared in the open literature.

Once prepared, the un-cross-linked poly(dichlorophosphazene) is soluble in several organic solvents including THF and benzene. Combined with this solubility, the high reactivity of the polar $P^{\delta+}–Cl^{\delta-}$ bonds makes $[Cl_2PN]_n$ amenable to chloride replacement, *without P–N bond cleavage*, by a wide variety of oxygen or nitrogen nucleophiles (eq 2–4). The first fully substituted, hydrolytically stable, un-cross-linked polyphosphazenes were prepared in this manner by Allcock and co-workers in the mid-1960s.[20] Since then, the substitution chemistry of poly(dichlorophosphazene) has grown to be an extremely diverse field and well over



$$[-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{P}}=N-]_n \xrightarrow{NaOR} [-\overset{\displaystyle OR}{\underset{\displaystyle OR}{P}}=N-]_n \quad (2)$$

$$[-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{P}}=N-]_n \xrightarrow{RNH_2} [-\overset{\displaystyle NHR}{\underset{\displaystyle NHR}{P}}=N-]_n \quad (3)$$

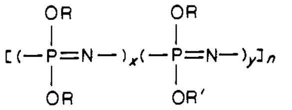
$$[-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{P}}=N-]_n \xrightarrow{R_2NH} [-\overset{\displaystyle NR_2}{\underset{\displaystyle NR_2}{P}}=N-]_n \quad (4)$$

TABLE I.

method	starting material	type of phosphazene product
A	poly(dichlorophosphazene), $[Cl_2PN]_n$	*P*-alkoxy, -aryloxy, and/or -amino substitution; often with functional groups
B	substituted *cyclic* phosphazenes, e.g., $\overline{P(Ph)(Cl)N{=}PCl_2N{=}PCl_2N{=}}$	*partial P*-alkyl, -aryl, or -metallocenyl substitution
C	*N*-silylphosphoranimines, e.g., $Me_3SiN{=}PMe_2(OCH_2CF_3)$	*complete P*-alkyl/aryl substitution
D	poly(alkyl/arylphosphazenes), e.g., $[(Ph)(Me)P{=}N]_n$	*complete P*-alkyl/aryl substitution plus functional groups

200 different polyphosphazenes of these types have been reported.

As mentioned earlier, the broad range of materials and associated properties that are available through this ring-opening/substitution approach have been previously reviewed.[8] Within the context of this review, however, there are some noteworthy features. First, the preparation of copolymers, in which two or more different side groups are incorporated into the same polymer, is generally possible. In fact, the inherent torsional flexibility of the P–N chain is enhanced by an irregular pattern of substituents. This is exemplified by the highly elastomeric nature of the commercial[12] fluoroalkoxy- and phenoxy-substituted polymers 1 and 2. In contrast, the corresponding homopolymers,



$$[(-P(OR)_2{=}N-)_x(-P(OR)(OR'){=}N-)_y]_n$$

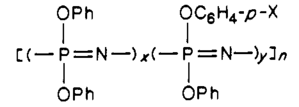
1: $R = CH_2CF_3$, $R' = CH_2(CF_2)_mCF_2H$ ($m = 1, 3, 5, 7, \ldots$)

2: $R = C_6H_5$, $R' = C_6H_4$-p-C_2H_5

$[(RO)_2PN]_n$ ($R = CH_2CF_3$, Ph), are semicrystalline thermoplastics with considerably higher glass transition temperatures. Since the nucleophiles used in this substitution process are usually comparable in reactivity, a random distribution of side groups is generally obtained. Only in a few cases when bulky nucleophiles[21] (e.g., R_2NH) are used is the process sufficiently controllable so that *nongeminal* substitution occurs [to give $[(R_2N)(Cl)P{=}N]_n$]. On the other hand, a regular substitution pattern of alkyl/aryl groups is more easily achieved through other preparative methods, especially via the condensation polymerization route, to be described below.

Second, the nucleophilic substitution reactions of the *cyclic* chlorophosphazenes, $[Cl_2PN]_n$ (n = 3, 4), are generally good models for the analogous chemistry of the high polymer.[22] Thus, new reactions can be explored initially with small molecules that mimic the structure and reactivity of the polymeric substrate. Reaction mechanisms, purification methods, and structure proofs can all be obtained readily with small molecule models, but similar studies of the polymers are more difficult in the absence of the model system data. Only reactions that proceed readily in high yield at the cyclic phosphazene level are feasible at the high polymer level since the coiling of the long chain polymer molecules in solution is likely to enhance the possibility of undesired side reactions such as cross-linking or P–N bond scission. This model system approach has been of particular value in elucidating the problems associated with the reactivity of poly(dichlorophosphazene) toward organometallic nucleophiles such as Grignard and organolithium reagents. As will be discussed later, the poly(alkyl/arylphosphazenes) also have useful small molecule models for their derivative chemistry.

A third feature of polyphosphazenes prepared by the ring-opening/substitution method is that, after all of the chlorine atoms are replaced by OR or NHR groups, the P–N skeleton is sufficiently stable to allow organic chemistry to be carried out on those side groups, usually without damage to the polymer backbone. This type of derivative chemistry has lead to the synthesis of many new types of polyphosphazenes which often contain biologically, catalytically, or electrically active side groups.[8,10,11] For example, the bromo- and nitrophenoxy moieties (3), introduced via reaction of $[Cl_2PN]_n$ with the corresponding aryl oxides, can be derivatized in several ways, a few of which are mentioned here. The bromophenoxy groups can be lithiated and treated with Ph_2PCl to yield pendent phosphine substituents ($X = PPh_2$). These polymers have been coordinated to various transition metal centers,[23] some of which have been studied as hydroformylation catalysts.[24] Interestingly, while the P–N polymer backbone is stable, the phosphine units become separated from the aryloxy side groups during the catalytic process.[24] The nitrophenoxy groups can be reduced to the synthetically useful aminophenoxy ($X = NH_2$) derivative. Coupling reactions of the NH_2 function either directly or following diazotization have produced polyphosphazenes bearing, e.g., Schiff bases,[25] azo dyes,[26] catecholamines,[27] and enzymes.[28]



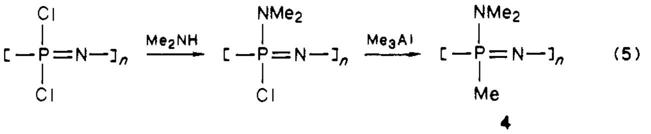
$$[(-P(OPh)_2{=}N-)_x(-P(OC_6H_4\text{-}p\text{-}X)(OPh){=}N-)_y]_n$$

3: X = Br, NO_2

Virtually all of this work as well as a great deal of related chemistry has been carried out by Allcock and co-workers and, for additional examples, the reader is referred to their reviews[8] and more recent papers.[29] The important point to be made is that, in all of these reactions, the polyphosphazene backbone remains intact. Clearly, such side-group modification greatly increases the variety of polymers which are ultimately available via the ring-opening/substitution approach to polyphosphazene synthesis. Similarly, as will be shown below, the poly(*alkyl*/*aryl*phosphazenes) can also undergo a wealth of derivatization processes to afford functionalized polymers in which all of the side groups are linked to the P–N backbone by phosphorus–carbon bonds.

Fourth, although the reactions of alkoxides, aryl oxides, and amines with poly(dihalophosphazenes) have been developed to a high degree, they all yield polymers in which the organic group is linked to the backbone through an oxygen or nitrogen atom. Because these P–O–R and P–N–R linkages are sometimes prone to thermal or chemical degradation,[30] the possibility of preparing polyphosphazenes with alkyl and/or aryl groups connected directly to the skeleton through phosphorus–carbon bonds is of considerable interest. Moreover, such poly(alkyl/arylphosphazenes) would be the exact isoelectronic and isostructural analogues of the polysiloxanes. Unfortunately, numerous studies have shown that the reactions of poly(dihalophosphazenes) with organometallic nucleophiles (e.g., Grignard and organolithium reagents) are not useful for the preparation of *fully* substituted poly(alkyl/arylphosphazenes). For example, treatment of $[Cl_2PN]_n$ with PhLi results in P–N bond cleavage in addition to chloride replacement once the degree of phenyl substitution exceeds ca. 10%.[31] The reasons for not cleanly achieving complete substitution in such reactions are now fairly well understood, largely from mechanistic studies on the cyclic model compounds.[32] The complex reaction pathway involves metal–halogen exchange, metalation of alkyl groups already attached to the backbone, and cross-linking (probably through the formation of intermolecular P–P bonds), in addition to simple halogen replacement by alkyl or aryl groups. Some of the synthetically useful reactions of organometallic reagents with the cyclic trimer, $[Cl_2PN]_n$, will be reviewed in more detail in the next section.

Better results are obtained with $[F_2PN]_n$ as the substrate so that, upon sequential treatment with PhLi and $NaOCH_2CF_3$, polymers of the type $[(Ph)_x(CF_3CH_2O)_yPN]_n$ are produced in which the ratio x:y reaches ca. 1.6:1 (60–70% phenyl substitution) before the molecular weight begins to decrease rapidly.[33] As noted above, however, there are significant drawbacks to the use of the fluorinated polyphosphazene as the starting material for these substitution reactions.[18] More recently, a new approach (eq 5) to polyphosphazenes with 50% *P*-methyl substitution (**4**) has been reported.[34] This method takes advantage of the coordination of the methylating agent, Me_3Al, to the NMe_2 groups that are first attached to the P–N backbone by treatment of poly(dichlorophosphazene) with dimethylamine.



$$[-\overset{Cl}{\underset{Cl}{P}}=N-]_n \xrightarrow{Me_2NH} [-\overset{NMe_2}{\underset{Cl}{P}}=N-]_n \xrightarrow{Me_3Al} [-\overset{NMe_2}{\underset{Me}{P}}=N-]_n \quad (5)$$

4

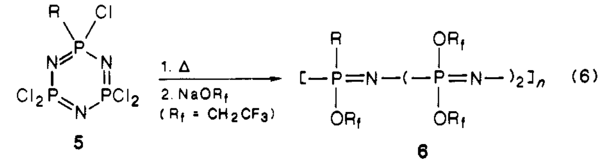
In summary, the synthesis of polyphosphazenes via substitution reactions of poly(dichlorophosphazene) is a versatile and widely used method for the preparation of alkoxy, aryloxy, amino, and *partially* alkyl/aryl substituted materials. Indeed, it is the method of choice when those types of polyphosphazenes are the target compounds. For *completely* alkyl/aryl substituted polyphosphazenes, however, alternative methods, notably the condensation polymerization of *N*-silylphosphoranimines, must be employed.

B. Ring-Opening of Substituted Cyclic Phosphazenes

Although the use of substitution reactions of $[Cl_2PN]_n$ has been highly successful as a general synthetic route to polyphosphazenes, there are useful alternative methods. One alternative process involves the initial introduction of organic side groups at the cyclic trimer or tetramer stage, followed by a ring-opening polymerization of the cyclic organophosphazene. Such a synthetic method is especially attractive because substitution reactions carried out on cyclic phosphazenes, and the associated product isolation and purification, are generally much easier than the corresponding processes for the high molecular weight polymers.

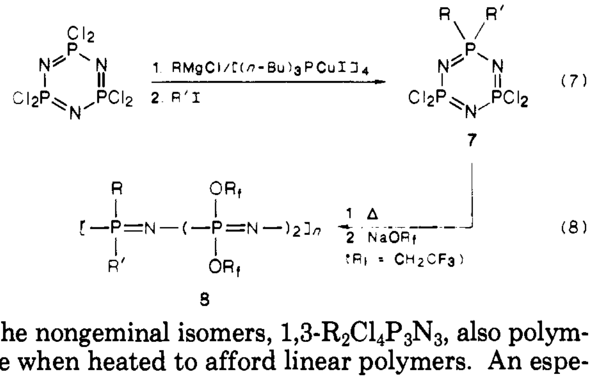
Thus far, however, all attempts to polymerize cyclic trimers or tetramers which are *fully* substituted with organic groups have failed to yield linear high polymers. Cyclic species bearing alkyl, aryl, or fluoroalkoxy side groups merely undergo ring–ring equilibration reactions at elevated temperatures.[35] The alkoxy derivatives decompose at first via alkyl group migration from oxygen to nitrogen [i.e., $-N{=}P(OR)_2- \rightarrow -N(R)P({=}O)(OR)$],[36] while the amino-substituted compounds undergo more complicated intermolecular condensation processes to yield ceramic-like residues.[37]

The situation is quite different if both halogen and organic substituents are present within the same cyclic phosphazene ring. Generally, in these cases, thermally induced ring-opening polymerization does occur. For example, a fairly wide variety of organopentachlorocyclotriphosphazenes **5** have been polymerized, with subsequent chlorine replacement by trifluoroethoxy groups (eq 6), to yield high molecular weight elastomers **6** which contain not only simple alkyl or aryl groups[38] but also more complex functionalities such as metallocenyl,[39] carboranyl,[40] and organosilyl[41] substituents.

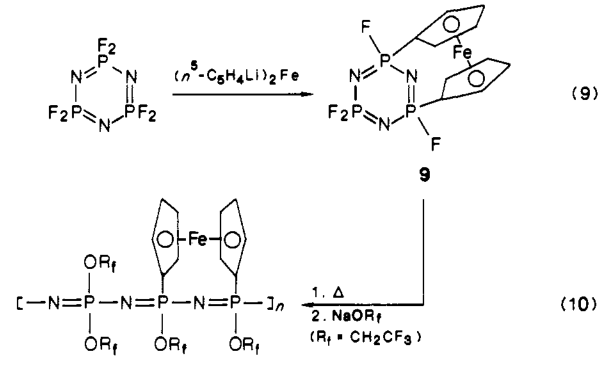


R = alkyl, aryl, metallocenyl, carboranyl, CH_2SiMe_3, etc.

