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# Linear, cyclic and polymeric phosphazenes

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CONTENTS

## ABSTRACT

An assessment of the diversity of phosphazene chemistry is presented with an emphasis on recent developments and their significance. Fundamental properties of phosphazenes are examined such as structure, nomenclature and bonding, and the various synthetic procedures are catagorized. In addition, the more important reactivity patterns are detailed and analysed. The review compares all systems containing the phosphazene bond, and makes extensive reference to previous reviews on specific types of phosphazene.

## A. INTRODUCTION

The ammonolysis of main group halides is one of the most important reactions of the representative elements. In addition to preparation of the phosphazenes, ammonolysis

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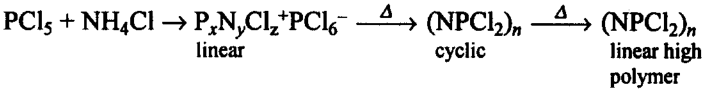
routes lead to many of the most important inorganic ring systems [1–3]. Specific examples include the borazines [2,4] and related Group IIIB entities [2], cyclosilazanes [2] and sulfur-nitrides [2,3]. In the case of the phosphazenes, the range of systems of interest is encompassed by the species involved in the ammonolysis of phosphorus pentachloride and the subsequent thermolysis of the initial reaction products.



$$PCl_5 + NH_4Cl \rightarrow \underset{\text{linear}}{P_xN_yCl_z{}^+PCl_6{}^-} \xrightarrow{\Delta} \underset{\text{cyclic}}{(NPCl_2)_n} \xrightarrow{\Delta} \underset{\text{linear high polymer}}{(NPCl_2)_n}$$

At each step, one has phosphorus(V) with a formal double bond to a two coordinate nitrogen atom and three additional $\sigma$ bonds ($\equiv P=N-$). There are three related systems employing this functionality: the short chain linear acyclic phosphazenes, the cyclophosphazenes and the long chain linear phosphazenes more commonly known as poly(phosphazenes). In this review, all three systems are discussed with the emphasis, however, being on the cyclophosphazenes. In order to give some idea of the expanding diversity of these systems, a (considerably) less detailed coverage of cyclo- and poly(phosphazenes) which incorporate other atoms into the phosphazene ring system is also discussed. The chemistry of the phosphazenes has been the subject of an authoritative monograph [5], numerous reviews of which two are of particular interest: one summarizes significant details of over eight hundred cyclophosphazene derivatives [6] and the other is a relatively recent, comprehensive review of cyclophosphazene chemistry [7]. With the exception of a few years respite, the phosphazene literature has been comprehensively surveyed on a yearly basis since 1969 [8–10].

## B. STRUCTURE

### *(i) Geometric structure and nomenclature*

#### *(a) Acyclic phosphazenes*

Acyclic, short chain, linear phosphazenes which are also referred to as phosphine imines or phosphoranimines have been subjected to numerous structural studies. For the generalized molecule, $R_3P=NR'$, there are three fundamental structural parameters of interest: the phosphorus–nitrogen (PN) bond length, the geometry at the nitrogen atom and the PNR' bond angle. The generally accepted phosphorus–nitrogen (PN) single distance is 177 pm which is found in the phosphoramidate anion, $NH_3PO_3^-$. The PN distances found in acyclic phosphazenes are uniformly shorter, generally in the range of 150–164 pm (Table 1). The geometry at the nitrogen atom is generally planar or only slightly distorted from planarity and the PNR' angle is in the range of 119–143° (for single P=N units) The structural data are thus supportive of some multiple bond character, the nitrogen atom of the PN unit being at least $sp^2$ and possibly having more s character. These arguments are based, in part, on the validity of the phosphorus–nitrogen distance in the phosphoramidate

TABLE 1

X-Ray diffraction data for selected acyclic phosphazenes

| Compound | PN[a] | PNX[b] | Comments | Reference |
|---|---|---|---|---|
| $\mathrm{Ph_3P{=}NMe}$ | 164.1 | 119.1 | X = C | 11 |
| $\mathrm{Ph_3P{=}NC_6H_4}$-*p*-Br | 165.7 | 124.2 | X = C | 12 |
| $\mathrm{Cl_3P{=}NC(CF_3)_2}$ | 150.5 | 142.9 | X = C | 13 |
| $\mathrm{Ph_3P{=}N_1{-}N_2{=}N_3{-}C_6H_4}$-*o*-$\mathrm{CO_2H}$ | 156.1 | 109.5 | X = N<br>$N_1N_2 = 132.8$<br>$N_2N_3 = 127.9$ | 14 |
| $\mathrm{Ph_3P{=}NPh}$ | 160.2 | 130.4 | X = C | 15 |
| $\mathrm{(Cl_3PNPCl_3)^+MoCl_6^-}$ | 154 | 139 | X = P | 18 |
| $\mathrm{[Ph_3PNPPh_3]^+V(CO)_6^-}$ | 153.9 | 180 | X = P, linear | 17 |
| $\mathrm{[Ph_3PNPPh_3]^+Fe(CO)_4C_3H_7^-}$ | 157, 158 | 145.9 | X = P, bent | 18 |
| $\mathrm{[Ph_2P(NH_2)NP(NH_2)Ph_2]^+Cl^-}$ | 157, 158 | 136 | X =<br>$\mathrm{PPNH_2}$ 164, 166 | 19 |
| $\mathrm{[Cl_3PNPCl_2NPCl_2NPCl_2]^+PCl_6^-}$ | 149.8, 157.2<br>152.7 | PNP =<br>143.1,<br>144.8<br>NPN = 110.9 | Planar,<br>*trans-trans* | 20 |

[a]Phosphorus–nitrogen distances in picometers. [b]Bond angles in degrees.

anion as being truly representative of a single bond. The structural data in Table 1 show that when a formal single PN bond is also present in the molecule, it is slightly longer than the formal PN double bond hence reinforcing the suggestion of multiple bond nature of the phosphazene. The bond angles and planarity at nitrogen are, of course, subject to the same debate as other second-row nitrogen derivatives (e.g. trisilylamine).

More complex acyclic phosphazenes also show interesting structural features. A general tendency to planarity of the $P_xN_y$ unit and a short phosphorus–nitrogen bond is observed. The most common higher acyclic phosphazenes are the $\mathrm{R_3PNPR_3^+}$ cations, several of which are presented in Table 1. The short and equivalent phosphorus–nitrogen bonds as well as the very large bond angles at nitrogen are strongly indicative of a delocalized PNP unit involving the nitrogen lone pair in addition to the P$\pi$ electrons. Due to its often utilized ability to crystallize with large anions, the $\mathrm{Ph_3PNPh_3^+}$ (PNP) cation has been examined by X-ray crystallography a number of times. Two such structures are presented in Table 1 and show both bent and linear forms of the cation. The linear species exhibits the shorter PN bond as would be expected for the configuration which maximizes $\pi$ bonding. The structures of several longer chain species have been reported in a comprehensive study by Allcock [20]. The general trends noted above are observed with variations relating to charge and end group effects being noted. Structurally, these long chain species are good models for the linear phosphazene polymers.

### (b) Cyclophosphazenes

Per-substituted cyclophosphazenes, $(NPX_2)_n$, exist in a wide range of ring sizes and conformations, selected examples of which may be found in Table 2. The most common species are the trimer ($n = 3$) and tetramer ($n = 4$) both of which are commercially available in the chloride series. The pentamer is also easily obtained. The series $(NPF_2)_n$ has been separated chromatographically up to $n = 17$ [21] and higher rings are believed to occur [22]. The trimeric species are planar (or nearly so) with phosphorus–nitrogen distances in the range of 157 pm. A slight decrease in the bond length with increased sub-