While attachment of a single organic group to the cyclic trimer (e.g., **5**) is usually easily accomplished by treating $[Cl_2PN]_n$ with a Grignard or organolithium reagent, the selective introduction of two or more organic moieties requires other methods. Allcock et al.[42] have extensively studied the reactions of $[Cl_2PN]_n$ with organocopper-modified Grignard reagents and have developed workable syntheses (eq 7) of a variety of 1,1-dialkyl-3,3,5,5-tetrachlorocyclotriphosphazenes **7**. The same types of compounds are accessible via cleavage of the P–P bond in the diphosphazene $[(Ph)Cl_4P_3N_3]_2$ by treatment with $Li[Et_3BH]$.[43] These geminally dialkylated trimers **7** also undergo ring-opening polymerization at high temperatures to afford, after the remaining chlorine atoms are replaced by OCH_2CF_3 groups (eq 8), lower molecular weight hybrid polymers **8** in which one-third of the side groups are attached by direct P–C bonds.[44]



The nongeminal isomers, $1,3\text{-}R_2Cl_4P_3N_3$, also polymerize when heated to afford linear polymers. An especially interesting example of this process is the facile ring opening (eq 10) of the cyclic fluoro trimer **9** in which two phosphorus sites are linked in a transannular fashion by a ferrocene moiety.[45] After fluoride re-

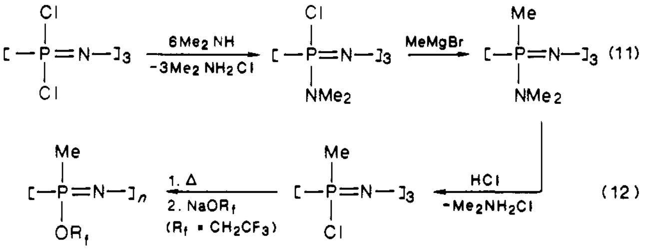


9

10

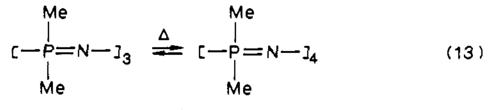
placement by OCH_2CF_3 groups, the resulting ferrocene/phosphazene polymer **10** was obtained as a high molecular weight, film-forming elastomer. Similar chemistry has been used to prepare the ruthenocene analogue, copolymers containing both iron and ruthenium, and lower molecular weight materials containing both bridging and pendent metallocene units.[45] Allcock et al.[46] have also systematically studied the synthesis, reaction mechanisms, and X-ray crystallographic structures of the starting cyclic trimers (e.g., **9**), tetramers, and related species.

The next step toward increasing the degree of alkylation of the polyphosphazene backbone involves the use of 1,3,5-trialkyl-1,3,5-trichlorocyclotriphosphazenes **11**. Although their behavior in ring-opening polymerizations has not been extensively studied due to difficulties in their synthesis (eq 11, 12),[47] these trimers do, in fact, yield relatively low molecular weight polymers **12** upon thermolysis.[48]



12 **11**

Even more highly alkylated cyclic phosphazenes (e.g., $Me_4Cl_2P_3N_3$) have also been prepared[49] but their thermolysis reactions have not been reported. The *fully* substituted cyclics, e.g., $[Me_2PN]_n$ (n = 3, 4, ..., 12), have been studied quite thoroughly in terms of preparative chemistry,[50] reactivity,[51,52] and X-ray structure determinations.[53] None of these peralkyl derivatives, however, have been successfully ring opened to the corresponding high polymers. Indeed, a detailed study[35] of the thermolytic behavior of the permethylated cyclic trimer and tetramer (with and without catalysts) has shown that ring–ring equilibration (eq 13), rather than



polymerization, occurs readily with the tetramer being the thermodynamically more stable species. In spite of their failure to undergo ring-opening polymerization, the peralkyl-substituted cyclic phosphazenes are useful as model systems for many of the structure and reactivity aspects of the poly(alkyl/arylphosphazenes). Relevant details of such chemistry will be mentioned in later parts of this review.

Finally, it has been pointed out[8,15] that, in addition to providing many new partially alkylated polyphosphazenes, these studies of the substituted cyclic trimers and tetramers have shed considerable light on the question of the mechanism of the ring-opening polymerization. The evidence accumulated to date indicates that the initiation step involves ionization of a halide ion from phosphorus. This is then followed or accompanied by P–N bond scission and a rapid cationic chain growth process. The work with trimers which contain both organic and halogen substituents demonstrates that the three P–N units from each trimeric ring enter the polymer as a unit; thus, decyclization to a monomeric $R_2P{\equiv}N$ species[54] does not precede polymerization. The question of the possible existence of a phosphazene monomer, $R_2P{\equiv}N$, and potential methods of generating such a reactive species are relevant to the third method of preparing polyphosphazenes as discussed in the next section.

C. Condensation Polymerization of *N*-Silylphosphoranimines

Both of the synthetic routes to polyphosphazenes discussed thus far involve ring opening of either completely or partially halogen substituted cyclic compounds to produce a reactive polymeric intermediate. Nucleophilic substitution reactions on this substrate polymer are then used to generate a great variety of stable derivatives. While the ring-opening aspect of these methods is, in fact, prevalent throughout main group element polymer chemistry [e.g., polysiloxanes, poly(sulfur nitride), polymeric sulfur, etc.], the concept of derivatizing a reactive intermediate polymer is unique to the polyphosphazenes. The prospect of extending this principle to other inorganic polymer systems is an important area for future investigation.

In order to design other preparative methods for polyphosphazenes in particular and inorganic polymers in general, it is instructive to first consider the most common polymerization reactions—addition polymerization (eq 14) and condensation polymerization (eq 15)—that are used in the field of organic polymer chemistry. In principle, both of these methods could be used for the synthesis of new inorganic polymers. In practice, however, there are some critical, fundamental problems which must be overcome before these will be generally useful in inorganic polymer chemistry.

$$\text{addition:} \quad nA{=}B \rightarrow [A{-}B]_n \qquad (14)$$

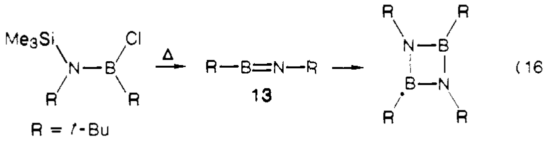
$$\text{condensation:} \quad nE{-}A{-}B{-}X \rightarrow [A{-}B]_n + nEX \qquad (15)$$

First, a major problem common to both approaches is the pronounced stability of the cyclic oligomers (e.g., phosphazenes, borazenes, silazanes, etc.) relative to the linear chain polymers. To be used successfully, these methods will require that precursors and reaction conditions be specifically designed to bypass the formation of cyclic products so that the linear polymers are directly produced. This is, at best, a difficult task, but some of the information gained from the studies of small molecule model compounds and from the successful preparation of polyphosphazenes via the condensation route (see below) should be very helpful in the ultimate solution of this problem.

A second factor hindering the application of organic polymer methodology to inorganic polymer synthesis is the scarcity of *useful* unsaturated monomers, A═B, for addition polymerization (eq 14). Such species, containing a variety of multiply bonded main-group elements [e.g., P═E (E = C, N, P, Si, etc.), Si═C, Si═Si, and B═N], are known and have been extensively studied in recent years.[55] The preparation of isolable compounds of these types, however, generally requires the use of sterically demanding substituents that are specifically incorporated to *prevent* polymerization from occurring. With less hindering groups in the compounds, one is relegated to working with transient intermediates which, although interesting for more fundamental studies, are impractical as polymer precursors. Moreover, there seems to be a general hesitancy on the part of investigators interested in the monomers, A═B, to extend their studies to the corresponding polymer systems. The work of West and coworkers on the polysilanes,[3] $[R_2Si]_n$, as well as the disilenes,[55b] ($R_2Si{=}SiR_2$), however, is a noteworthy exception, illustrating the close relationship that should exist between the unimolecular and the macromolecular systems.

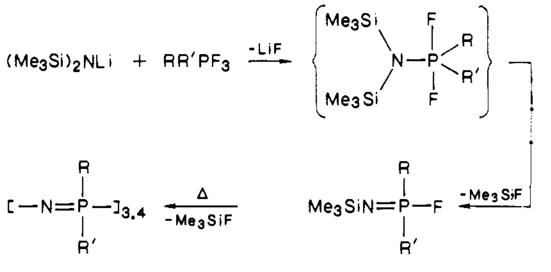
Third, in regard to the method of condensation polymerization (eq 15), a direct analogy to organic polymer chemistry is actually detrimental since the typical "inert" byproducts (e.g., EX = H_2O, HOR, HCl, NH_3, etc.) are often reactive toward the main group element bonds (A–B) that are being formed. Thus, some degree of depolymerization may result, leading to the formation of a thermodynamically stable ring system instead of the analogous polymer which may well be kinetically favored. In the inorganic systems, especially with phosphazenes, the elimination of silanes (e.g., Me_3SiF, Me_3SiCl, Me_3SiOR, etc.) is a very good alternative for several reasons. Silicon forms very strong bonds with many potential leaving groups (X = halogen, OR, etc.) which provides a good driving force for the condensation and helps to suppress the reverse reaction. Moreover, there are workable synthetic routes to many of the necessary silylated condensation "monomers" containing, e.g., Si–N–P, Si–C–P, Si–N–B, and Si–N–S linkages. Some of the small molecule preparative chemistry, especially as it applies to polyphosphazene precursors, will be covered later in this review.

Aside from these fundamental problems, it should also be noted that there is, however, a close relationship between these seemingly different polymerization methods (i.e., addition and condensation). It is possible for the condensation reaction to actually occur via a unimolecular elimination of EX in which case an unsaturated addition polymerization monomer A═B is generated. Many of the sterically stabilized species such as the monomeric boron imine 13 (eq 16)[56] are, in fact, prepared in this manner. As in this case, however, the self-association of the unsaturated species normally stops at the small ring stage. Phosphorus–nitrogen rings which have been prepared by the elimination of silyl halides include a few cyclic phosphazanes,[57] $(RPNR)_n$ (n = 3, 4), and several diazadiphosphetidines,[58] $(RNPR_xF_{3-x})_2$, and, more recently, the trifluoromethyl-substituted cyclic phosphazenes, $[(CF_3)_2PN]_n$ (n = 3, 4).[59]



(16)

The first strong evidence that phosphazenes could be prepared by a condensation process involving elimination of a small molecule silane resulted from our studies of the reactions of lithium bis(trimethylsilyl)amine with fluorophosphoranes[60] (eq 17). Instead of yielding the



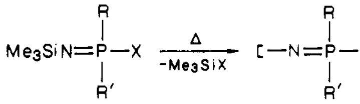
(17)

(18)

14: R = R' = Ph, Me, F, NMe2

desired five-coordinate Si–N–P compounds,[61] these reactions occurred with the spontaneous elimination of Me_3SiF to afford the *N*-silyl-*P*-fluorophosphoranimines 14. These compounds all underwent further fluorosilane elimination, either at room temperature or when heated, to give cyclic phosphazenes. Mass spectroscopic analysis showed that the products were predominately trimers and tetramers.

These preliminary results led us to propose that the thermal elimination of volatile silanes from suitably constructed *N*-silylphosphoranimines (eq 19) could be used as a new, general synthesis of phosphazene polymers, especially those containing alkyl and/or aryl side groups attached directly to the backbone by P–C bonds.



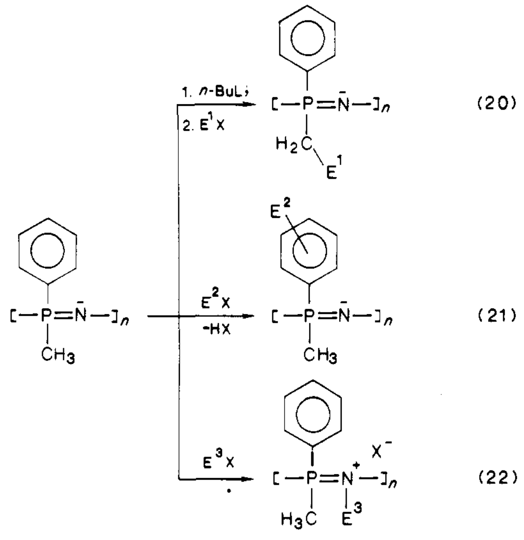
$$\mathrm{Me_3SiN{=}}\overset{\mathrm{R}}{\underset{\mathrm{R'}}{\mathrm{P}}}\mathrm{{-}X} \xrightarrow[-\mathrm{Me_3SiX}]{\Delta} [\mathrm{{-}N{=}}\overset{\mathrm{R}}{\underset{\mathrm{R'}}{\mathrm{P}}}\mathrm{{-}}]_n \qquad (19)$$

The major advantage of this approach over the ring-opening/substitution method is that it would permit 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 and avoiding the difficulties of its substitution reactions with organic nucleophiles (i.e., RMgX, RLi, etc.). In an independent study, Flindt and Rose[62] reported that the tris(trifluoroethoxy)phosphoranimine, $Me_3SiN{=}P(OCH_2CF_3)_3$, underwent elimination of $Me_3SiOCH_2CF_3$ when heated at ca. 200 °C to give poly[bis(trifluoroethoxy)phosphazene] in relatively low yield and low molecular weight ($M_w \approx 10\,000$). As will be described herein, subsequent work in our laboratories has verified the initial hypothesis that the condensation polymerization of *N*-silylphosphoranimines would be a general synthetic route to poly(alkyl/arylphosphazenes).

D. Derivatization of Preformed Poly(alkyl/arylphosphazenes)

In contrast to the ring-opening/substitution methods described in sections II.A and II.B above, the condensation polymerization (eq 19) is well suited to the synthesis of polyphosphazenes which are *fully* substituted with alkyl and/or aryl groups along the polymer backbone. The condensation method, however, is not generally useful for the preparation of poly(alkyl/arylphosphazenes) that also bear functional groups. Nevertheless, such materials are highly desirable because the direct P–C bonds should serve as thermally and chemically stable links between the reactive functional groups and the polymer skeleton. The availability of these functionalized poly(alkyl/arylphosphazenes) would expand even further the range of potential applications for phosphazene polymers as carrier molecules for reactive functional groups.

Recent work at Southern Methodist University has shown that preformed polymers such as poly(methylphenylphosphazene), obtained via the condensation polymerization of the appropriate *N*-silylphosphoranimine, can be derivatized by three general methods (eq 20–22). Functional groups (represented by E^1, E^2, etc.) can be introduced at three different sites: (1) at the *P-methyl* groups via deprotonation/substitution reactions (eq 20), (2) at the *P-phenyl* ring via electrophilic substitution reactions (eq 21), and (3) at the *backbone nitrogen* atoms via coordination of Lewis acids (eq 22). Illustrative examples of each of these types of reactions, and the relevant small molecule model chemistry, are discussed in section IV of this review.