TABLE 2

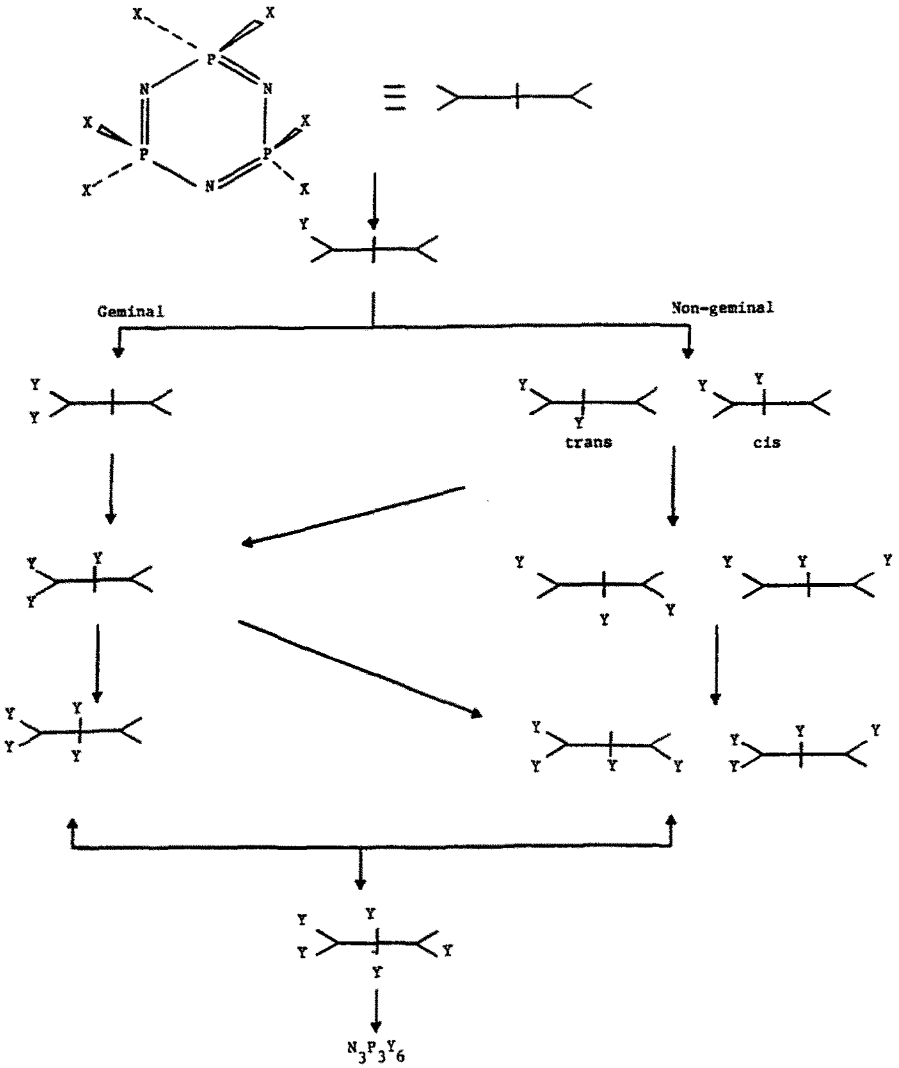
X-Ray diffraction for selected cyclophosphazenes

| Compound | Comments | Ref. |
|---|---|---|
| $N_3P_3F_6$ | Planar; PN 157; PNP 120.3; NPN 119.4 | 23 |
| $N_3P_3Cl_6$ | Almost planar; PN 158; PNP 121.4; NPN 118.4 | 24 |
| $N_3P_3Br_6$ | Slight chair; PN 157.6; NPN 118.5 | 25 |
| $N_3P_3Me_6$ | Distorted chair; PN 159.9–161.2 | 26 |
| $N_3P_3(NMe_2)_6$ | Slight boat; PN 158.8; $PN_{(exo)}$ 165.2; NPN 116.7 | 27 |
| $N_3P_3(NC_2H_4)_6 \cdot 3CCl_4$ | Planar; PN 159.2; $PN_{(exo)}$ 167.6 | 28 |
| $N_4P_4F_8$ | Planar; PN 151; PNP 147.2 NPN 122.7 | 29 |
| $N_4P_4Cl_8$ (K) | Boat; PN 157; PNP 113.3; NPN 121.2 | 30 |
| $N_4P_4Cl_8$ (T) | Chair; PN 156; PNP 135.6; NPN 120.5 | 31 |
| $N_4P_4Me_8$ | Puckered; PN 160; PNP 131.6; NPN 119.8 | 32 |
| $N_4P_4(NMe_2)_8$ | Puckered; PN 158; PNP 133; NPN 120.0 | 33 |
| $N_5P_5Cl_{10}$ | Nearly planar; PN 152; PNP 148.6; NPN 118.4 | 34 |
| $N_8P_8(NMe_2)_{16}$ | Centrosymmetric with two nearly planar seven-atom segments joined by step at N; PN 154.8; $PN_{(exo)}$ 165.1 | 35 |
| $Ph_2P^1N^1P^2F_2NP^3F_2N^3$ | $P_1$ out of plane; $P_1N_1$ 161.7, $N_1P_2$ 153.9; $P_2N_2$ 155.5 | 36 |
| *cis*- $(NMe_2)ClP^1N^1P^2(NMe_2)ClN^2P^3Cl_2N_3$ | Slight chair; $P_1N_1$ 157.5, $N_1P_2$ 158.3; $N_2P_3$ 156.8; $PN_{(exo)}$ 161.5–161.7 | 37 |
| $Me_2P^1N^1P^2F_2N^2P^3F^2N^3P^4F_2N^4$ | Saddle conformation; $P_1N_1$ 158.4, $N_1P_2$ 147.0, $P_2N_2$ 153.2, $N_2P_3$ 148.7 | 38 |

stituent electronegativity is observed. Endocyclic bond angles are in the range of 120. The per-substituted tetramers present an interesting study in structural variation with the nature of the substituent. The fluoro derivative, $(NPF_2)_4$, is planar while two conformations of the chloro derivative, $(NPCl_2)_4$, a tub and a chair form are known. The PN distances in the tetrameric series are generally shorter than in the corresponding trimeric analogs. The permethyl series, $(NPMe_2)_n$ ($n = 3$–$12$), is the largest known series of structurally characterized rings. The details of conformational variation in this series are discussed in a comprehensive paper dealing with this subject [22] and, contrary to several earlier suggestions, appear to be controlled primarily by steric interactions of the methyl groups. In spite of the vastly different electronic structures of the two series the conformations, especially of the larger rings, can be correlated with the analogous cycloalkane [22].

The structures of cyclophosphazenes with more than one type of substituent are far too numerous to be collected or discussed in this article and indeed the subject could form the basis for a review on its own. Selected data for all known structurally characterized cyclophosphazenes are available by combining the resources of several reviews [5,7–10]. Several significant and striking observations are, however, pertinent in the present context. The range of structural variation (bond lengths and to a lesser degree bond angles) imparted by substituent variation is far beyond anything found in carbocyclic or even other cyclic main group ring systems. Ring conformations also vary widely with the nature of the exocyclic group. The distance between a phosphorus center and an exocyclic substituent is also subjected to significant variation.

Before indicating any specific variations of the type noted above, the multiplicity of isomeric possibilities presented by these materials needs to be addressed. In Scheme 1, the positional and geometric isomers presented by the trimeric series are shown. While only one structure is possible for the per- and mono-substituted derivatives, the di-substituted derivatives, $N_3P_3X_4Y_2$, exhibit a range of structural possibilities due to the relative placement of the two Y substituents. If both substituents are on the same phosphorus atom, a geminal isomer is obtained while placement on adjacent phosphorus atoms leads to non-geminal species. In the non-geminal case, both *cis* and *trans* isomers about the plane (or average plane) of the ring are possible. Therefore, there are three possible regio- and stereoisomers for the generalized $N_3P_3X_4Y_2$ series of phosphazenes. A careful examination of the appropriate symmetry elements, or more appropriately the lack of same, in the *trans* non-geminal isomers shows that the possibility of optical isomerism exists due to the absence of superimposable mirror images. To date, only one reported resolution of the diastereomeric materials has been obtained by cyclization of a linear phosphazene (see Section C(ii)(b)) rather than from a substitution reaction of a preformed cyclophosphazene. Proceeding on to tri-substituted materials, $N_3P_3X_3Y_3$, again the possibility of regio- (geminal versus non-geminal) and stereoisomers (*cis* versus *trans*) occurs. In this case, the geminal product has the potential for optical isomerism. The tetra-substituted materials, $N_3P_3X_2Y_4$ obviously repeats the pattern of the di-substituted species and the penta-substituted material, $N_3P_3XY_5$ is analogous to the mono-substituted derivative.