III. Synthesis of Poly(alkyl/arylphosphazenes)

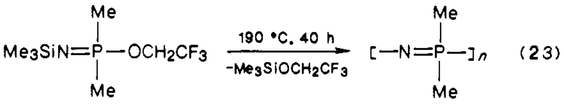
The development of preparative routes to poly(alkyl/arylphosphazenes), i.e., phosphazene polymers in which all of the side groups are attached by direct P–C bonds, has been a prime objective in phosphazene chemistry for several reasons. First, it is expected that the stability of the P–C bonds will enhance the thermal and/or chemical stability of the polymers and give rise to interesting physical and/or mechanical properties. Second, the extent of the analogy between polyphosphazenes such as $[Me_2PN]_n$ and the isoelectronic/isostructural polysiloxanes, $[Me_2SiO]_n$, would be very interesting to explore. Third, the electron-releasing nature of alkyl/aryl substituents, relative to the usual alkoxy, aryloxy, and amino groups, should enhance the basicity of the backbone nitrogen atoms and, thus, introduce a host of unique chemical and solubility properties to the polyphosphazenes.

A survey of the literature on phosphazenes reveals relatively few publications dealing with attempted syntheses of *fully* alkyl/aryl substituted compounds. Early claims (prior to 1966) in the patent literature of polymers with $[R_2PN]_n$ compositions can be discounted since these materials, having been prepared from the crosslinked form of $[Cl_2PN]_n$, are totally insoluble and virtually uncharacterized. Considerably better evidence was cited by Sisler et al.[63] for some low molecular weight (3500–12 500) samples of a soluble form of poly(dimethylphosphazene), prepared by the thermolysis of the phosphonium salt, $[Me_2P(NH_2)_2]^+Cl^-$. A subsequent reinvestigation of this reaction by Allcock and Patterson[35] indicated, however, that the initial thermolysis product of this salt is a short-chain linear phosphazene, probably with a structure of the type $H_2N[Me_2PN]_nPMe_2Cl$ (where $n \approx 20$). Continued pyrolysis afforded a high-yield sublimate consisting of the cyclic phosphazenes, $[Me_2PN]_n$ ($n = 3, 4$). Variations of this reaction have, in fact, been the most commonly used method for preparing the permethylated cyclic trimer and tetramer.[50,51]

In contrast to this general lack of information on the poly(alkyl/arylphosphazenes), numerous papers, notably those of Paddock, Oakley, and co-workers,[50–53] have dealt with the synthesis, derivative chemistry, and structures of the cyclic analogues. In addition to the trimer and tetramer just mentioned, the larger ring compounds, $[Me_2PN]_n$ (n = 5–12), have been prepared by treating the fluoro cyclics, $[F_2PN]_n$, with methyllithium. As noted earlier, these cyclics are useful as model systems for the structures and reactivity of the linear high polymers that have recently been prepared in our laboratories.

A. Condensation Polymerization of *N*-Silylphosphoranimines

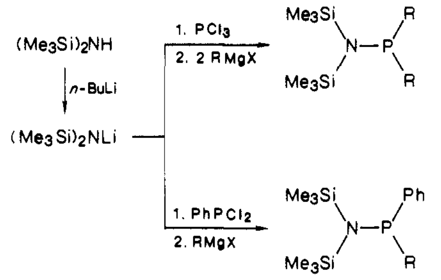
In 1980, we reported[64] that *N*-(trimethylsilyl)-*P*,*P*-dimethyl-*P*-(trifluoroethoxy)phosphoranimine (**15**) undergoes a smooth thermal decomposition (eq 23) to afford poly(dimethylphosphazene) **16** in essentially quantitative yield, free of the cyclic analogues. The



$$\underset{\textbf{15}}{Me_3SiN{=}\overset{Me}{\underset{Me}{P}}{-}OCH_2CF_3} \xrightarrow[-Me_3SiOCH_2CF_3]{190\ °C,\ 40\ h} \underset{\textbf{16}}{[{-}N{=}\overset{Me}{\underset{Me}{P}}{-}]_n} \quad (23)$$

product **16**, a white film-forming thermoplastic (T_g = −46 °C, T_m = 143 °C), bore a superficial resemblance to the material reported by Sisler[63] but it had a substantially higher molecular weight (M_w = 50 000) and was better characterized by NMR spectroscopy and thermal analysis. Subsequent work in our laboratories, some of which has been reported,[65–70] has demonstrated that the thermal decomposition of *N*-silyl-*P*-(trifluoroethoxy)phosphoranimines is indeed a general, high-yield synthesis of poly(alkyl/arylphosphazenes). By designing the appropriate precursors, it is possible to widely vary the pattern of alkyl/aryl substituents along the polymer backbone and, therefore, to essentially tailor the properties of the polyphosphazene products.

Most of the *N*-silyl-*P*-(trifluoroethoxy)phosphoranimine reagents, used as "monomers" in this polymer synthesis, are readily prepared from either PCl_3 or $PhPCl_2$ in a straightforward three-step reaction sequence (eq 24–26).[68,71,72] These compounds are obtained as colorless, distillable, air-sensitive liquids in yields of 50–75% based on starting PCl_3 or $PhPCl_2$. Some of the precursors (e.g., R = Me, R′ = Et, CH_2CH_2Ph) are actually obtained by a side-group modification of a simpler phosphoranimine such as **15**. Further details of the preparative chemistry of these precursors and related compounds will be discussed in section V of this review.



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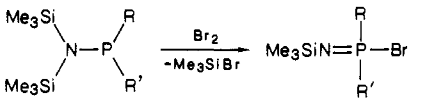

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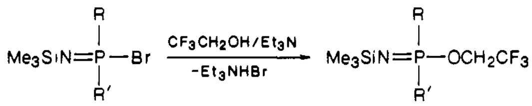
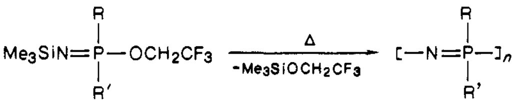


$$\mathrm{Me_3SiN{=}\underset{R'}{\overset{R}{P}}{-}Br \xrightarrow[-Et_3NHBr]{CF_3CH_2OH/Et_3N} Me_3SiN{=}\underset{R'}{\overset{R}{P}}{-}OCH_2CF_3} \quad (26)$$



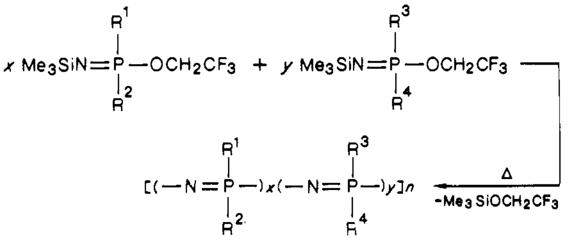
$$\mathrm{Me_3SiN{=}\underset{R'}{\overset{R}{P}}{-}OCH_2CF_3 \xrightarrow[-Me_3SiOCH_2CF_3]{\Delta} [{-}N{=}\underset{R'}{\overset{R}{P}}{-}]_n} \quad (27)$$

R =	Me	Et	n-Pr	Me	Me	Me	Me	CH_2Ph
R′ =	Me	Et	n-Pr	Et	n-Pr	CH_2CH_2Ph	Ph	Ph

On heating at ca. 160–220 °C for 2–12 days in sealed, evacuated glass or stainless steel vessels, these phosphoranimines quantitatively eliminate the silyl ether byproduct, $Me_3SiOCH_2CF_3$, to form the poly(alkyl/arylphosphazenes). The synthesis of a representative series of the homopolymers (i.e., products derived from a single precursor) is shown in eq 27. As will be discussed in more detail later, the properties of these polymers are found to be very dependent upon the nature of the substituents along the polymer backbone.

In addition to the synthesis of a wide variety of homopolymers, the condensation polymerization of *N*-silyl-*P*-(trifluoroethoxy)phosphoranimines can also be used to prepare other types of poly(alkyl/arylphosphazenes) including (1) copolymers of variable composition, (2) polymers containing certain functional groups such as pendent phosphine ligands, and (3) cross-linked polymers. Each of these variations will be briefly described below.

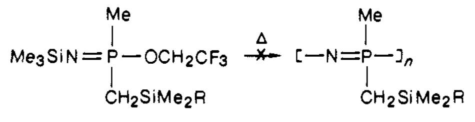
Copolymers are easily prepared by heating a mixture of two (or presumably more) *N*-silylphosphoranimines containing the desired combination of alkyl/aryl groups.[65-67] Since most of the precursors decompose at comparable rates, the polymer composition is easily controllable by adjusting the stoichiometry (*x*:*y*) of the starting mixture. Several of the types of copolymers prepared in this manner are summarized in eq 28. In most cases, the monomer ratio (*x*:*y*) has been varied from ca. 1:5 to 5:1, thereby yielding a large number of copolymers having a broad spectrum of properties (i.e., solubilities, glass transition temperatures, viscosities, thermal stabilities, etc.). Typically, the molecular weights (M_w) of both the homo- and copolymers are in the range of ca. 50000–250000 and the molecular weight distributions are relatively narrow ($M_w/M_n \approx 1.5$–2.5). The detailed characterization of a representative series of these poly(alkyl/arylphosphazenes) is discussed in the next section.



$$\mathrm{x\,Me_3SiN{=}\underset{R^2}{\overset{R^1}{P}}{-}OCH_2CF_3 + y\,Me_3SiN{=}\underset{R^4}{\overset{R^3}{P}}{-}OCH_2CF_3 \xrightarrow[-Me_3SiOCH_2CF_3]{\Delta} [({-}N{=}\underset{R^2}{\overset{R^1}{P}}{-})_x({-}N{=}\underset{R^4}{\overset{R^3}{P}}{-})_y]_n} \quad (28)$$

R^1 =	Me	Me	Me	Me	Me	Me	Me	Me	Me	Et
R^2 =	Me	Me	Me	Me	Me	Me	Ph	Ph	Ph	Et
R^3 =	Me	Et	n-Pr	Me	Me	Me	Me	Me	n-Pr	Et
R^4 =	Ph	Et	n-Pr	Et	n-Pr	CH_2CH_2Ph	CH_2CH_2Ph	n-Pr	n-Pr	Ph

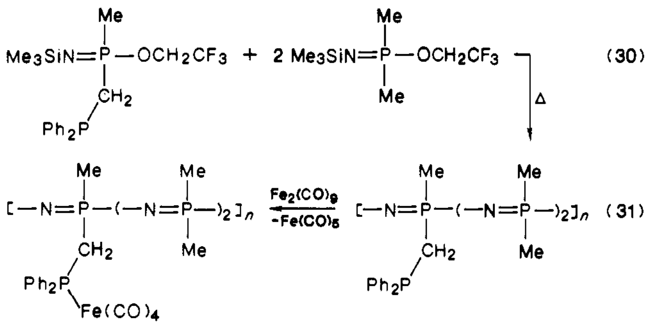
Poly(alkyl/arylphosphazenes) that contain chemically reactive substituents can, in principle, be prepared by introducing the desired functional groups either prior to polymerization by chemical modification of the simple *N*-silylphosphoranimines, or after polymerization by suitable derivative chemistry of a preformed poly(alkyl/arylphosphazene). The preparation of a variety of functionalized monomers and polymers are discussed, respectively, in sections V and IV of this review. In practice, we find that, although a wide variety of functional groups can be readily incorporated into the monomers, many of these functionalized monomers do not polymerize cleanly. A case in point is the general failure of the C-silylated precursors[73,74] to undergo condensation polymerization (eq 29). For reasons that are not yet clear, these silylated precursors are much more thermally stable than the parent dimethylphosphoranimine **15** and, under forcing conditions (ca. 220 °C, for up to 21 days), they decompose to unidentified, intractable black solids rather than linear polymers. On the other hand, silyl groups can be easily attached to the preformed polymer $[(Ph)(Me)PN]_n$ to give interesting, fully characterized materials (see section IV).



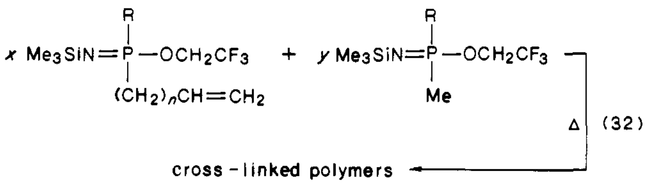
$$\mathrm{Me_3SiN{=}\underset{CH_2SiMe_2R}{\overset{Me}{P}}{-}OCH_2CF_3 \xrightarrow{\Delta}\!\!\!\!\!\!/\;\; [{-}N{=}\underset{CH_2SiMe_2R}{\overset{Me}{P}}{-}]_n} \quad (29)$$

R = Me, Ph, H, $CH{=}CH_2$, $(CH_2)_3CN$, etc.

The problem with the polymerization of the silyl-substituted monomers is probably not steric in nature, since other precursors with fairly bulky groups do polymerize. For example, *N*-silylphosphoranimines bearing the (diphenylphosphino)methyl group, Ph_2PCH_2, undergo facile copolymerization with **15** to afford novel poly(alkyl/arylphosphazenes) of moderate molecular weight (ca. 50000) which contain pendent phosphine ligands (eq 30 and 31).[75,76] The ability of such polymers to coordinate to metal centers, without chain degradation or cross-linking, was shown by their reactions with $Fe_2(CO)_9$, which gave the fully $Fe(CO)_4$ complexed derivatives (eq 31). These results indicate that it should be possible to use the skeleton of a poly(alkyl/arylphosphazene) as the substrate for selective attachment of a wide variety of transition-metal centers.

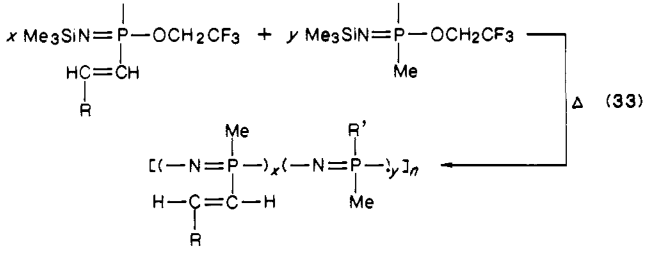


A third variation in the condensation polymerization of *N*-silylphosphoranimines involves the preparation of cross-linked polymers. This is an important objective because the capability of cross-linking the polyphosphazene chains, in a controlled fashion, is essential to their ultimate use as elastomers or structural materials. We have recently prepared a series of vinyl-,[77] allyl-,[75,76] and butenyl-substituted[74] phosphoranimines and have studied their cothermolysis reactions (eq 32) with both the dimethyl and the methylphenyl derivatives. In all cases which involve an *unsubstituted* group, attached either directly to phosphorus or through $(CH_2)_n$ spacers, the *cross-linking occurs during the polymerization process* itself. The products from such reactions are generally insoluble, tough, rubbery materials that form highly swollen gels upon treatment with organic solvents. This type of elastomeric behavior is characteristic of lightly cross-linked polymers. The degree of cross-linking in these systems, however, has not been determined.



n = 0, 1, 2; R = Me, Ph; $x{:}y$ = 1:1, 1:2, 1:5, 1:10, 1:20, ...

An alternative method,[70] which should ultimately permit much better control over the degree of cross-linking in the poly(alkyl/arylphosphazenes), is based on the use of monomers containing *1,2-disubstituted olefinic groups.* Such precursors have recently become readily available through simple derivative chemistry of the dimethyl precursor **15**, as will be described later (section V). Cothermolysis of these substituted monomers yields a series of soluble, un-cross-linked poly(alkyl/arylphosphazenes) ($M_w \approx 100\,000$) which contain pendent vinyl groups (eq 33). Subsequent curing of the materials with, for example, peroxides can then produce the desired *cross-linking after polymerization.*

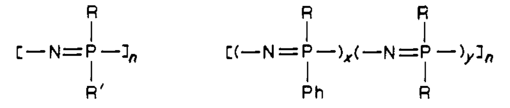


R, R′ = Me, Ph: $x{:}y$ = 1:2, 1:5, 1:10, 1:20, ...

In summary, the condensation polymerization is a general, high-yield synthesis of poly(alkyl/arylphosphazene) homopolymers, a wide variety of copolymers with easily controlled compositions, some types of functionalized polymers (e.g., with pendent phosphine ligands or substituted vinyl groups), and cross-linked, elastomeric materials.

B. Characterization and Properties of Poly(alkyl/arylphosphazenes)

Recently, we have reported[67] the results of a reasonably complete study of the properties of a representative series of poly(alkyl/arylphosphazene) polymers (**16–19**) and copolymers (**20** and **21**), prepared by the condensation polymerization method. These new materials were characterized by high-field NMR spectroscopy, dilute solution techniques (viscosity, membrane osmometry, light scattering, and size exclusion chromatography), thermal analysis (DSC and TGA), and X-ray diffraction measurements. Some of the key findings, which present a fairly clear picture of the nature of these materials, are summarized in this section.



16: R = R′ = Me
17: R = R′ = Et
18: R = Me, R′ = Ph
19: R = Et, R′ = Ph

20: R = Me
21: R = Et
$x = y$

Solubility Properties. As is the case with most poly(phosphazenes), the physical properties of these alkyl/aryl derivatives are found to be very dependent upon the nature of the substituents along the polymer backbone. This fact is illustrated, for example, by their solubility behavior. With the exception of poly(diethylphosphazene) (**17**),[78] which is insoluble in all common solvents, the new polymers are readily soluble in CH_2Cl_2 and $CHCl_3$, facilitating their characterization by NMR spectroscopy. In addition, the phenyl-substituted compounds (**18–21**) are soluble in THF and various aromatic solvents. While none of the polymers are water-soluble, $[Me_2PN]_n$ (**16**) is soluble in a 50:50 water/THF mixture.

NMR Spectral Data. All of the soluble polymers (e.g., **16** and **18–21**) give high-resolution NMR spectra that are completely consistent with their proposed structures.[67] The ^{31}P NMR spectra of the homopolymers **16**, **18**, and **19** consist of single peaks (with some fine structure noted for **18** and **19**) as expected, while those of the copolymers **20** and **21** contain two distinct sets of resonances, corresponding to the two different structural environments of the phosphorus centers along the polymer backbone. As observed for other types of poly(phosphazenes),[8] the ^{31}P chemical shifts of these alkyl/aryl substituted polymers are consistently ca. 15–30 ppm upfield from those of the analogous cyclic trimers and tetramers.

The ^1H NMR spectra of these polymers generally consist of relatively broad, featureless signals with the exception of the dimethyl compound **16** for which a sharp doublet is observed. In contrast, some important structural information is provided by ^{13}C NMR spectroscopy, particularly for the phenyl/alkyl derivatives

18 and **19**. These materials are rare examples[79] of poly(phosphazenes) that *contain two different substituents at each phosphorus atom in the chain and, thus, have the possibility of being stereoregular.* The fact that the structures are completely *atactic*, however, is clearly shown by the ^{13}C NMR spectral data. In particular, the high-field ^{13}C NMR spectrum of **18** contains three doublets in the P–Me region (ca. 22 ppm) in a 1:2:1 intensity ratio. This spectral feature clearly indicates a random stereochemistry of the side groups along the polymer backbone. The same reasoning accounts for the observation of three doublets (ca. 140 ppm) for the P-bonded phenyl carbon.

Dilute Solution Characterization. This series of poly(alkyl/arylphosphazenes) was also studied[67] by a variety of standard dilute solution techniques including viscosity measurements, membrane osmometry, size exclusion chromatography, and light scattering. Taken together, these studies demonstrate that *the poly(alkyl/arylphosphazenes) exist as extended, flexible chains in good solvents such as THF or* $CHCl_3$, *with average chain lengths of several hundred to a thousand repeat units and symmetrical molecular weight distributions* $M_w/M_n \approx 2$).

For all of the soluble polymers, plots of reduced viscosity vs. concentration were quite linear at low concentration (ca. 0.1–1.0%) with Huggins constants in the range (ca. 0.30–0.45) characteristic[80] of good polymer/solvent interactions. In order to investigate solvent effects in more detail, the viscosity of the phenyl/methyl polymer **18** was measured in a series of solvents (THF, $CHCl_3$, toluene, DMF, and THF containing 0.1% tetra-*n*-butylammonium bromide). The intrinsic viscosity ($[\eta] \approx 0.41$ dL/g) and the Huggins constant remained essentially the same in $CHCl_3$, toluene, and THF (with or without the ammonium salt additive), thus showing all of these to be very good solvents for the polymer. In DMF, however, $[\eta]$ decreased to 0.24 dL/g and the Huggins constant increased to 0.71, consistent with the polymer having a more tightly coiled structure in this polar solvent.

The absolute number average molecular weights (M_n) of the same series of polymers were determined by membrane osmometry.[67] The molecular weights (M_n) fall in the general range of 20 000–100 000 with those of the dimethyl (**16**) and phenyl/methyl (**18**) polymers and the corresponding copolymer (**20**) typically being greater than 50 000. The analogous phenyl/ethyl compounds (**19** and **21**) have somewhat lower molecular weights, but since they have not been studied as extensively, it is not known whether this is due to the greater steric bulk of the ethyl group or to other factors such as reaction time and/or temperature.

Until recently, the rapid and routine characterization of these poly(phosphazenes) was hindered by their anomalous behavior in size exclusion chromatography (SEC) experiments. The analysis of these materials was attempted on commercial columns, with either μStyragel or glass bead packings, at a variety of temperatures and concentrations. In addition, several different solvents including mixed solvent systems were investigated. In almost all cases, grossly distorted, severely tailing, nonreproducible chromatograms were obtained, suggestive of an adsorption type of interaction between the polymer and the column materials. We have found, however, that *these SEC problems are completely circumvented by the addition of a small amount (ca. 0.1 weight percent) of an ionic species such as* $(n\text{-}Bu)_4NBr$ *to the THF mobile phase.* Under these conditions, classic SEC behavior is observed and consistent, nontailing chromatograms are obtained. Moreover, the molecular weights measured by SEC, relative to narrow molecular weight polystyrene standards, agree very well (within ca. 20–30%) with the values determined by membrane osmometry. Similar effects were observed with other ammonium salt additives in THF as well as in $CHCl_3$ and CH_2Cl_2 solution. The fact that the solution viscosity, as mentioned above, is unaffected by the presence of the salt shows that there has been no significant change in the nature of the polymer/solvent interaction. The exact reason for this dramatic improvement in the chromatography is not known, but we speculated[67] that the ionic solute simply prevents whatever type of polar interaction was occurring in the prior experiments. Other new findings (see section IV.C), relevant to this question, indicate that the backbone nitrogen sites in these poly(alkyl/arylphosphazenes) are more easily protonated than those in the more conventional polymers bearing alkoxy, aryloxy, or amino substituents.

The absolute weight average molecular weights (M_w) of several samples of $[Ph(Me)PN]_n$ (**18**) from different preparations were determined by light scattering measurements in dilute THF solutions. The M_w values, which ranged from 73 000 to 202 000, were consistently (ca. 30%) higher than those obtained by SEC determinations. These results, when combined with the membrane osmometry data, confirmed that the SEC experiments provide valid representations of the molecular weight distributions of these poly(alkyl/arylphosphazenes). The second virial coefficients A_2 determined by light scattering are quite consistent with the osmometry values. The radius of gyration $\langle S^2\rangle_z{}^{1/2}$ of the highest molecular weight sample was found to be 249 Å and the calculated ratio $\langle S^2\rangle_x/M_w$ (ca. 0.31 Å^2·mol/g) is essentially identical with the value obtained for high molecular weight poly(dichlorophosphazene).[17] Also, a good correlation between M_w (light scattering) and intrinsic viscosity was observed for $[Ph(Me)PN]_n$ (**18**) over the molecular weight range noted above. Thus, the Mark–Houwink relationship, $[\eta] = K(M_w)^a$, gave values of $K = 1.44 \times 10^{-4}$ (with $[\eta]$ in dL/g) and $a = 0.66$. These data again indicate a well-solvated, extended-chain structure of the polymer in THF.

Thermal Analysis Results. Not surprisingly, thermal analysis experiments (DSC and TGA)[67] demonstrated that the nature of the substituents along the polymer backbone has a pronounced effect on properties such as glass transition and melting temperatures and on the overall thermal stability of these poly(alkyl/arylphosphazenes). The symmetrically substituted poly(dialkylphosphazenes) **16** and **17** showed sharp endothermic melt transitions, indicating a fairly high degree of crystallinity in the materials. On the other hand, none of the phenyl-substituted polymers (**18** and **19**) or copolymers (**20** and **21**) showed a melt transition; therefore, the side group asymmetry disrupts the crystalline order in the solid state. The general amorphous nature of the phenyl/alkyl homopolymers **18** and **19** is consistent with their structures being assigned as atactic on the basis of ^{13}C NMR spectroscopy (see above).

In DSC experiments, poly(dimethylphosphazene) (**16**) showed a glass transition of −46 °C which increased to −3 and 37 °C for the 25% (**20**) and 50% (**18**) phenyl substituted analogues. A similar trend was noted for the phenyl/ethyl derivatives **19** and **21**, although poly(diethylphosphazene) itself did not exhibit a discernible glass transition. Studies of a much larger series of polymers and copolymers (eq 27 and 28) are currently under way in order to better understand the structure/property relationships common to the poly(alkyl/arylphosphazenes).

Thermogravimetric analysis (TGA) of these poly(phosphazenes) showed their decomposition onset temperatures in an inert atmosphere to be ca. 350–400 °C, depending on the side group. These temperatures are ca. 25–70 °C higher than that reported for commercial materials based on the fluoroalkoxy-substituted polymer, $[(CF_3CH_2O)_2PN]_n$.[81] Preliminary indications, therefore, are that the incorporation of directly P–C bonded alkyl and/or aryl groups does enhance the thermal stability of poly(phosphazenes), as anticipated. Interestingly, methyl rather than phenyl side groups yield the more stable materials, as shown by the results for polymers **16**, **18** and **20**, which were found to have the highest decomposition temperatures. We have also recently reported[82] that silylmethyl groups (i.e., Me_3SiCH_2) have a significant stabilizing influence.

X-ray Diffraction Studies. In our work, samples of the poly(dialkylphosphazenes) **16** and **17** displayed X-ray powder diffraction patterns characteristic of crystalline regions in the materials. The peaks in the diffraction of **16** were of lower amplitude and greater angular breadth than those of **17**, indicating that poly(diethylphosphazene) (**17**) is highly crystalline while poly(dimethylphosphazene) (**16**) is more amorphous with smaller crystalline zones. This high degree of crystallinity is probably responsible for the insolubility of **17** as noted above. All of the phenyl-substituted polymers **18**–**21** were found to be amorphous in the X-ray diffraction studies, a result that is further evidence for an atactic structure of the poly(alkylphenylphosphazenes) **18** and **19** and for a random substitution pattern in the copolymers **20** and **21**.

Recently, Riecke and Magill[83] have used transmission electron microscopy for lattice imaging studies of single crystals of poly(dimethylphosphazene) (**16**) grown from dilute solution. They found that the polymer has a hexagonal crystal morphology with unit cell parameters of $a = b = 0.513$ nm and $c = 0.585$ nm. They also pointed out that $[Me_2PN]_n$ (**16**) does not exhibit the thermotropic behavior which is quite common among other types of polyphosphazenes such as $[(PhO)_2PN]_n$. Further studies along these lines are needed in order to improve understanding of these morphological features and their relationship to the bulk physical properties of the poly(alkyl/arylphosphazenes).

C. Polymerization Mechanism

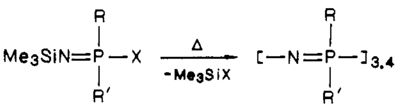
The successful synthesis of poly(alkyl/arylphosphazenes) by the condensation polymerization process leads to a number of questions concerning the mechanism of this reaction (eq 19). For example, are cyclic or monomeric phosphazenes involved in the mechanism, or does the polymerization occur via a step-growth or a chain-growth process, and if so, what are the actual initiation, propagation, and termination steps? Although no detailed studies specifically aimed at elucidating the mechanism have been conducted, there are a number of experimental observations that are noteworthy in this context.

The possibility of cyclic trimers or tetramers being formed as intermediates can probably be eliminated from consideration. Allcock[35] has already shown that the permethylated cyclics do not thermally polymerize under a wide variety of conditions. Moreover, we have found[84] that thermolysis of the dimethyl precursor **15** in the presence of the corresponding cyclics $[Me_2PN]_{3,4}$ affords a mixture of unreacted cyclics and the dimethyl polymer **16** (presumably formed by the polymerization of **15**), indicating that condensation polymerization and ring–ring equilibration[35]/ring opening occur by different mechanisms. It is more difficult to conclusively rule out the possibility of a monomeric phosphazene (e.g., $Me_2P{\equiv}N$) intermediate, especially since there is evidence for the existence of such a species, although it is stabilized by two bulky $[(CH_3)_2CH]_2N$ substituents on phosphorus.[54] The formation of an unstable, monomeric $R_2P{\equiv}N$ species in this polymerization process, however, is very unlikely. The major problem with this possibility is that it does not account for the preferential formation of polymers rather than the thermodynamically more stable cyclic trimers and tetramers. In fact, other transient, multiply bonded species (e.g., the isoelectronic silanones, $R_2Si{=}O$[85]) invariably form cyclic oligomers rather than linear polymers when they are generated in the absence of trapping agents. A monomeric intermediate also seems to be inconsistent with the leaving group effects that are described below.