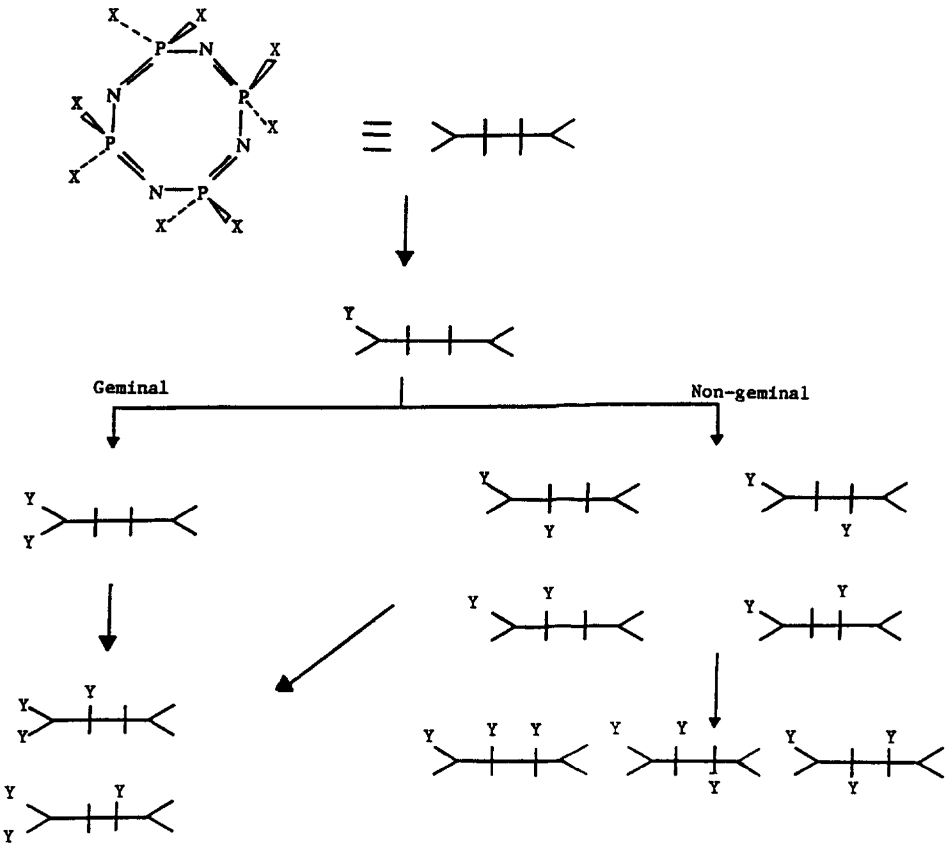
Scheme 1.

The extensive array of structures available for partially substituted systems requires a precise but non-cumbersome system of nomenclature. An older system wherein these materials are given the root name phosphonitrile has all but fallen into disuse. The Chemical Abstracts system refers to the PN unit as an azaphosphorine. This system rapidly becomes impractical when even the simplest materials are considered, e.g. $N_3P_3Cl_6$ would be referred to as 2,2,4,4,6,6-hexachloro-2,2,4,4,6,6-hexahydro-1,3,5,2,4,6-triazatriphosphorine. The system which is in general usage was originated by Shaw and takes phosphazene as the root for the ≡P=N– unit. Thus, a system with three coordinate nitrogen atoms, ≡P–N=, would be a phosphazane. The presence of a ring is indicated by the prefix cyclo and the number of units is also indicated by a prefix. In this system, $N_3P_3Cl_6$ would be referred to as hexachlorocyclotriphosphazene. Regio- and stereoisomers and specified by a numerical sequence starting with nitrogen and the standard *cis/trans* designation. Thus, a *trans* non-geminal bis(dimethylamino) derivative of $N_3P_3Cl_6$ would be referred to as 2,4-*trans*-bis(dimethylamino)tetrachlorocyclotriphosphazene and designated as 2,4-*trans*-$N_3P_3(NMe_2)_2Cl_4$.

Moving on to the tetrameric series, in Scheme 2 one can see an increase in structural complexity. While there is only one geminal isomer at the bis stage of substitution, there are two non-geminal sites, one at the adjacent phosphorus center (vicinal or 2,4 substitution) or on a non-adjacent phosphorus center (antipodal or 2,6 substitution). Each of the two non-geminal centers has possible *cis* and *trans* orientations of the two groups. The structural variations outlined at the bis stage of substitution continue in a fashion analogous to that outlined for the trimeric series (Scheme 1).

Returning to the structural data found in Table 2, it is clear that extensive variations of ring conformation and bond lengths occur as a function of substituent. Some generalizations, however, can be drawn from these and related data [5,7–10]. The larger the difference in electron donating/withdrawing ability between substituents in a mixed substituent ring system, the greater tendency for bond length inequality and deviation from planar geometry. The bond length variations do show a regular pattern. This variation is most clearly shown in geminal derivatives such as 2,2-$N_3P_3Ph_2F_4$ [36] where the PN distances starting from the ≡$PPh_2$ center are 161.7, 153.9 and 155.5 pm, respectively. These distances correspond to a long bond, a short bond and one in the range of the parent ($N_3P_3F_6$) compound. The origins of this variation are discussed in Section B(ii)(b). Variations are also noted in the tetrameric series where a long-short alteration can continue across the ring. A final structural feature of interest involves the exocyclic groups. Given the focus on PN bonds, the exocyclic distance to substituents derived from amines are of interest for most systems which have been examined by X-ray methods; two salient features are noted. The first is the exocyclic nitrogen atom which is observed (with one exception) to be approximately trigonal planar. The second feature of interest is the exocyclic PN distance which while longer than most endocyclic distances, is shorter than the 177 pm value assigned to a PN single bond. These observations suggest some back donation of exocyclic lone pair electrons to the phosphorus atom. Two types of substituents are of interest with regards to this model.

The first is the pair 2,2-$N_3P_3Cl_4(NHEMe_3)_2$ (E = C, Si). The structures of both are known and the exocyclic PN distances are essentially equivalent thus indicating that the phosphazene is a better lone pair acceptor than the organosilicon moiety [39]. The other system is the aziridino ($NC_2H_4$) derivatives. Several of these have been examined structurally and one example is included in Table 2. The exocyclic nitrogen atom is pyramidal and the exocyclic PN distance is slightly longer than those observed in other aminophosphazenes. The ring strain inherent in a three-membered ring will not allow for a trigonal

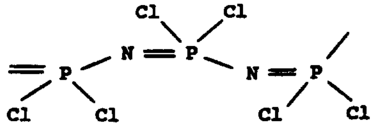


Scheme 2.

planar nitrogen. The pyramidal nitrogen forces the lone pair away from the acceptor center and hence the long exocyclic PN bond.

### (c) Poly(phosphazenes)

The fiber diffraction data for $(NPCl_2)_n$ has been examined several times [40,41] with both helix 2/1 [40] and glide conformations [41] being proposed as best fits for the data. In either case, the gross features of the planar chain are as follows:



Various indirect approaches to understanding this, and related, structures have been explored. These include conformational energy calculations [42] and modeling with short chain linear phosphazenes [20]. The nature of the PN units in the chain is also controversial with equal bond lengths [20,40] and alternating single (167 pm) and double (144 pm) PN bonds [41] being proposed. Dielectric relaxation times for $[NP(OPh)_2]_n$ have been interpreted in terms of single-double bonds [43]. Fiber diffraction data for $[NPR_2]_n$ (R = F [44], $OC_6H_4$-*p*-Cl [45], $OC_6H_3Me_2$ [46]) have indicated a 2/1 helix conformation.

The structural complexities of various phase transformations of poly(phosphazenes) have been a major subject of study in recent years and go far beyond the scope of this article. The relationship of side chain orientations to structure provide for mesophases [47,48] including liquid crystalline materials [49]. In addition to the references cited above, surveys of the original literature [10] should be consulted for details in this area.

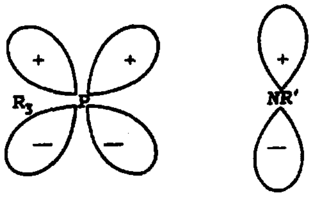
### (ii) Electronic structure

#### (a) Acyclic phosphazenes

A simple monophosphazene, $R_3PNR'$, could potentially be represented by the following two resonance forms:

$$R_3P{=}\bar{N}R' \longleftrightarrow R_3\overset{\oplus}{P}{-}\overset{\ominus}{\underline{\bar{N}}}R'$$

Since phosphorus is four coordinate, the double bond requires an expanded octet at phosphorus. Traditionally, the most accessible model for the double bond incorporates $d_\pi$ orbitals on phosphorus which can combine with the $P_\pi$ orbital on an $sp^2$ nitrogen center.

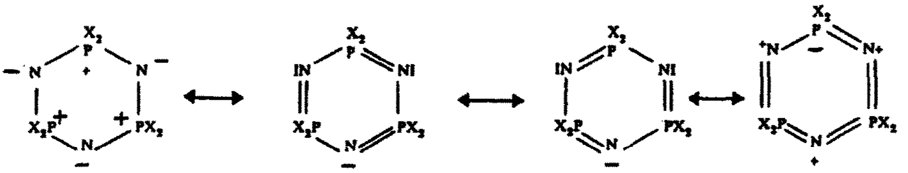


Even in the event of this interaction occurring, the $\pi$ system would be polarized towards the nitrogen center due to the significant electronegativity difference between the participating atoms. In the absence of any $\pi$ interactions, the ylidic or zwitterionic form would represent the electron distribution. Ab initio calculations have been carried out for the hypothetical species $H_3PNH$ [50]. The model that emerges from these studies is reminiscent of the phosphorus–carbon bond in ylides. The highly polar PN $\sigma$ bond is counterbalanced, in part, by a $N_{p\pi}/P_{d\pi}$ interaction. The resulting bond retains significant dipolar character with calculated charges of P, +0.73 and N, −1.02. Moving to molecules with substituents which are of chemical interest, semi-empirical MO (PRDDO) calculations on $Ph_3P{=}NC_6H_4$-*m,p*-R (R = $NO_2$, CN, $CF_3$, Cl, F, H, $CH_3$, $OCH_3$, $NMe_2$) suggest that the $\sigma^*_{PN}$ orbital is close enough in energy to compete with d orbitals in $\pi$ bond formation [51]. Extensive correlations of NMR parameters ($^{31}P$, $^{15}N$, $^{13}C$) with Hamment constants have been obtained for the arylphosphazenes [51–53]. The one bond coupling constants *J*(PN) and *J*(PC) correlate with $P_\pi$–$d_\pi$ and $P_\pi$–$\sigma^*_{pc}$ interactions, respectively. The $Ph_3PN$ group is found to be a strong electron donor [53]. Evidence for the high formal charges in $Ph_3PNPPh_3^+$ (N, −0.5, P, +0.9) has been obtained from IR intensity and ESCA measurements [54].

Less attention has been give to longer chain acyclic phosphazenes. However, recent *ab initio* MO calculations on $OP(F_2)NP(F_2)NPF_3$ [55] and $H_3P(NPH_2)_nNH$ ($n$ = 1–4) [56] have been reported. The inclusion of d type functions on phosphorus improved the calculations. There are two components to the $\pi$ system, an in-plane and out-of-plane interaction similar to those found in cyclic phosphazenes. The $\pi$ systems are highly polarized with charge essentially localized in PNP fragments maximized at the nitrogen center. End group effects induce a very small bond alternation in the chain [55]. The calculations on the oligomeric series indicate that the bond alternation may continue through to the large limit for $n$, however the differences are too small to give rise to separate single and double bonds [56]. The ability of the end group to stabilize a charge separated structure is the key to the proposed bond alternation. Experimental verification of this effect has been claimed by noting the small differences in bond lengths observed for short chain phosphazenes [20,56] but it is important to note that these variations are comparable to those seen in polyenes rather than being indicative of single/double bond isolation.

### (*b*) *Cyclophosphazenes*

The range of possible electronic interactions in cyclophosphazenes is conveniently presented by considering classical resonance structures.



Three bonding interactions can be considered in these systems. The first of these is the $\sigma$ system using $sp^3$ phosphorus and $sp^2$ nitrogen centers. As noted above, this will be a highly polar bond due to electronegativity differences. From an orbital symmetry perspective there are two sets of $\pi$ interactions, an in-plane ($\pi'$) and an out-of-plane ($\pi$) set. The $\pi$ system can be viewed in two ways depending on which orbitals on the phosphorus center participate in electron delocalization. Taking the $z$ axis perpendicular to the plane of the ring and the $y$ axis bisecting the ring, the combination of a $d_{xz}$ orbital on phosphorus with a $p_z$ orbital on nitrogen allows for the unpaired electron from nitrogen to combine to form a two electron $\pi$ bond. Since three such interactions are possible, a six $\pi$ electron system is generated. A careful inspection of orbital signs will show one sign mismatch in the trimer thus disrupting "aromatic" delocalization in the six-membered ring [57]. Alternatively, it has been suggested by Dewar [58] that a linear combination of $d_{xz}$ and $d_{yz}$ orbitals will generate two orbitals of $\pi$ symmetry directed along the bond axes and thus maximize overlap. Since these two orbitals are orthogonal, there will be no $\pi$ communication through the phosphorus atom and the $\pi$ system will be restricted to three atom PNP segments or islands. The in-plane $\pi'$ system allows for interaction of the nitrogen lone pair with phosphorus $d_\pi$ acceptor orbitals. Lastly, an electron pair on the exocyclic atom could interact with the phosphorus $d_z{}^2$ orbital.

With the advent of powerful ab initio methods which can accommodate heavy atoms, a series of high level calculations on linear and cyclophosphazenes have appeared [55,56,59–61]. For details, one can consult the original literature but some salient points bear consideration. There are significant d orbital contributions [59,61] which primarily focus overlap in the bonding region [61]. The $\pi$ and $\pi'$ systems are both significant. While characteristics of both models appear in the results of the calculations, the island model seems to be the best qualitative fit [61]. In any case, the high $\sigma$ bond polarity results in all $\pi$ systems being strongly polarized towards nitrogen centers [55,60,61]. Photoelectron and Auger data support highly polarized centers [62]. Thus, when all endocyclic interactions are considered, the four resonance forms shown above give a reasonable description of the range of interactions which occur but the range of the $\pi$ system is largely restricted to PNP islands. The role of exocyclic interactions has been explored in calculations on the model compound $[NP(NH_2)]_2$ [60]. While the exocyclic nitrogen atom has inductive acceptor abilities, mesomeric interactions between the exocyclic nitrogen lone pair and the phosphorus center require d orbital contributions on phosphorus. In this particular model, endo and exocyclic PN bonds have similar overlap populations. This discussion is designed only as an introduction to the intricacies of bonding in cyclophosphazenes. For detailed discussions of the qualitative aspects, comprehensive reviews [5,57] are available. Summaries of experimental evidence for various bonding models are available [7,57]. It should be noted that experiments which unambiguously show conjugations beyond a PNP fragment are not available.

It is of value to explore some of the structural observations in the context of bonding models. The requirement of planarity as a prerequisite for delocalization does not carry over from carbocyclic systems to phosphazenes. The incorporation of d orbitals into the bonding scheme means that rehybridization to fit any observed direction can occur. Alternatively, if the island model is operative there is flexibility at each phosphorus atom. The bond length alternation in mixed substituent cyclophosphazenes can be best understood in terms of variations in the $\pi$ systems. Consider for example, a geminally di-substituted material, 2,2-$N_3P_3X_4Y_2$, where X is more strongly electron-withdrawing than Y. Given this situation, $\equiv PX_2$ centers will be more effective in attracting $\pi$ and $\pi'$ electron density than $\equiv PY_2$ centers. Therefore, in a $Y_2PNPX_2$ fragment, the $Y_2PN$ bond will be long and the $NPX_2$ bond will be short. The bonds in the $X_2PNPX_2$ fragment are unchanged and thus intermediate between the long and short values (see Table 2).

The question of exocyclic $\pi$ interactions is an important one. The fact that exocyclic PN bonds are shorter than the value for the phosphoramidate anion has been taken as evidence for $\pi$ interactions. The pyramidal character of the exocyclic nitrogen center and the somewhat elongated exocyclic PN bond in aziridinophosphazenes lends support to the $\pi$

model for the (non-aziridino) derivatives. Evidence exists for exocyclic lone pair delocalization for phosphazenes with carbanionic substituents [63]. Phosphazenes with substituents derived from oxyanions would be expected to have minimal lone pair delocalization due to the large phosphorus–oxygen electronegativity difference. Mesomeric interaction between exocyclic organic $\pi$ systems and the phosphorus centers in phosphazenes have been considered by several workers. NMR data can be interpreted in terms of the presence [64,65] or absence [66] of such interactions. Other diverse methods such as PE spectroscopy [67] and polymerization reactivity ratios [68,69] show that little or no exocyclic delocalization occurs. Whatever the origin of the effect, exocyclic substituents strongly influence the properties of the ring system. The fact that these effects are so much in evidence compared to carbocyclic systems is directly related to the large polarizability of the $(p\text{–}d)_\pi$ $\pi$ system. The perturbation of the ring system is demonstrated both in structural properties such as ring conformation and bond lengths (Table 2) and in chemical properties such as basicity. The basicity of the endocyclic nitrogen atoms varies extensively with the exocyclic group [70]. The perhalo derivatives, $(NPX_2)_3$ (X = F, Cl), show minimal basic behavior (as detected by titration with perchloric acid) while in systems with electron-donating groups, $(NPX_2)_3$ (X = $CH_3$, $NMe_2$), stable Lewis acid–base adducts form and show significant titrometric behavior.

### (c) Poly(phosphazenes)

There has been relatively little work on the electronic structure of long chain poly(phosphazenes). One approach to this problem has been extrapolation of the results from short-chain species (Section B(ii)(a)) to the long chain limit [55,56]. The main points of interest here are the comparison of the cyclic and linear molecular orbitals and the question of bond length alternation. If the $\pi$ system behaves essentially as PNP "island" fragments, then the short chain model is reasonable. This behavior is indicated in the calculations [55,56] and in fact the opening of the PNP bond angle has been shown to reduce overlap over multiple centers, thereby favoring the "island" description [55]. Bond length alternation has been estimated to be in the range of 4–5 pm which is consistent with polyenes but should not be considered as distinct single and double PN bonds [56]. An approach to analysis of the band structure of poly(phosphazenes) by considering the sum of individual bond contributions calculated at the semi-empirical CNDO/2 level has been produced [71]. The series $(NPX_2)_n$ (X = H, F, Cl) has been examined by this technique. The calculated band gap is too large for semiconductor behavior. The HOMO ($\pi$) system energy depends on both the side groups and the backbone while the LUMO ($\pi^*$) energy depends only on the PN backbone.