In organic polymer chemistry, most condensation polymerizations occur via a step-growth mechanism in which the reactive functional groups condense with each other at a rate that is independent of molecular size.[80] As a consequence, the reaction mixture consists of mainly short-chain oligomers until very high degrees of conversion are achieved (e.g., when ca. 99% of the functional groups have reacted, the average polymer chain is only about 10 monomer units long). On the other hand, in a chain-growth mechanism, the important reaction is that between the functional end of a growing polymer chain and a monomer molecule. This leads to the formation of high molecular weight polymer at the early stages of the reaction sequence.

Initially, in our work, it was assumed that a typical step-growth mechanism was operative for the polymerization of *N*-silylphosphoranimines since the polydispersity (M_w/M_n) values of the poly(alkyl/arylphosphazenes) are close to the theoretical limit of 2.0, as expected for a step-growth process. The possibility of a step-growth mechanism is precluded, however, by results of experiments in which the polymerization was stopped prior to completion.[67] Even when the reaction is only ca. 20–50% complete, the reaction mixture consists of fairly high molecular weight polymer ($M_w \approx 60\,000$) and unreacted monomer. No indication of the presence of linear or cyclic oligomers is found in the NMR spectroscopic and SEC studies of these reaction mixtures. These data clearly indicate that some type of a *chain-growth mechanism must be occurring.*

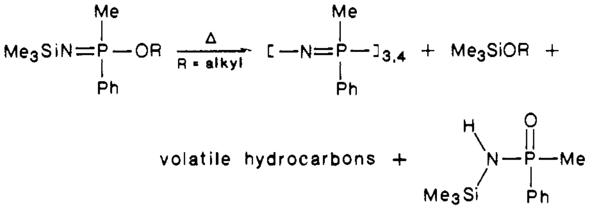
Information is also available on how the nature of the leaving group (X) at phosphorus effects the thermal stability and/or decomposition products of the *N*-silylphosphoranimines, $Me_3SiN{=}P(X)R_2$. The tendency of these precursors to thermally eliminate Me_3SiX follows the approximate order: X = halogen > aryloxy ≈ fluoroalkoxy > alkoxy ≈ amino. Thus, greater polarity of the $P^{\delta+}–X^{\delta-}$ bond and the corresponding leaving-group ability of X^- generally favor the elimination of Me_3SiX. As a result, the *P-halo*phosphoranimines often decompose during distillation when heated at relatively low temperatures (ca. 150 °C or less) while most of the other types of phosphoranimines can routinely be distilled without decomposition.[64,72] The leaving group also has a pronounced influence on the type of phosphazene—cyclic or polymeric—that is formed in these condensation processes. For example, the *N*-silyl-*P*-*halo*phosphoranimines decomposed to yield *cyclic* phosphazenes (eq 34), normally mixtures of trimers and tetramers, rather than polymers as obtained in the thermolyses of the trifluoroethoxy analogues (eq 27 and 28). At first glance, such a dramatic leaving-group effect might be interpreted as an indication that two different mechanisms were involved. Other work,[84] however, showed that Me_3SiBr reacts with $[Me_2PN]_n$, prepared from the P-OCH_2CF_3 derivative, at high temperature (ca. 180 °C) to cause chain degradation and formation of cyclic phosphazenes. This observation illustrates the principle mentioned in section II.C that condensation reactions must produce an "inert" byproduct in order to be useful for polymerization reactions. Apparently, trifluoroethoxy- but not halosilanes are suitable elimination products in this sense.



$$Me_3SiN{=}\overset{R}{\underset{R'}{P}}{-}X \xrightarrow[-Me_3SiX]{\Delta} [{-}N{=}\overset{R}{\underset{R'}{P}}{-}]_{3,4} \qquad (34)$$

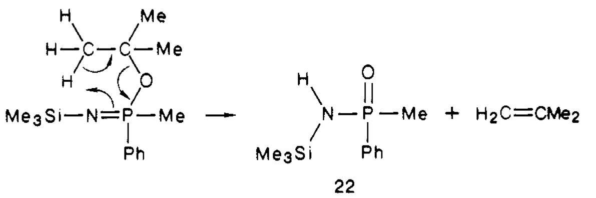
R = R' = alkyl, Ph; X = F, Cl, Br

These mechanistic questions, as well as the relatively high price of trifluoroethanol, led to an investigation of other alkoxy and aryloxy substituents as possible leaving groups.[69,70,86] Some unexpected as well as some useful results were obtained. When nonfluorinated *alkoxy* groups are attached to phosphorus, the precursors are much more thermally stable than the OCH_2CF_3 derivatives. Furthermore, when more drastic conditions are used, the *P-alkoxy* compounds decompose to yield *cyclic* phosphazenes along with other products (eq 35). For example, in the thermolysis of the *tert*-butoxy derivative (eq 36), the formation of the (silylamino)phosphine oxide **22** probably occurs via a β-elimination of isobutylene.



(35)

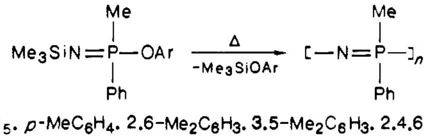
22



(36)

22

We have also prepared a large series of *P*-(*aryloxy*)phosphoranimines by treatment of the *P*-bromophosphoranimine, $Me_3SiN{=}P(Me)(Ph)Br$, with the appropriate phenol derivative in the presence of Et_3N.[70,86] In contrast to the results obtained with the alkoxy analogues, *the thermal decomposition of the aryloxy-substituted monomers is an efficient, high-yield, and inexpensive new preparative route to the poly(alkyl/arylphosphazenes)* (eq 37). The difference between these systems (i.e., alkoxy vs aryloxy leaving groups) can be attributed to the inability of the aryloxy (or OCH_2CF_3) groups to undergo β-elimination and to the fact that ArO^- is a better leaving group than RO^-.



$$Me_3SiN{=}\overset{Me}{\underset{Ph}{P}}{-}OAr \xrightarrow[-Me_3SiOAr]{\Delta} [{-}N{=}\overset{Me}{\underset{Ph}{P}}{-}]_n \qquad (37)$$

Ar = C_6H_5, p-MeC_6H_4, 2,6-$Me_2C_6H_3$, 3,5-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, p-ClC_6H_4, 2,4,6-$Cl_3C_6H_2$, p-$MeOC_6H_4$

In a general sense, therefore, the formation of poly(alkyl/arylphosphazenes) by the thermolysis of *N*-silylphosphoranimines appears to occur via a chain-growth process involving bimolecular reactions of the polar $P^{\delta+}–X^{\delta-}$ and $N^{\delta-}–Si^{\delta+}$ functional groups. Studies of the effects of variation of the leaving group (X) suggest that initiation may involve heterolytic cleavage of the P–X bond (i.e., formation of X^-). Further conclusions about the exact nature of the propagation and termination steps (and, eventually, a means of controlling the degree of polymerization) will require more detailed mechanistic studies.

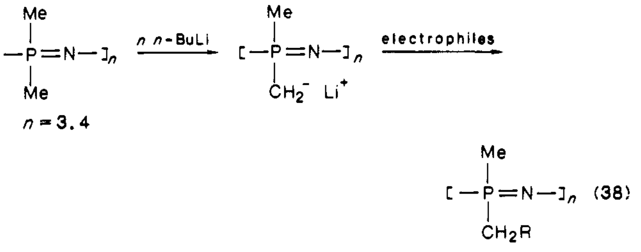
IV. Chemistry of Poly(alkyl/arylphosphazenes)

With the ready availability of a large number of poly(alkyl/arylphosphazenes), it is of interest to study the chemistry of these polymers in order to compare their reactivity to the amino-, alkoxy-, and aryloxy-substituted polymers and to diversify the types of substituents that can be attached directly to the backbone by P–C linkages. The latter reason is particularly important because the thermal, solubility, mechanical, surface, and chemical properties can be drastically altered by changing the nature of the side groups on the backbone. Furthermore, the attachment of various functional groups to the polymers offers potential sites for cross-linking, binding of transition-metal catalysts, and interaction with biological systems. Indeed, it is the numerous examples of the variety of properties of, and the incorporation of reactive functional groups into, the derivatives of $[Cl_2PN]_n$ that account for the uniqueness of polyphosphazenes among polymer systems. The results to be discussed in this section indicate that the more recently discovered poly(alkyl/arylphosphazenes) are likely to have a derivative chemistry which is similar in diversity and utility to that of poly(dichlorophosphazene).

As noted earlier (section II.D, eq 20–22), there are three potentially reactive sites in the simple poly(alkyl/arylphosphazenes): (1) the methyl group, (2) the phenyl group, and (3) the lone pair of electrons on the backbone nitrogen atom. Reactions at both the nitrogen atom[51] and the methyl group[52] in methyl and methyl/phenyl substituted cyclic phosphazenes (e.g., $[Me_2PN]_{3,4}$ and $Ph_4Me_2P_3N_4$) have been reported and serve as excellent models for reactions on the corresponding polymers. There is, however, very little work reported on the substitution reactions of the phenyl group in the cyclic phosphazenes.

A. Deprotonation/Substitution Reactions of *P*-Methyl Groups

The cyclic phosphazenes $(Me_2PN)_3$, $(Me_2PN)_4$, and $Ph_4Me_2P_3N_3$ have been deprotonated by butyllithium and the resulting anions quenched with electrophiles to yield phosphazenes with a variety of PCH_2R substituents (e.g., eq 38).[52] Surprisingly, the deprotonation reaction of the permethylated cyclics occurs completely, even if a deficiency of n-BuLi is used, so that 100% substitution (i.e., one R group per PN monomer unit) is easily achieved. Only with the tetraphenyl derivative $Ph_4Me_2P_3N_3$ is it possible to obtain monosubstituted rings.



$$[-P(Me)_2=N-]_n \xrightarrow{n\ n\text{-BuLi}} [-P(Me)(CH_2^-\ Li^+)=N-]_n \xrightarrow{\text{electrophiles}} [-P(Me)(CH_2R)=N-]_n \quad (38)$$

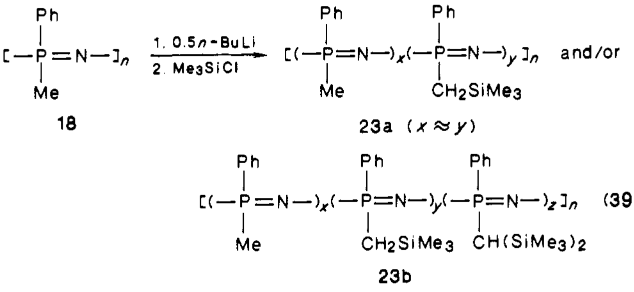
$n = 3, 4$

R = Me, Br, I, PhC(O), CO_2H, $AsMe_2$, MMe_3 (M = Si, Ge, Sn)

Similar reactions can be carried out on the N-silylphosphoranimine precursors to the poly(alkyl/arylphosphazenes)[73-76] (see section V.B. below) and, like the cyclic systems, can be used as models for the reactivity of poly(alkyl/arylphosphazenes). Related deprotonation/substitution reactions of the preformed polymers are under investigation in our laboratories and have resulted in the preparation of silylated polymers with reactive functional groups, polymers with alcohol side groups, carboxylated polymers and a water-soluble derivative, and polystyrene grafted copolymers. In contrast to the chemistry of the permethylated cyclic phosphazenes, however, it has not yet been possible to achieve more than ca. 50% substitution (i.e., one functional group per two PN units). Several types of these reactions are discussed below.

1. Reactions with Halides

In 1986, we reported[82] the first derivatization reaction of a poly(alkyl/arylphosphazene). In this study, one-half of the methyl groups in $[Ph(Me)PN]_n$ (chosen for its solubility in THF as opposed to $[Me_2PN]_n$, which is insoluble in THF and other ether solvents favorable for the deprotonation reaction) were deprotonated by treatment with 0.5 equiv of n-BuLi at −78 °C. Subsequent addition of 0.5 equiv of Me_3SiCl at −78 °C afforded the 50%-silylated derivative **23** (eq 39). (A few other polyphosphazenes bearing CH_2SiMe_3 groups have been reported.[41]) While elemental analysis indicated complete incorporation of the Me_3Si group into the polymer, it is especially noteworthy that SEC (size exclusion chromatography) analysis showed that *no cleavage of the P–N backbone occurred.* In fact, the M_w of the Me_3Si derivative **23** was 26% higher than that of the parent polymer as expected for complete incorporation of the silyl groups. The molecular weight distributions as well as the intrinsic viscosities of the parent polymer **18** and the silylated product **23** were virtually identical. Presumably, it is the mild conditions of this reaction (i.e., −78 °C) that prevent chain degradation which occurs when poly(halophosphazenes) are treated with organolithium reagents.[31,33]



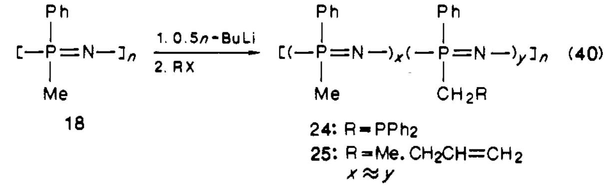
$$[-P(Ph)(Me)=N-]_n \xrightarrow[2.\ Me_3SiCl]{1.\ 0.5n\text{-BuLi}} [(-P(Ph)(Me)=N-)_x(-P(Ph)(CH_2SiMe_3)=N-)_y]_n \text{ and/or } [(-P(Ph)(Me)=N-)_x(-P(Ph)(CH_2SiMe_3)=N-)_y(-P(Ph)(CH(SiMe_3)_2)=N-)_z]_n \quad (39)$$

While the simplest representation of the silylated polymer is **23a**, the ^1H and ^{13}C NMR spectra suggested that deprotonation occurred more than once on some of the methyl groups, producing polymer **23b** with $CH(SiMe_3)_2$ groups as well as CH_2SiMe_3 and unreacted methyl groups. The number of $CH(SiMe_3)_2$ groups increases when the reaction is carried out under more dilute conditions (i.e., less than ca. 0.6 M) and when $[Ph(Me)PN]_n$ is treated first with 0.5 equiv of n-BuLi and then with two 0.25-equiv portions of Me_3SiCl at 1-h intervals. These conditions presumably favor the rearrangement (via H^+ migration from a pendent $P-CH_2SiMe_3$ to a $P-CH_2^-$ center) of the polymeric anion to a more thermodynamically stable form containing a significant number of $P-C(SiMe_3)H^-$ sites.

The thermal stability of the silyl-substituted polymers **23** is very interesting since the onset of decomposition (391 °C) is ca. 30 °C higher than that of the parent polymer, $[Ph(Me)PN]_n$ (**18**). This is analogous to the higher thermal stability of the phosphoranimine $Me_3SiN{=}P(OCH_2CF_3)(CH_2SiMe_3)Me$ relative to its nonsilylated analogue **15**.[73,74]

A series of related polymers $\{[Ph(Me)PN]_x[Ph(RMe_2SiCH_2)PN]_y\}_n$ [where R = H, $CH{=}CH_2$, and $CH_2(CH_2)_2C{\equiv}N$] have been prepared in the same fashion. These materials offer the possibility of further derivatization via the Si–H bond, the unsaturated vinyl moiety, or the cyano group and indicate that many other functional groups may be attached to the backbone through the CH_2Si spacer group. Several polymers with the same RMe_2Si substituents on 20% of the PN monomer units have also been prepared by treatment of **18** with 0.2 equiv of n-BuLi/RMe_2SiCl.

These deprotonation/substitution reactions have also been carried out with other inorganic halides[87] (i.e., Ph_2PCl) and with several organic[88] halides (e.g., MeI, $CH_2{=}CHCH_2Br$) (eq 40). The attachment of phosphine moieties (**24**) in this manner compliments that discussed in section III.A, in that it allows for the preparation of high molecular weight polymers with as many as one phosphine substituent per two PN repeat units. Similarly, use of allyl bromide permits attachment of the vinyl functional group (**25**: R = $CH_2CH{=}CH_2$), which can be used as a cross-linking site.



$$[-P(Ph)(Me)=N-]_n \xrightarrow[2.\ RX]{1.\ 0.5\,n\text{-BuLi}} [(-P(Ph)(Me)=N-)_x(-P(Ph)(CH_2R)=N-)_y]_n \quad (40)$$

18

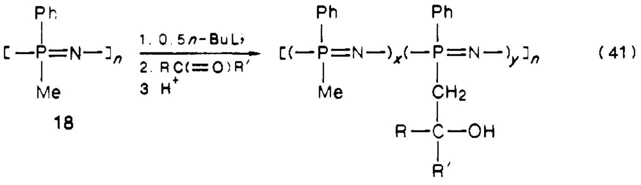
24: R = PPh$_2$

25: R = Me, CH$_2$CH=CH$_2$

$x \approx y$

2. Reactions with Carbonyl-Containing Electrophiles

The reactivity of the polymeric anion toward electrophiles has been further demonstrated by its reactions with aldehydes and ketones (eq 41).[89,90] Treatment of the anion with these carbonyl compounds, containing both aliphatic and aromatic groups, and subsequent quenching of the alkoxy anion with a saturated aqueous solution of NH_4Cl resulted in a series of new polymers **26** in which 30–50% of the methyl groups were functionalized. In general, when the reactions were carried out by generation of the polymer anion at −78 °C with 0.5 equiv of n-BuLi, stirring 1 h, and adding the quench at −78 °C, the aldehydes reacted cleanly to give 45–50% substitution while the ketones typically produced polymers with only 20–30% of the methyl groups substituted. If, instead, the anion was allowed to warm to 0 °C before addition of the ketone, higher degrees of substitution were obtained (30–40%). This implies that the polymer anion is more thermally stable than expected and that nucleophilic attack at the carbonyl carbon is favored over quenching of the anion by abstraction of a proton from the carbon α to the carbonyl group, a problem which does not exist with the aldehydes. These polymers were fully characterized by ^1H, ^{13}C (including DEPT experiments which allowed for assignments of all chemical shift values), and ^{31}P NMR spectroscopy, IR spectroscopy, elemental analysis, and SEC, with the latter again confirming that no chain degradation occurred as was shown with the silylation reactions.



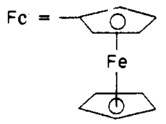
$$[-P(Ph)(Me)=N-]_n \xrightarrow[2.\ RC(=O)R'\ \ 3.\ H^+]{1.\ 0.5\,n\text{-BuLi}} [(-P(Ph)(Me)=N-)_x(-P(Ph)(CH_2C(R)(R')OH)=N-)_y]_n \quad (41)$$

18

26 ($x \approx y$)

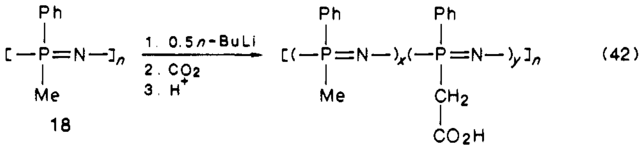
	a	b	c	d	e	f
R	H	H	Me	Me	H	Me
R′	Ph	Me	Me	Ph	Fc	Fc

Fc =



Perhaps the most interesting of these derivatives is **26e**, which contains approximately one ferrocenyl moiety for every two PN repeat units.[89] By thermogravimetric analysis, the onset of decomposition of this compound was ca. 360 °C, with a slight deflection at ca. 100 °C. More importantly, the weight retained above 800 °C (53%) is remarkably high for polyphosphazenes, which generally tend to form cyclics that sublime, leaving very little residue after thermolysis.

Poly(alkyl/arylphosphazenes) containing the carboxylate functional group (**27**) have also been prepared by a similar reaction sequence in which CO_2 is used as the electrophile (eq 42). At the 50% substitution level, the polymer is insoluble in water, but readily becomes soluble on conversion to its sodium salt. Recent experiments suggest that even the carboxylic acid derivatives are somewhat water soluble if the degree of substitution is increased (i.e., above 50%) by using 1 or more equiv of n-BuLi and stirring at 0 °C rather than at −78 °C, conditions which favored higher degrees of substitution for the ketone reactions discussed above. The carboxylic acid derivatives **27** provide access to many other types of functionalization reactions, including cross-linking by typical organic condensation polymerization reactions.



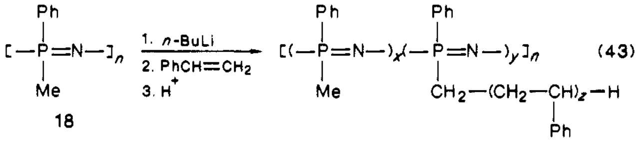
$$[-P(Ph)(Me)=N-]_n \xrightarrow[2.\ CO_2\ \ 3.\ H^+]{1.\ 0.5\,n\text{-BuLi}} [(-P(Ph)(Me)=N-)_x(-P(Ph)(CH_2CO_2H)=N-)_y]_n \quad (42)$$

18

27 ($x \approx y$)

3. Graft Copolymers

The anions generated on $[Ph(Me)PN]_n$ have also been used to initiate the anionic polymerization of styrene,[86,91] resulting in graft copolymers **28** (eq 43) with both organic and inorganic components.[92] On the basis of control experiments which were carried out simultaneously with the grafting reactions, copolymers with chain lengths of ca. 150, 50, and 20 styrene monomer units have been attached to 10–20% of the PN monomer units. Size exclusion chromatographic analysis indicated significant molecular weight increases as a result of grafting (ca. 300 000 to 650 000), whereas physical blends of polystyrene and **18** had SEC traces clearly representative of mixtures of the two components. Moreover, the viscosities of the grafts (ca. 1.4–3.3 dL/g) were markedly different from that of similar blends (ca. 0.2 dL/g). These reactions demonstrate the feasibility of using poly(alkyl/arylphosphazenes) as backbones in other inorganic/organic and inorganic/inorganic graft copolymers.



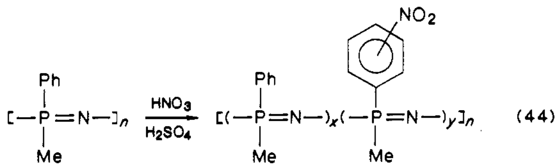
$$[-P(Ph)(Me)=N-]_n \xrightarrow[2.\ PhCH=CH_2\ \ 3.\ H^+]{1.\ n\text{-BuLi}} [(-P(Ph)(Me)=N-)_x(-P(Ph)(CH_2-(CH_2-CH(Ph))_z-H)=N-)_y]_n \quad (43)$$

18

28

B. Substitution Reactions of *P*-Phenyl Rings

The attachment of the substitutents in poly(alkyl/arylphosphazenes) by direct P–C bonds should enhance the chemical stability of the P–N backbone, thus making possible the use of a greater variety of reagents and rather severe reaction conditions in derivatization reactions. An example of this is the nitration of the phenyl substituent in $[Ph(Me)PN]_n$ (**18**) with nitric and sulfuric acids at 50 °C (eq 44).[93] Reaction times of 15, 30, 60, 90, and 170 min produced the nitrated deriva-



$$[-P(Ph)(Me)=N-]_n \xrightarrow[H_2SO_4]{HNO_3} [(-P(Ph)(Me)=N-)_x(-P(C_6H_4NO_2)(Me)=N-)_y]_n \quad (44)$$

18

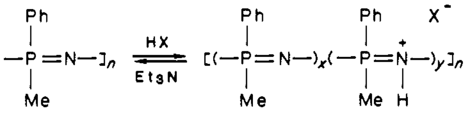
29

tives **29** as light yellow, film-forming materials. Both ^{31}P NMR spectroscopy and SEC analysis indicated that these products were still polymeric. The SEC molecular weights were, however, lower and the molecular weight distributions were narrower than that of the parent polymer. Interestingly, the *apparent* molecular weight showed a very small, but steady, decrease (from ca. 60 000 to 50 000 over the entire range of times) with the reaction time. These results suggest that the solution properties of the derivatized polymers have been altered by the polar NO_2 groups, while the actual polymer chain length is probably unchanged.

C. Reactions of the Backbone Nitrogen Atoms

The third potentially reactive site in polyphosphazenes is the backbone nitrogen. A good example of donation of the nitrogen lone pair electrons to Lewis acids is found in the biologically active platinum complexes of methylamino-substituted polyphosphazenes.[94] Several transition-metal complexes of the cyclic methylphosphazenes have also been prepared,[51] indicative of the donor properties of the nitrogen centers in these systems. In fact, the backbone nitrogens in poly(alkyl/arylphosphazenes) should be particularly good donors because of the electron-releasing nature of the organic substituents attached directly to phosphorus. This is indeed the case for the cyclic methyl phosphazenes, $[Me_2PN]_n$ (n = 3–5), which form stable salts with HCl, $HClO_4$, and alkyl iodides.[51] Interestingly, the cyclic trimer undergoes protonation or methylation at only one of the nitrogen atoms per ring, whereas the tetramer and pentamer can readily take on either one or two substituents per ring at the nitrogen centers.

The analogous chemistry of the *polymeric* alkyl/arylphosphazenes has not yet been extensively studied. Preliminary work in our laboratories,[86,93] however, strongly suggests that the same types of reactions are possible. For example, treatment of CH_2Cl_2 or THF solutions of poly(methylphenylphosphazene) (**18**) with several acids (either anhydrous or aqueous) leads to precipitation of protonated polymers **30** (eq 45). Addition of excess Et_3N results in regeneration of the parent polymer as confirmed by NMR spectroscopic and SEC analysis. In the case of the HI salt, the degree of protonation was found to be ca. 68% both by the mass balance of the reaction and by the elemental analysis of the protonated polymer. Similarly, poly(dimethylphosphazene) (**16**) can be protonated to yield, in this case, a water-soluble polymeric salt. The reaction of **16** with MeI has also been studied by NMR spectroscopy, although the maximum degree of methylation has not yet been determined.



$$[-\overset{\displaystyle Ph}{\underset{\displaystyle Me}{P}}=N-]_n \underset{Et_3N}{\overset{HX}{\rightleftharpoons}} [(-\overset{\displaystyle Ph}{\underset{\displaystyle Me}{P}}=N-)_x(-\overset{\displaystyle Ph}{\underset{\displaystyle Me}{P}}=\overset{+}{\underset{\displaystyle H}{N}}-)_y]_n\ X^- \quad (45)$$

18 30

Such reactions do not always occur without damage to the polymer chain. As mentioned in section III.C, the high-temperature interaction of preformed poly(alkyl/arylphosphazene) with Me_3SiBr results in complete cleavage of the polymer chains to give cyclic phosphazenes. In fact, this reaction occurs even under milder conditions (refluxing benzene solution). It seems likely that P–N bond cleavage could result from nucleophilic attack of the counter ion (e.g., Br^-) on a phosphorus center that is adjacent to a silylated nitrogen, although this hypothesis has not been verified experimentally.

V. Precursors to Poly(alkyl/arylphosphazenes)

The synthesis of poly(alkyl/arylphosphazenes) is essentially a four-step process (see eq 24–27, section III.A) that involves (1) synthesis of a (disilylamino)phosphine, $(Me_3Si)_2NPRR'$, bearing the desired substituents at phosphorus, (2) oxidation of this phosphine to the P^V state, i.e., the *N*-silylphosphoranimine, $Me_3SiN{=}P(X)RR'$, with elimination of one Me_3Si group, (3) modification of the leaving group (X) and/or the side groups (R, R′) to give the immediate precursor to the poly(alkyl/arylphosphazene), and (4) condensation polymerization of this precursor via the thermally induced elimination of a volatile silane (Me_3SiX) to afford the desired polymer, $(RR'PN)_n$. The development of this condensation polymerization process was made possible by, and, in fact, was a direct result of, our more fundamental studies of the preparative chemistry of small molecule silicon–nitrogen–phosphorus compounds. Two types of Si–N–P systems—the (silylamino)phosphines and the *N*-silylphosphoranimines—are of particular importance in this context. Various aspects of both the synthesis and reactivity of each of these classes will be discussed in this section of the review.

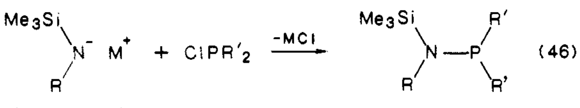
It is important to note that the chemistry of compounds which contain the Si–N–P linkage is usually markedly different from that of their nonsilylated analogues. On the one hand, the steric bulk and π-acceptor ability of the silyl group help to stabilize many types of unusual phosphorus compounds and, in many cases, to prevent cleavage of the P–N bond. On the other hand, the polarity of the silicon–nitrogen bond ($Si^{\delta+}$–$N^{\delta-}$) and the fact that silicon forms very strong bonds with, for example, oxygen and the halogens make the Si–N bond very susceptible to cleavage via nucleophilic attack at silicon. Thus, in addition to the "normal" modes of reactivity found in phosphorus chemistry, the preparative chemistry of Si–N–P compounds often involves silyl group elimination or rearrangement processes. As will be described in this section, these features of the chemistry of Si–N–P compounds are quite significant in the overall synthesis of poly(alkyl/arylphosphazenes) and their precursors.