## C. SYNTHESIS OF PHOSPHAZENES

### (i) Acyclic phosphazenes

The synthetic chemistry of processes leading to monophosphazenes, $R_3P{=}NR'$, and short chain species has been an active area of investigation for most of the twentieth century. An attempt to be comprehensive in this regard would far exceed the bounds of this review. The topic has been covered in previous monographs on phosphorus chemistry [71–73] and uncited work may be found in these sources.

The Staudinger reaction allows for conversion of a phosphorus(III) derivative to a phosphazene via reaction with an azide through the intermediacy of a phosphazide, $R_3PN_3R'$.

$$R_3P + R'N_3 \rightarrow [R_3P{=}N{-}N{=}N{-}R'] \rightarrow R_3P{=}NR'$$

$R_3 = Ph_3, (OR)_3, Cl_3, Ph_2Cl, PR_2Cl, (NMe_2)_3, Me_3$

$R' = Ar, RSO_2, PhCO, Me_3Si$

The range of substituents on phosphorus is large [74] thus making the Staudinger reaction the method of choice in many preparations. In certain cases, the use of highly electron withdrawing groups on the azide (e.g. $2,4,6\text{-}(O_2N)_3C_6H_2$) allows for isolation of the intermediate [75].

The structures, as determined by X-ray crystallography, show the alternating double–single bonds for the phosphazide (Table 1). Diphosphines such as $Ph_2PCH_2PPh_2$ can be converted to either monophosphazenes, $Ph_2P({=}NSiMe_3)CHPPh_2$ [76] or diphosphazenes, $Ph_2P({=}NC_6H_4R)CH_2P({=}NC_6H_4R)Ph_2$ [77] by exercising stoichiometric control. The kinetics of certain Staudinger reactions show that steric hindrance due to substituents on the phosphine is not a significant barrier to this process [78]. The application of the Staudinger reaction to low coordinate (coordination number < 3) phosphorus(III) derivatives leads to low coordinate (coordination number < 4) phosphazenes. Two classes of low coordinate phosphorus(III) entities can be considered, cations and formally unsaturated species. Both iminophosphonium and bisphospho cations are available from the reactions of chlorophosphenium ions with organoazides [79].

$$R_2NPN{=}P(X)NR_2 \xleftarrow{Me_3SiN_3} R_2NPCl^+AlCl_4^- \xrightarrow{PhN_3} R_2NP(Cl){=}NPh^+AlCl_4^-$$

$X = Cl, N_3$ $\qquad R = Ph, Me_3Si$

While not low coordinate species, it is relevant to note at this point that anionic phosphorus(III) species also undergo the Staudinger reaction [80].

$$PhP(CN)_2Cl^- + RN_3 \rightarrow RN{=}P(Ph)(CN)_2Cl^-$$

Azide addition to formally unsaturated phosphorus(III) compounds produce the novel three coordinate phospha(v)zenes, $RP({=}NR')({=}X)$ [81]. Unsaturated units in these reactions include phosphorus–carbon [82], phosphorus–nitrogen [83] and phosphorus–phosphorus [84] double bonds.

$$RP{=}NSiMe_3 + Me_3SiN_3 \rightarrow RP({=}NSiMe_3)_2$$

where R = 2,2,6,6-tetramethylpiperidine

$$(Me_3Si)_2NP{=}CHSiMe_3 + Me_3SiN_3 \rightarrow (Me_3Si)_2NP({=}CHSiMe_3){=}NSiMe_3$$

$$(Me_3Si)_2NP{=}PN(SiMe_3)_2 + Me_3SiN_3 \rightarrow Me_3Si)_2NP({=}NSiMe_3){=}P(NSiMe_3)_2$$

An examination of the chemistry shown above suggests an alternative non-azide route to phosphazenes by the oxidative addition reactions of low coordinate species such as $RP{=}NR'$ or $R_2P{\equiv}N$. The chemistry of these systems goes far beyond the straightforward examples indicated below. The numerous exciting aspects of low valent phosphazene chemistry can be obtained by consulting the yearly surveys of phosphazene chemistry [10] with particular focus on the work of Bertrand, Majoral and Niecke. The addition of dipolar reagents to the two coordinate phosphazene leads to phospha(v)zenes [84,85].

$$RP{=}NSiMe_3 + XY \rightarrow RP(X)(Y){=}NSiMe_3$$

where R = 2,2,6,6-tetramethylpiperidine and XY = $HNMe_2$, MeOH, $CCl_3Br$, $Br_2$, $Cl_2$, RI.

An exciting entry into phosphazene chemistry comes from the reactivity of phosphazynes, $R_2P{\equiv}N$, which are available from photolysis of the corresponding phosphorus(III) azides [86]. A clever combination of these two reaction types

$$R_2PN + XY \rightarrow R_2P(X){=}NY$$

where R = isopropyl, XY = MeNH, $Me_3SiCl$, $Me_3SiN_3$, PhN, PhNCO, using iminophosphanes, $RP{=}NR'$ to trap the phosphazene provides an additional route to three coordinate phospha(v)zenes [87].

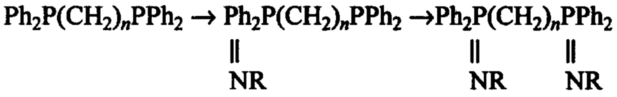
$$RP{=}NR' + R''_2PN \rightarrow RP({=}NR'){=}NPR_2''$$

The chemistry in this system is quite complicated and subtle changes in substituents can lead to different pathways than those outlined above. Oxidation of iminophosphanes with ozone sulfur or selenium also gives phospha(v)zenes [88].

$$RP{=}NR' + En \rightarrow RP({=}E){=}NR'$$

where R = mesityl, R' = $CMe_3$, E = O, S, Se

Another recently developed route to acyclic phosphazenes is a redox condensation reaction involving a phosphine, an organic or inorganic entity with a $NH_2$ group and diethylazodicarboxylate (DAD) [89,90].



$$Ph_2P(CH_2)_nPPh_2 \rightarrow Ph_2\underset{\underset{NR}{\|}}{P}(CH_2)_nPPh_2 \rightarrow Ph_2\underset{\underset{NR}{\|}}{P}(CH_2)_n\underset{\underset{NR}{\|}}{P}Ph_2$$

where $n = 1,2$, R = $p$-$MeC_6H_4SO_2$, $Ph_2P(O)$, CN. Alternatively, the reactions of the $(EtO)_3P/CCl_4$ mixture with acid, cyanimides [91] or acid amides [92] leads to $(EtO)_3P{=}NR$. The addition of $CCl_4$ [93] or $Br_2$ [94] to silylaminophosphines is followed by hydrogen halide elimination to give the appropriate phosphazene.

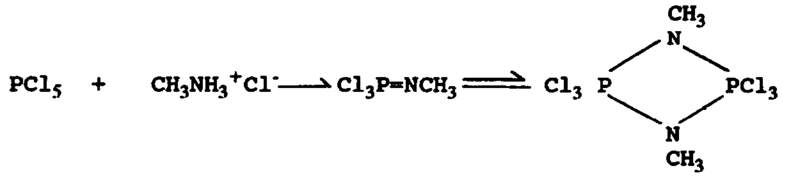
$$(Me_3Si)_2NP(R)NHSiMe_3 \xrightarrow{XY} \xrightarrow{-HY} (Me_3Si)_2NP(R)(X){=}NSiMe_3$$

where XY = $CCl_4$, $Br_2$.

The reactions presented so far all use phosphorus(III) derivatives as starting points in the synthesis of phospha(v)zenes. Another important set of reactions starts with phosphorus(v) derivatives. The most important of these is the Kirsanov reaction which involves halophosphoranes and primary amines [71–73]. Typical phosphorus reagents include

$$R_3PX_2 + R'NH_2 \rightarrow R_3P{=}NR'$$

$PCl_5$, $Ph_3PX_2$ (X = Cl, Br), $PF_3Cl_2$, $(PhO)_3PCl_2$, while a broad range of nitrogen derivatives (e.g. $NH_4Cl$, $RNH_2$ (R = Me, Ph, RC(O), ArSO2) have been employed. The monophosphazene which is formed in the Kirsanov reaction often dimerizes.



The range of substituents in the Kirsanov and Staudinger reactions to some degree complement each other so that a given monophosphazene can often be prepared by one or the other of these two reactions.

The Kirsanov reaction of $PCl_5$ with $NH_3$ (in the form of $NH_4Cl$) which at first glance would appear to be the simplest is actually the most complex in that it leads to linear phosphazenes [95] and ultimately cyclophosphazenes (Section A(ii)(a)).

$$PCl_5 + NH_4Cl \longrightarrow Cl_3P{=}NPCl_3{}^+PCl_6{}^-$$

$$Cl_3P{=}NPCl_3{}^+PCl_6{}^- + NH_4Cl \rightarrow Cl_3P{=}N{-}PCl_2{=}N{-}PCl_3{}^+PCl_6{}^-$$

An important member of the linear phosphazene series is $Cl_3P(O)NPCl_3$ which can be obtained by a wide variety of reactions, the most common of which is the reaction of $PCl_5$ with $(NH_4)_2SO_4$ [96]. Longer phosphazene chains can be prepared by a variation of a few reactions, the most important of these is the sequential treatment with $HN(SiMe_3)_2$ and $PCl_5$ [97].

$$\mathrm{Cl_2P(O)NPCl_3 + HN(SiMe_3)_2 \longrightarrow Cl_2P(O)NPCl_2N(SiMe_3)_2}$$

$$\mathrm{\xrightarrow{PCl_5} Cl_2P(O)NPCl_2NPCl_3}$$

The reaction of the $\equiv PN(SiMe_3)_2$ center with longer chain phosphazenium ions, such as $Cl_3PNPCl_2PCl_3{}^+PCl_6{}^-$ and $Cl_3PN(PCl_2N)_2PCl_3{}^+PCl_6{}^-$ (available from $N_3P_3Cl_6 + PCl_5$ [96]) allows for further chain extension [20]. The reaction of the phosphazenium ions with $SO_2$ allows for conversion to the phosphoryl derivative [20].

$$\mathrm{(Cl_3PNPCl_2NPCl_2NPCl_3)^+PCl_6{}^- \xrightarrow{SO_2} Cl_2P(O)NPCl_2NPCl_2NPCl_3}$$

A number of less general reactions also have been developed for the synthesis of monophosphazenes. Certain of these are mentioned below. A logical approach to consider would be deprotonation of aminophosphonium ions [72,73,98,99].

$$\mathrm{PPh_3 + NH_2SO_3H \longrightarrow Ph_3PNH_2{}^+HSO_4{}^- \xrightarrow[NH_{3(\mathit{l})}]{NaNH_2} Ph_3P{=}NH}$$

$$\mathrm{(C_2H_4N)_\mathit{n}(Et_2N)_{3-\mathit{n}}PNH_2{}^+ \xrightarrow[NH_{3(\mathit{l})}]{Na} (C_2H_4N)_\mathit{n}(Et_2N)_{3-\mathit{n}}P{=}NH}$$

The addition of haloamines to phosphorus tribromide is an interesting route to phosphazenes [101].

$$\mathrm{Me_3CNBr_2 + PBr_3 \longrightarrow Me_3CN{=}PBr_3}$$

Reactions of preformed acyclic phosphazenes which leave the PN bond unchanged represent another route to new phosphazenes. These processes are considered in Section D(i). Additional, less general routes may be found in the yearly summaries of phosphazene chemistry [8–10].

### *(ii) Cyclophosphazenes*

#### *(a) Ammonolysis of phosphoranes*

Fortunately, the most commonly employed starting materials in cyclophosphazene chemistry, hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene, $(NPCl_2)_{3,4}$, are commercially available. The preparation of these materials uses phosphorus pentachloride and ammonium chloride in halogenated solvents. The reaction produces linear phosphazenes (Section C(i)) in the early stages. Chain growth continues until the four phosphorus fragment, $Cl_3P(NPCl_2)_2NPCl_3{}^+$ is formed. At this point, cyclization to $(NPCl_2)_3$ with the elimination of $PCl_4{}^+$ occurs [102]. Since $(NPCl_2)_3$ is a precursor to poly(dichlorophosphazene), $(NPCl_2)_n$, extensive efforts, primarily found in the patent literature [10], still continue to optimize this process in terms of yield, purity and cost. Numerous mixed substituent chlorophosphoranes (alkyl, aryl, dialkylamino) also undergo ammonolysis to give the appropriate cyclophosphazene [5,6,103].

$$RPCl_4 + NH_4Cl \longrightarrow [NP(Cl)R]_n$$

$$R_2PCl_3 + NH_4Cl \longrightarrow (NPR_2)_n$$

This process has been used to produce the only example of spiroorganophosphazenes containing phosphorus carbon bonds [104].

$$(CH_2)_4PCl_3 + NH_4Cl \longrightarrow [(CH_2)_4PN]_{3,4}$$

The use of N-15 labeled ammonium chloride allows for the preparation of N-15 labeled cyclophosphazenes [105].

The reaction of $PCl_5$ with primary amines or other amine derivatives normally gives acyclic phosphazenes (Section C(i)) or their dimers. In selected cases where the amine contains a good leaving group, elimination of the chloride of the leaving group occurs and cyclophosphazenes are obtained.

$$PCl_5 + PhCH_2NH_3^+Cl^- \xrightarrow{-PhCH_2Cl} (NPCl_2)_{3,4}$$

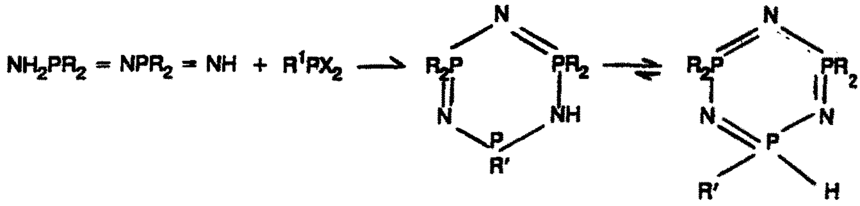
Bromophosphazenes are also available via the ammonolysis route although the lability of bromophosphoranes often requires the in situ preparation from phosphorus(III) bromides and bromine. Fluorophazenes are most commonly prepared from cyclic precursors as are the few reported iodophosphazenes.

### (b) Cyclization of linear fragments

Another synthetic strategy for the construction of the phosphazene ring system is cyclization of a preformed linear material. Several mixed substituent cyclophosphazenes have been obtained using this methodology [5,6,72]. A typical example involves the synthesis of 2,2-$N_3P_3Ph_4Me_2$ from $[NH_2PPh_2NPPh_2NH_2]^+Cl^-$ (the most commonly employed linear precursor).

$$Me_2PCl_3 + [NH_2PPh_2NPPh_2NH_2]^+Cl^- \longrightarrow 2,2\text{-}N_3P_3Ph_4Me_2$$

It should be noted that ligand exchange (Ph/Me) also occurs in the reaction [106]. The cyclization of the resolved chiral cation, $[NH_2P(MeC_6H_4)PhNP(MeC_6H_4)PhNH_2]^+$, with $PCl_5$ gave the first (and only) resolved optically active cyclophosphazene. The reactions of phosphorus(III) derivatives with linear fragments can also lead to phosphazenes as shown in the reaction of 1-amino-3-imino-1,1,3,3-tetraorganophosphazenes in which tautomerism leads to the formation of the cyclophosphazene [107].



Other, more complex reactions of phosphorus(III) reagents with linear fragments have been reported [7].

In recent years, the cyclization of linear precursors has been most widely applied to the synthesis of heterocyclophosphazenes, i.e. rings with at least one phosphazene unit and other ring atoms such as carbon, sulfur or transition metals. While a detailed presentation of the chemistry of these materials is beyond the scope of this review, typical syntheses will be indicated to establish both the range of heterocyclophosphazenes and the generality of this type of reaction. Detailed reviews of phospha(thia)zenes containing four coordinate [3,108] and two or three coordinate [3,109,110] sulfur and of metallocyclophosphazenes [111] are available.

The phosphatriazenes (azaphosphorins, triazaphosphinimines), which are intermediate between cyclophosphazenes and cyclotriazines, have both ≡CR and $\equiv PR_2$ groups in the ring. The reaction of fluoroalkyl imidoylamines with chlorophosphoranes provides monophosphatriazenes [112].

$$R_fC(=NH)N{=}CR_fNH + RPCl_4 \longrightarrow Cl(R)\overline{PNCR_fNCR_fN}$$

(R = Ph, Cl). The construction of diphosphatriazenes requires a fragment containing two phosphorus atoms with a carbon-nitrogen source such as an amidine [113,114].

$$R_fC(=NH)NH_2 + Cl_3P(Ph)N{=}P(Ph)Cl_2 \longrightarrow Cl(Ph)\overline{PNP(Ph)(Cl)NCR_fN}$$

$$[H_2NC(Ph){=}NH_2]Cl + [N(PCl_3)_2] + SbCl_6 \longrightarrow Ph\overline{C{=}NPCl_2{=}NPCl_6{=}N}$$

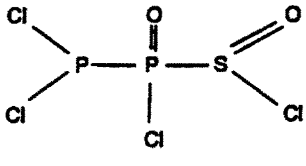
If the linear fragment can undergo carbon chlorine bond formation in addition to cyclization, the perchloro monophosphatriazene can be obtained [115].

$$NH_2C(O)NHC(O)CH_3 + PCl_5 \longrightarrow Cl_2\overline{PNC(Cl)NC(Cl)N}$$

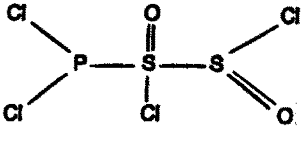
The numerous reactions leading to phospha(thia)zenes are conveniently divided between those providing four coordinate sulfur derivatives and those providing two and three coordinate sulfur materials. The $Cl_3PNPCl_3^+$ cation is a good PN source and reaction with $NH_2SO_3H$ provides an entry into the four coordinate sulfur series [107,109].

$$(Cl_3PNPCl_3)^+PCl_6^- + NH_2SO_3H \rightarrow NPCl_2(NSOCl)_2 + (NPCl_2)_2NSOCl$$

The two isomers (*cis* and *β*) of the monophosphazene which are obtained are shown below (using the structural designation similar to that in Scheme 1).