Since such a large number of reports dealing with the synthesis, structure, reactivity, and stereochemistry of Si–N–P compounds have appeared in the last two decades, a complete survey of the field is well beyond the scope of this review. Instead, we will concentrate on those aspects of the chemistry that are most related to the topic of poly(alkyl/arylphosphazenes).

A. (Silylamino)phosphines

1. Synthesis

During the 1960s and 1970s, the most commonly used method of preparing (silylamino)phosphines involved treating silyl amides with an appropriate chlorophosphine (eq 46). The yields of such reactions are

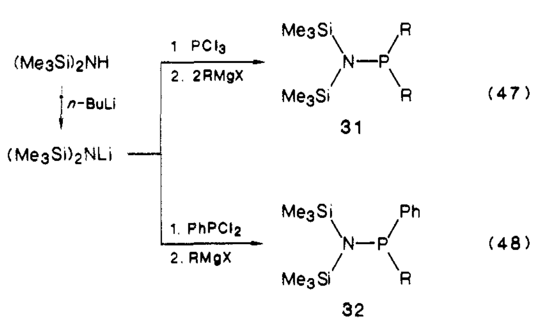


(M = Li, Na)

R	R'	ref
Me_3Si	Ph	95
alkyl	Ph	96
Me_3Si	Me	97, 98
Me_3Si	CF_3	99

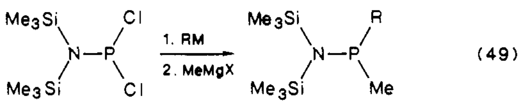
generally quite high, and, in fact, this is still the method of choice for preparing (silylamino)*diphenyl*phosphines, since Ph_2PCl is an inexpensive, readily available reagent. The method is not well suited, however, to the synthesis of the *P-alkyl* derivatives due to the technical problems (e.g., low yield, multistep syntheses, flammability, toxicity, etc.) encountered in preparing, storing, and handling large quantities of reagents like Me_2PCl. These problems become nearly insurmountable when unsymmetrically substituted reactants such as Ph(Me)PCl are required. Nevertheless, several of these (silylamino)phosphines were used for various preparative[95-98] and structural/stereochemical studies.[99] A few of the "parent" compounds containing H_3Si rather than Me_3Si groups on nitrogen were also prepared and structurally characterized.[99,100]

The major disadvantages of this synthetic approach to (silylamino)phosphines all stem from the fact that the phosphorus substituents (R, R') must be introduced prior to formation of the P–N bond. More recently, we have reported an alternative approach,[68,71] now known as the Wilburn method (developed by and named in honor of our late co-worker, J. C. Wilburn) (eq 47 and 48). This process is essentially a "one-pot" method in which the chlorine atoms in PCl_3 or $PhPCl_2$ are sequentially replaced by the bis(trimethylsilyl)amino and alkyl groups. The method typically produces the (silylamino)phosphine products as thermally stable, distillable liquids in overall isolated yields of ca. 70–95%. These reactions are routinely carried out on 1–3 mol scales with conventional laboratory glassware. The procedure is also extremely versatile in that virtually any symmetrical *dialkyl*phosphine (**31**) or unsymmetrical *phenyl/alkyl*phosphine (**32**) can be readily synthesized.[68,71,75,77]



R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, CH_2Ph, $CH{=}CH_2$, $CH_2CH{=}CH_2$, CH_2SiMe_3

The Wilburn method is also useful for the synthesis of some unsymmetrically substituted dialkylphosphine derivatives **33** (eq 49)[77,101-103] as long as the first substituent (R) is sufficiently bulky such that an intermediate chlorophosphine, $(Me_3Si)_2NP(Cl)R$, is cleanly produced. This variation of the method has, therefore, not been successfully used in cases such as the *methyl/ethyl*phosphine. Fortunately, it is also possible to incorporate more complicated side group arrangements at a later stage in the overall synthesis of the poly(alkyl/arylphosphazenes).



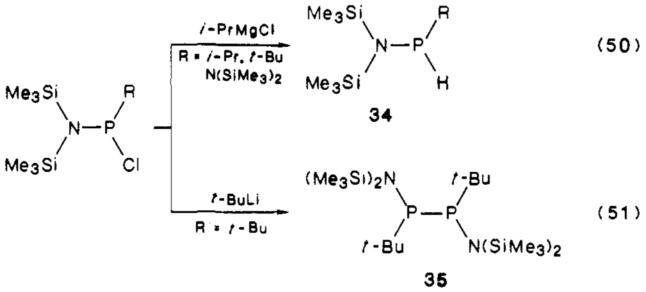
(M = MgX or Li)

33

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

Other useful modifications of the basic "one-pot" method have involved, for example, the use of 2 equiv of the silyl amide in the first step followed by 1 equiv of a Grignard reagent to give the bis[bis(trimethylsilyl)amino]phosphines, $[(Me_3Si)_2N]_2PR$ (R = Me, Et, $CH{=}CH_2$, CH_2SiMe_3, etc.).[104,105]

Interestingly, when attempts are made to introduce two sterically demanding groups on phosphorus by using the Wilburn method, unexpected products are sometimes observed. For example, when an isopropyl Grignard reagent is used in the second step, reduction to the P–H phosphine **34** (eq 50), via a β-elimination of propylene, is the major reaction pathway rather than simple nucleophilic substitution. These P–H substituted (silylamino)phosphines have been found to have some interesting derivative chemistry involving P–H to N–H rearrangements.[106] Still another mode of reactivity was observed when we attempted to prepare the di-*tert*-butyl derivative by reaction of the *t*-Bu/Cl substituted (disilylamino)phosphine with a second equivalent of *tert*-butyllithium (eq 51).[87] In this case, a high yield of the P–P coupled product **35** was obtained.

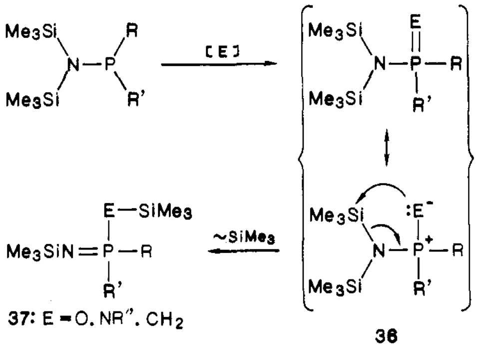


In summary, the Wilburn method is a convenient, high-yield "one-pot" synthesis of a wide variety of dialkyl and alkyl/phenyl substituted (disilylamino)phosphines from readily available and inexpensive reagents. Indeed, it is this process and the alkyl/arylphosphines that it affords which form the basis of the synthesis of poly(alkyl/arylphosphazenes). Some of the common types of reactivity exhibited by these (silylamino)phosphines are described in the next section.

2. Reactivity

In order for the (disilylamino)phosphines to be used as precursors to poly(alkyl/arylphosphazenes), the phosphorus must be oxidized to the P^V state. It is in this oxidation process that the unique chemistry of the Si–N–P linkage plays a major role. The reactions of (silylamino)phosphines with a large number of oxidizing reagents have been studied in considerable detail both prior to and after the discovery of the condensation polymerization route to poly(alkyl/arylphosphazenes). In general, these oxidation reactions fall into two general classes: (1) those involving simple oxidation at phosphorus accompanied by a silyl group migration, and (2) those involving oxidative halogenation at phosphorus followed by elimination of a halosilane.

The first of these types of oxidations can be summarized in the manner of eq 52. Such reactions clearly demonstrate the difunctional character of the (silylamino)phosphines in which oxidation of phosphorus (or *nucleophilic attack by phosphorus* on the oxidant) is accompanied by or followed by *electrophilic attack by silicon* on the electron rich P=E functionality. In any event, the products isolated from such reactions are phosphoranimines **37** resulting from the 1,3-shift of a silyl group from nitrogen to oxygen,[107] nitrogen,[108] or carbon.[109] These rearrangements have been shown, in several cases, to be *intra*molecular processes and the pertinent steric and electronic factors have been studied in some detail.

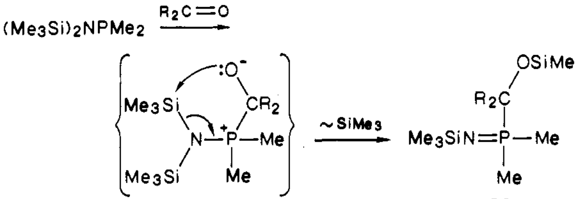


(52)

37: E = O, NR'', CH2

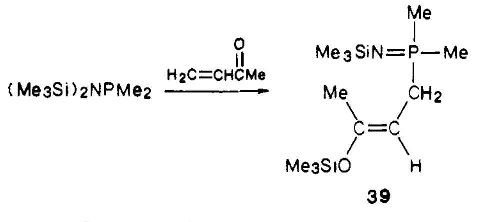
36

Similarly, the strong tendency of silyl groups to migrate from nitrogen to oxygen provides a driving force for the facile reaction of (silylamino)phosphines with aldehydes and ketones (eq 53).[110] These reactions proceed via nucleophilic attack by phosphorus followed by a 1,4-silyl shift to afford high yields of the CR_2OSiMe_3-substituted phosphoranimines **38**. With α,β-unsaturated carbonyl compounds, 1,4-addition to the conjugated system occurs, leading to novel silyl enol ether derivatives such as **39** (eq 54).[110]



(53)

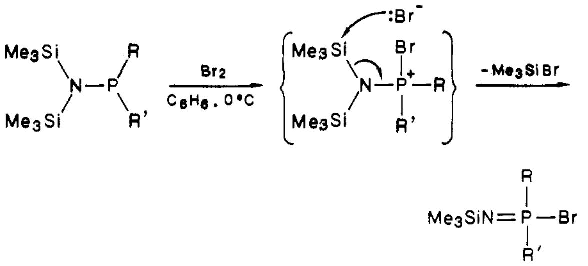
38



(54)

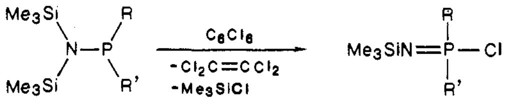
39

The second general type of reaction that (silylamino)phosphines readily undergo involves *elimination* (usually as a halosilane) rather than migration of a silyl group. This is best illustrated by the synthetically useful bromination reaction (eq 55) which quantitatively converts the (silylamino)phosphines into phosphazene precursors, i.e., the *P*-bromo-*N*-silylphosphoranimines (**40**).[72] Most simple organophosphines, R_3P, form phosphonium salts, $[R_3PBr]^+Br^-$, upon treatment with Br_2. It seems likely that the (silylamino)phosphines react similarly except that the Si–N bond in such an intermediate is easily cleaved by nucleophilic attack of the counter ion (Br^-) on silicon, thus accounting for the observed products. This is a very general reaction that has been successful for (silylamino)phosphines with a wide range of substituents on phosphorus.[74-78] In a similar manner, the analogous *P-chloro*phosphoranimines **41** are produced when alkyl/arylphosphines are treated with hexachloroethane, a mild source of Cl_2 (eq 56).[111]



(55)

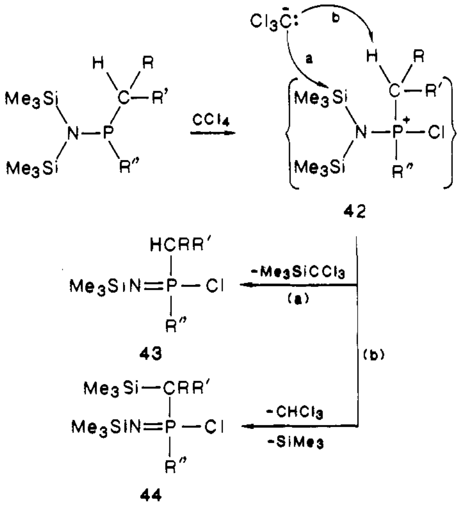
40: R = R' = alkyl, aryl, alkoxy, aryloxy, dialkylamino, etc.



(56)

41: R = R' = alkyl, Ph

The reactions of (silylamino)phosphines with CCl_4 (eq 57 and 58)[104,112] have also been studied in detail and are further examples of the two general modes of reactivity of these Si–N–P systems. In this case, the counterion (CCl_3^-) of the phosphonium salt intermediate **42** can either attack at silicon (pathway a, eq 57) with Si–N bond cleavage leading to phosphoranimine **43** or, instead, it can abstract a proton from the carbon α to phosphorus (pathway b, eq 58) to yield chloroform and the C-silylated phosphoranimine **44**. This latter product is probably formed via a 1,3-silyl shift from nitrogen to carbon in an ylide intermediate (see eq 52, E = CH_2). The type of product (i.e., **43** or **44**) which is favored in such reactions depends on a number of factors including solvent polarity, relative acidity of the α-hydrogen(s), and the number of Si–N bonds present in the (silylamino)phosphine. In many cases, the conditions can be adjusted so as to allow for the selective formation of a single desired product. Thus, these CCl_4 reactions are sometimes useful synthetic alternatives to the bromination process described above.



(57)

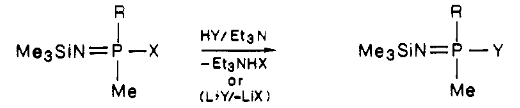
(58)

(Silylamino)phosphines also react with various organic halides including ethyl bromoacetate, allyl bromide, and chloroformates.[113] The initially formed phosphonium salts readily eliminate halosilanes to yield functionalized *N*-silylphosphoranimines of the type $Me_3SiN{=}P(R)Me_2$, where R = $CH_2C(O)OEt$, $CH_2CH{=}CH_2$, or $C(O)OR'$. The reactions of these phosphines with carbon disulfide, which yield zwitterionic products without silyl migration to sulfur, have also been reported.[114]

B. Functionalized *N*-Silylphosphoranimines

Virtually all of the products of the oxidation reactions of the (silylamino)phosphines described in the preceding section are *N*-silylphosphoranimines of general formula $Me_3SiN{=}P(X)RR'$. As we have discussed earlier (section III), some of these types of compounds are very useful precursors to both cyclic (X = halogen or alkoxy) or polymeric (X = fluoroalkoxy or aryloxy) phosphazenes. Because of their importance as precursors to poly(alkyl/arylphosphazenes), we have undertaken an extensive survey of the derivative chemistry of these *N*-silylphosphoranimines.[115] The major objectives of this work are (1) to study the effects of leaving group (X) variation in order to improve and optimize the polymerization process and to further elucidate the polymerization mechanism and (2) to introduce functional groups into the polymer precursors. In principle, there are three sites for variation of the structure of the *N*-silylphosphoranimine: the leaving group (X), the silyl group attached to nitrogen, and the other substituents (R, R′) attached to phosphorus. All of these cases have been studied in some detail and examples of each are described below.

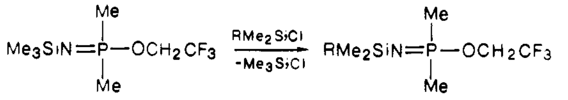
First, a wide range of potential leaving groups [e.g., Y = OR (45), OAr (46)][72,86] can be easily introduced by straightforward nucleophilic substitution reactions of the readily available *P*-bromo- or *P*-chlorophosphoranimines (40 and 41, respectively) (eq 59). The types of phosphazene products obtained from the thermolysis reactions of these phosphoranimines have been described earlier (section III). Dialkylamino[72] and PhS[86] groups can also be incorporated into the compounds by similar substitution reactions, although these phosphoranimines are too thermally stable to be useful as phosphazene precursors.



(59)

40: X = Br
41: X = Cl; R = Me, Ph
45: Y = OR′; R′ = any alkyl group
46: Y = OAr; Ar = as in eq 37

Second, the Si–N bond in these *N*-silylphosphoranimines is subject to cleavage by a variety of reagents via nucleophilic attack at silicon. A particularly straightforward example of this mode of reactivity is the process of transsilylation (eq 60)[116,117] in which the phosphazene precursor 15 is smoothly converted into a series of Si-functionalized derivatives 47. These reactions proceed rapidly at 0 °C in CH_2Cl_2 solution to give high yields (ca. 65–85%) of the transsilylated products. In similar fashion, compound 15 reacts in a 2:1 stoichiometry with dichlorosilanes to give the bis(phosphoranimino)silanes, $[Me_2(CF_3CH_2O)P{=}N]_2E$, where E = $-Me_2Si-$, $-SiMe_2CH_2CH_2SiMe_2-$, and $-SiMe_2(OSiMe_2)_nSiMe_2-$ (n = 0–4).[116]

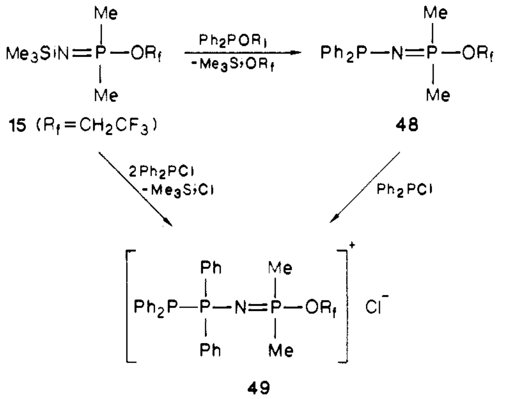


(60)

15

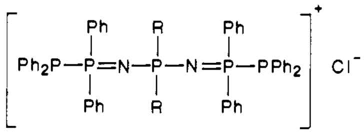
47: R = Ph, $CH{=}CH_2$, CH_2Cl, $CH_2(CH_2)_2C{\equiv}N$, $CH_2CH_2OC(O)Me$

The Si–N bond in phosphoranimines such as 15 is also susceptible to cleavage by other polar reagents. Diphenyl(trifluoroethoxy)phosphine, for example, reacts cleanly with 15 to yield the $P^{III}{-}N{=}P^{V}$ derivative 48 (eq 61), which in turn will add a molecule of chlorodiphenylphosphine (eq 62) to yield the phosphonium salt 49.[74,118] Alternatively, 49 can be produced in a single step by the reaction of 15 with 2 equiv of Ph_2PCl. This type of Si–N bond cleavage/quaternarization reaction had been reported earlier for simpler *N*-silylphosphoranimines, $Me_3SiN{=}PR_3$, without a functional group on phosphorus.[119] In related work,[118] we have found that more highly silylated phosphoranimines, e.g., $(Me_3Si)_2NPR_2{=}NSiMe_3$, undergo similar reactions with chlorophosphines to give novel multiphosphorus ionic species of the following type:



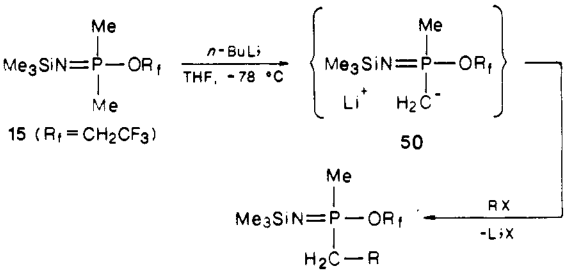
(61)

(62)



The third type of derivatization reaction of the *N*-silylphosphoranimines is the one most relevant to the synthesis of poly(alkyl/arylphosphazenes). This involves chemical modification of the phosphorus-bonded alkyl side groups in the actual condensation monomers such as $Me_3SiN{=}P(OCH_2CF_3)Me_2$ (15). There are two primary reasons for doing this type of derivative chemistry: (1) to obtain polymer precursors having a greater variety of functional groups and (2) to develop useful model reactions for similar chemistry to be later applied to the preformed poly(alkyl/arylphosphazenes) as discussed in section IV.

It was reported by Schmidbaur[120] that the permethylated *N*-silylphosphoranimine, $Me_3SiN{=}PMe_3$, could be converted to the silyl derivative, $Me_3SiN{=}P(CH_2SiMe_3)Me_2$, by treatment with *n*-BuLi followed by Me_3SiCl. As described earlier (section IV.A), similar deprotonation/substitution reactions can be carried out on methyl substituted cyclic and polymeric phosphazenes. Allcock[121] has reported, however, that phosphazenes bearing *trifluoroethoxy* groups undergo facile dehydrofluorination upon reaction with *n*-BuLi and various electrophiles. Recent work in our laboratories[73–76] has shown that, if mild conditions are employed, the methyl group in the phosphazene precursors such as $Me_3SiN{=}P(OCH_2CF_3)Me_2$ (**15**) can be selectively deprotonated by *n*-BuLi (eq 63) to yield the carbanion intermediate **50**. Solutions of the anion **50** in THF, which are stable up to ca. −50 °C, have been treated with a variety of alkyl,[122] phosphinyl,[75] and silyl[73] halides to afford high yields of the functionalized phosphoranimines **51**–**53**, respectively (eq 64). Quenching of the anion **50** with bromine produces the bromomethyl derivative **54** (eq 64).



15 ($R_f = CH_2CF_3$)

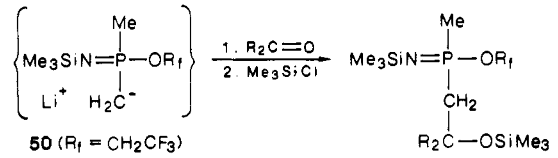
50

(63)

(64)

51: R=Me, CH_2Ph, $CH_2CH{=}CH_2$
52: R=PPh_2, $P(NMe_2)_2$
53: R=$SiMe_2R'$ [R′=Me (**a**), Ph (**b**), H (**c**), $CH{=}CH_2$ (**d**), $CH_2(CH_2)_2C{\equiv}N$ (**e**)]
54: R=Br

The carbanion **50** also reacts smoothly with other common organic electrophiles including aldehydes and ketones (eq 65).[122] In this series of reactions, the intermediate alkoxy anion was quenched with Me_3SiCl to give the *C*-siloxy derivatives **55**. This type of reaction is a good model system for the preparation of the alcohol substituted poly(alkyl/arylphosphazenes) (**26**, section IV.A, eq 41).



50 ($R_f = CH_2CF_3$)

55

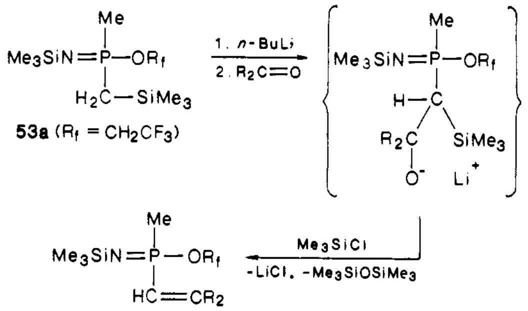
(85)

$R_2C(O)$ = MeC(O)Me, PhC(O)Me, PhC(O)H, $MeC(O)CH{=}CH_2$

The thermal decomposition reactions of most of these functionalized *N*-silylphosphoranimines have been studied. In many cases (e.g., the silylated compounds **53**), they are found to be more thermally stable than their simple precursors (e.g., **15**) and, thus, do not polymerize.[73] On the other hand, the diphenylphosphine derivative **52** does copolymerize with the dimethyl monomer **15** as described earlier (section III.A, eq 30 and 31) to yield poly(alkyl/arylphosphazenes) bearing phosphine ligands. Metal carbonyl complexes of both the polymer bound phosphines (eq 31) and the precursor model compounds **52** have been prepared.[75,76,86]

In spite of the fact that they do not undergo the condensation polymerization reaction, the C-silylated phosphoranimines **53** are synthetically useful compounds. For example, they can be used in the Peterson olefination reaction[123] in which the carbon α to silicon is easily deprotonated and then treated with carbonyl compounds (eq 66). The 1,2-elimination of $LiOSiMe_3$ (which is then quenched with Me_3SiCl) leads to high yields of the vinyl substituted *N*-silylphosphoranimines **56** (eq 67).[70,118]

Thus, by a combination of two successive deprotonation/substitution reactions (eq 63, 64 and 66, 67), the easily prepared dimethylphosphoranimine **15**



53a ($R_f = CH_2CF_3$)

(66)

(67)

56: R_2C = Me_2C, Ph(Me)C, Ph(H)C, $Ph(CF_3)C$, $Ph(H_2C{=}CH)C$, $(Me_2C{=}CH)C$, etc.

can be converted to a wide variety of new precursors to poly(alkyl/arylphosphazenes) which contain vinyl groups having virtually any substituent pattern that is desired. The condensation polymerization reactions of a few of these precursors **56** have been carried out, leading to several copolymers containing pendent vinyl groups (section III.A, eq 33).[70,118]

The chemistry of these *N*-silylphosphoranimines is, indeed, very diverse and has led to the synthesis of many different types of derivatives bearing functional groups at carbon, nitrogen, and silicon. Some of these compounds such as the phosphine derivatives **52** and the vinyl systems **56** are themselves very useful as condensation monomers for the synthesis of new functionalized poly(alkyl/arylphosphazenes), while others (e.g., the *C*-silyl derivatives **53**) are important as precursors to new monomers (e.g., **56**). Also, reactions involving cleavage of the Si–N bond in these systems can lead to many new element–nitrogen–phosphorus compounds such as transsilylation products and P_xN_y cations. A variety of other types of reactions of these multifaceted reagents are currently under investigation.

VI. Summary

This review has focused on the synthesis and characterization of polyphosphazenes with only P–C bonded substituents at phosphorus and on relevant chemistry of the Si–N–P precursors to these polymers. Polyphosphazenes with simple alkyl and aryl groups attached to the backbone are readily prepared in essentially quantitative yields by the condensation polymerization of *N*-silylphosphoranimines, $Me_3SiN{=}P(X)RR'$. This approach allows for the incorporation of the substituents at the small molecule stage, is facilitated by the ease of separation of the volatile silane byproducts from the polymers, and may potentially offer control of molecular weights through variation of leaving groups (X and R_3Si) and thermolysis conditions. The condensation method can also be used for the preparation of a variety of copolymers with certain functional groups that are unreactive at the polymerization temperature. In addition to its importance in the synthesis of poly(alkyl/arylphosphazenes), the condensation polymerization process may serve as a model for the preparation of other polymers with main group element backbones.

While the mechanism of this condensation polymerization is not fully understood, it appears to be a chain-growth process, probably initiated by heterolytic cleavage of the polar $P^{\delta+}$–$X^{\delta-}$ bond. Nonetheless, the poly(alkyl/arylphosphazenes) which result have been well characterized and exist as extended, flexible chains in solvents such as THF or $CHCl_3$ with average chain lengths of several hundred to a thousand repeat units and relatively narrow molecular weight distributions (i.e., $M_w/M_n \approx 2$).

Derivatization reactions of the simple poly(alkyl/arylphosphazenes), obtained from the condensation process, are also the source of new polymers with functionalized side groups. Through deprotonation/substitution reactions at the pendent methyl groups or electrophilic aromatic substitutions on the phenyl groups, ferrocenyl, alcohol, silyl and functionalized silyl, carboxylate, amino, nitro, and polystyrene groups have been attached to the polymers. The backbone nitrogen atoms are easily protonated, suggesting that Lewis acid coordination reactions may also be general processes for these systems. These straightforward reactions on the preformed polymers indicate that it should be possible to widely vary the chemical and physical properties of the P–C substituted phosphazenes by the attachment of many other functional groups, particularly those which cannot be attached to the phosphoranimine precursors, which do withstand the polymerization conditions, or which inhibit thermal polymerization.

The chemistry of the condensation polymer precursors has also been investigated. This has involved the synthesis of (silylamino)phosphines, $(Me_3Si)_2NPRR'$, with a variety of substituents (R and R′); studies of the most feasible methods of oxidizing these to the immediate polymer precursors, the *N*-silylphosphoranimines, $Me_3SiN{=}P(X)RR'$; and studies of the reactivity of the phosphoranimines, including transsilylation reactions, variation of the leaving group (X), and modification of the R and R′ side groups. This work has resulted in a less costly route to the polymers via the use of phenoxy rather than trifluoroethoxy leaving groups and in the preparation of functionalized phosphoranimines which can be easily converted to some new polymers. The side-group derivatization reactions also serve as models for reactions that can be carried out on the preformed polymers.

The P–C substituted polyphosphazenes offer another dimension to the already broad field of phosphazene polymers. The condensation polymerization and derivatization reactions of its products fully complement the ring-opening/substitution methods which have produced a large number of P–O and P–N substituted and several P–O/P–C substituted polyphosphazenes. It is clear, therefore, that phosphazenes are the most diverse class of inorganic polymers and that they will have a significant impact in the wide spread search for new materials. This relatively young class of polymers has already produced materials which can be used as electrical conductors, flame retardants, biomedical materials, and low-temperature elastomers. It is the very ease of attachment of such a large array of side groups by a variety of methods that allows for such diverse applications of polyphosphazenes and for the custom design of properties suitable for specific applications.

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