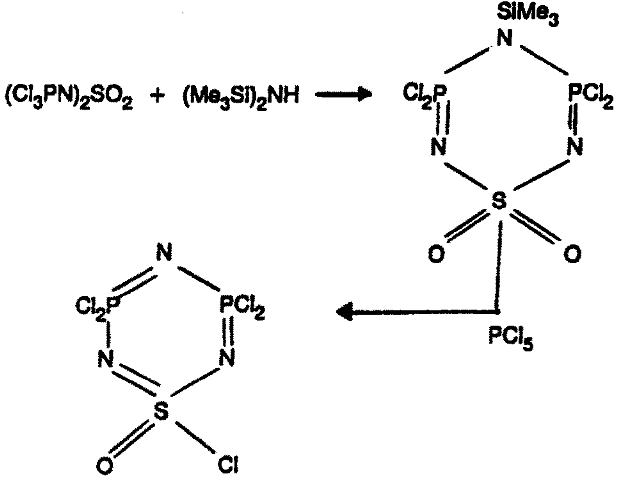


cis



β

An alternative synthesis, via another four coordinate sulfur ring system, of the disphosphazene has been developed [115].



There are several reactions leading to two and three coordinate phospha(thia)zenes and their selenium analogs. In these systems, the phosphorus atoms(s) have non-replaceable exocyclic groups (such as phenyl) and thus the chemistry is usually focused on the $EN_2$ (E = S, Se) region of the ring. Typical linear fragments employed in the syntheses of these heterocyclophosphazenes include: $ClPPh_2NPPh_2Cl^+$ [117], $R_2P[N(SiMe_3)_2]{=}NSiMe_3$ [118], $Me_3SiNSNSiMe_3$ [110] and $(Me_3SiNC(Ph){=}NPPh_2{=}N(SiMe_3)_2$ [117].

$$ClPPh_2NPPh_2Cl^+ + [(Me_3Si)_2N]_2E \longrightarrow \overline{ENPPh_2NPPh_2N}$$

(E = S, Se)

$$R_2P[N(SiMe_3)_2]{=}NSiMe_3 + PhSeCl_3 \longrightarrow Ph\overline{SeNPR_2NSe(Ph)NPR_2N}$$

(R = Ph, Me)

$$Me_3SiNSNSiMe_3 + PCl_5 \longrightarrow Cl\overline{SNPCl_2NPCl_2N}$$

$(Me_3Si)NC(Ph){=}NPPh_2{=}NSiMe_3 + ECl_n \longrightarrow ClSeNPPh_2NCPhN$

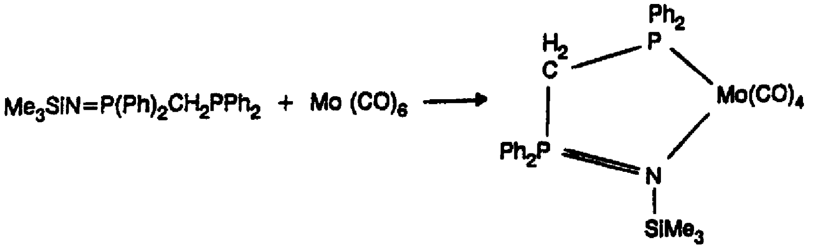
$(E = S, n = 2; Se, n = 4)$

Bicyclic and other complex structural units are also available using this method [10,109,110]. A cyclic source of the SNS unit, $S_4N_4$, has also been shown to provide a good entry into two and three coordinate phospha(thia)zenes [109,110].

$S_4N_4 + Ph_2PH \longrightarrow Ph_2PNSNSN$

$S_4N_4 + Ph_2PCl \longrightarrow Ph_2PNP(Ph)_2NS(Cl)N$

The synthesis of metallocyclophosphazenes is a topic of recent interest [111]. Many of these are available from the cyclization of $[NH_2PPh_2NPPh_2NH_2]Cl$ with high valent transition metal halides to give the six-membered rings with metal centers such as $MoCl_3$ [118], $NbCl_2$ [119], $VCl_2$ [120], $WX_3$ (X = Br, F) [121] and $ReCl_4$ [122]. Bicyclic species are also available [121]. Low valent transition metal centers can also be found in metallocyclophosphazenes [122].



*(c) Elimination reactions*

The thermal or photochemical elimination of molecular nitrogen from phosphorus azides has been used, on occasion, to generate cyclophosphazenes. The thermal process has been known for some time [5] and still receives some attention as shown in the synthesis of trifluoromethyl [123] and bromo [124] cyclophosphazenes.

$CF_3P(Me)N_3 \longrightarrow [NP(CH_3)CF_3]_n$

$PBr_3 + NaN_3 \longrightarrow (NPBr_2)_{3-5}$

Thermolysis and photolysis of certain phosphorus [111] azides has been examined in detail [125]. In both cases, a highly reactive phosphazyne, $R_2PN$, intermediate is obtained [125]. The expected high degree of polarity in the formal phosphorus–nitrogen triple bond renders it susceptible to attack by dipolar reagents. If none are available, dimerization to the first reported example of cyclodiphosphazenes occurs [126].

$(Me_3C)_2PN_3 \xrightarrow{\Delta \text{ or } h\nu} [(Me_3C)_2PN]_2 \longrightarrow [(Me_3C)_2PN]_n$

The dimer undergoes oligomerization to the trimer and higher rings [125].

Another significant elimination reaction leading to cyclophosphazenes is the thermolysis of *N*-silylphosphinimes which have a good leaving group (X) attached to the phosphorus atom [127,128].

$$Me_3SiNP(X)RR' \longrightarrow (NPRR')_n + Me_3SiX$$

The products may be either cyclic (X = F, Br) or high polymers ($X = OCH_2CF_3$) depending on the leaving group. This reaction is a good route to diorganocyclophosphazenes, $(NPRR')_{3-5}$ (R,R' = Ph, Me, etc.). Numerous other less useful syntheses of cyclophosphazenes have appeared [5,7] but they lack general interest.

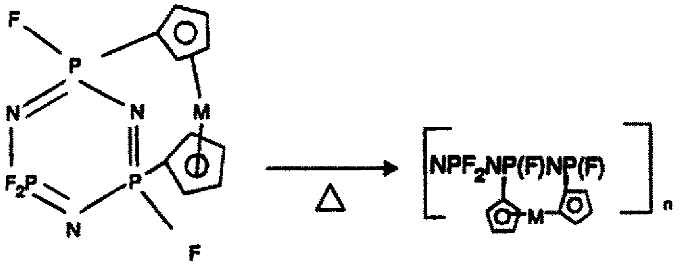
### *(iii) Poly(phosphazenes)*

#### *(a) Ring opening polymerization*

The classic method for the preparation of poly(dichlorophosphazene), $(NPCl_2)_n$, involves the melt polymerization of $(NPCl_2)_3$ at 250°C. Control of time and temperature are important if linear (soluble) rather than crosslinked (insoluble) polymer is to be obtained. This process has been studied numerous times [5,129]. The main features of the reaction are of a chain propagation process. The requirement of a trace amount of water suggests a cationic mechanism. Initiation is either a direct or catalyzed phosphorus–chlorine heterolytic bond cleavage. The actual end groups have not been detected. The molecular weight and polymerization rate of the melt polymerization has been followed in situ using light scattering and Raman spectroscopy [130]. The resulting polymer exhibits a high molecular weight (greater than one million Daltons) with moderate to high polydispersity which increases at high conversion along with an increase in branching [130]. The polymer is elastomeric which has resulted in it being referred to as “inorganic rubber”. The phosphorus–chlorine bonds are more susceptible to atmospheric moisture than is the case for the cyclic trimer thus $(NPCl_2)_n$ degrades in air.

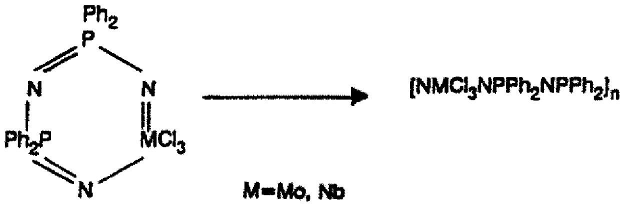
Although melt polymerization allows for successful preparation of $(NPCl_2)_n$, particularly on the laboratory scale, catalyzed solution polymerization is desirable for ease of preparation and scale up. A wide range of catalysts which promote ionic polymerization have been examined with the results appearing mostly in the patent literature [5,10]. Certain of these catalysts have been investigated in more detail. The use of $BCl_3$ with water as a co-catalyst allows for production of $(NPCl_2)_n$ having a high linear content with moderate molecular weight and polydispersity [132]. Rate measurements show dependence on both the monomer and catalyst. Small amounts of branching have been detected [133]. Repeated addition of monomer results in molecular weights of five to six million Daltons being obtained [134]. Another promising catalytic system is sulfonic acid (or related acids) with $CaSO_4 \cdot 2H_2O$ as a promoter. The actual catalyst is a decomposition product of the acid. High molecular weights and low polydispersity are obtained throughout the reaction, indicating an ionic chain propagation mechanism [135,136]. Radiation polymerization of $(NPCl_2)_3$ in solution in the presence of bulky electron acceptors to suppress chain transfer allows for high molecular weight and rate of polymerization [137].

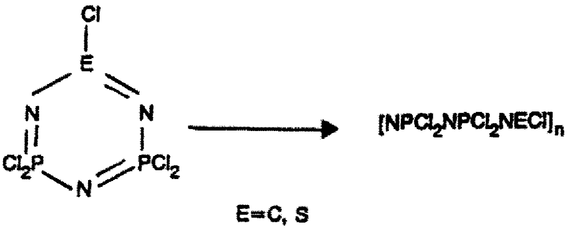
Attempts at ring opening polymerization of mixed substituent cyclotriphosphazenes have produced interesting results [138]. Chlorophosphazenes with one or two substituents such as $N_3P_3Cl_5R$ (R = Me, Ph) and 2,2'-$N_3P_3Cl_4(CH_2SiMe_3)R$ (R = alkyl, phenyl) [139] can be polymerized while high degrees of substitution suppress the ring opening ability [138]. Copolymers of substituted cyclophosphazenes and $N_3P_3Cl_6$ can be prepared [140]. Catalytic amounts of $N_3P_3Cl_6$ can induce polymerization for certain mixed substituent trimers which otherwise will not undergo the process [140]. Poly(phosphazenes) with organometallic substituents have been reviewed [141]. Mono-substituted materials such as $N_3P_3F_5C_5H_4RuCp$ (Cp = $\eta^5$-$C_5H_5$) give polymers with a metallocene substituent [142]. The transannular bridged derivatives, 2,4-$N_3P_3F_4[(C_5H_4)_2M]$, give polyphosphazenes with metallocene bridged phosphorus atoms [142].



The one example of a fully substituted cyclophosphazene undergoing ring opening polymerization is seen in the reaction of $N_3P_3(OCH_2CF_3)_4[(C_5H_4)_2Fe]$ in the presence of catalytic amounts of $(NPCl_2)_3$ [142].

An exciting recent development is the ring opening polymerization of heterocyclophosphazenes to give linear heterophosphazene polymers. Bulk polymerization of metallocyclophosphazenes [144], phosphatriazenes [145] and phospha(thia)zenes [146] has been reported.





*(b) Alternative routes*

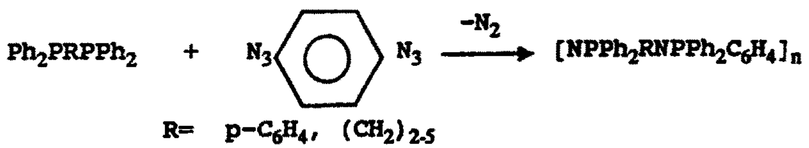
Several alternatives to ring opening polymerization have been explored as routes to poly(phosphazenes). The poly condensation of $Cl_3PNP(O)Cl_2$ leads to $(NPCl_2)_n$ exhibiting good molecular weight and polydispersity characteristics [147].

$$n\mathrm{Cl_3P{=}NP(O)Cl_2} \longrightarrow \mathrm{Cl_3PN(PCl_2N)}_{n-1}\mathrm{P(O)Cl_2} + (n-1)\mathrm{P(O)Cl_3}$$

The reaction has been followed by $^{31}P$ NMR and rates determined by measurement of released $P(O)Cl_3$ [148]. The previously mentioned thermal decomposition of *N*-silyphosphoranimines, $Me_3SiNP(X)RR'$ (Section C(ii)(c)), leads to poly(phosphazenes) when $X = OCH_2CF_3$ [127,128]. This is the only good route to poly(phosphazenes) with phosphorus–carbon bonds to the substituents. High molecular weights are obtained early and continuously in the reaction indicating a chain growth process [149]. Copolymers can also be obtained by the process as shown by the formation of $[(NPMe_2)_x(NP(Me)CH_2E)_y]_n$ ($E = R_2P$, $RMe_2Si$) from the thermolysis of a mixture of $Me_3SiNP(OCH_2CF_3)Me_2$ and $Me_3SiNP(OCH_2CF_3)(Me)CH_2E$ [150]. The action of anionic initiations (e.g. alkoxides) on $Me_3SiNP(OCH_2CF_3)_3$ leads to high yields of the trifluoroethoxy polymer at temperatures well below those required for ring opening polymerization [151].

$$\mathrm{Me_3SiNP\ (OCH_2CF_3)_3} \xrightarrow{X^-} \mathrm{[NP(OCH_2CF_3)_2]}_n$$

Finally, an alternative route to heterophosphazenes which contain an organic group in the chain using the Staudinger reaction (III.A) has been developed.



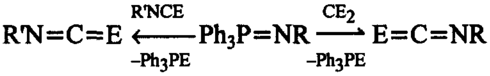
The polymers are insoluble in common solvents and end group analysis indicates fairly low values (1800–2600 Da) for the molecular weights [152].

## D. REACTIONS OF PHOSPHAZENES

The extraordinarily broad range of chemistry involved in the reactions of phosphazenes would necessitate an entire monograph for a complete survey. In view of space restrictions only selected highlights are presented. As previously noted, the interested reader may consult reviews [5,7] or the yearly comprehensive literature surveys [9,10] for a more complete survey.

*(i) Acyclic phosphazenes*

There are a broad range of reactions of monophosphazenes. A recent review of the Staudinger reactions focuses and a broad spectrum of the "organic" reactions of acyclic phosphazenes [153]. One of the most exciting and widely applicable processes is the aza-Wittig process [74,153]. By analogy with the classic Wittig reaction in which a phosphorus ylide functions as =CRR' transfer agent to form olefins, the phosphazene functions as a =NR transfer reagent to form imines. The high polarity of the PN bond is significant in this reaction. A variety of carbonyl and thiocarbonyl substrates have been employed in the aza-Wittig reaction. In addition to organic substrates with a single functional group, recent interest has been shown in additions of conjugated groups to give products such as carbodiimides. The aza-Wittig process has proven to be a valuable methodology for the synthesis of heterocyclic compounds [74,153].

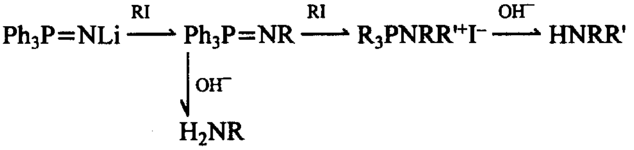


$$R'N{=}C{=}E \xleftarrow[-Ph_3PE]{R'NCE} Ph_3P{=}NR \xrightarrow[-Ph_3PE]{CE_2} E{=}C{=}NR$$

(E=O,S)

The usual approach is to generate, via the aza-Wittig reaction, a reactive imine or carbodiimide *ortho* to a reactive organic functionality in order to favor an intramolecular ring closure. The imine nitrogen atom is thus incorporated into a new ring system.

The high polarity of the PN bond leads to facile addition of electrophiles. The resulting phosphonium compounds are easily hydrolyzed leading to amines thus providing a pathway from organohalides to amines. Primary, and secondary amines or amino acids can be obtained by this route [154, 155].



$$\begin{tikzcd}
Ph_3P{=}NLi \arrow[r, "RI"] & Ph_3P{=}NR \arrow[r, "RI"] \arrow[d, "OH^-"] & R_3PNRR'^{+}I^{-} \arrow[r, "OH^-"] & HNRR' \\
& H_2NR & &
\end{tikzcd}$$

The high polarity of the phosphazene bond is accentuated by electron donating substituents, such as amines, on the phosphorus center. If the amine itself is a phosphazene and hence a potentially strong electron donor, one might expect the central phosphazene to be a very basic material. Materials of this type have been prepared [156].

$$(Me_2N)_3P{=}NH + Me_2NH + Cl_3P{=}NCMe_3 \rightarrow [(Me_2N)_3P{=}N]_n(Me_2N)_{3-n}P{=}NCMe_3 \qquad n = 0\text{–}3$$

These linear phosphazenes are among the strongest known neutral bases with the $n = 2$ material having a p$K$ of 32.66. The high degree of steric crowding results in low nucleophilicity so they have considerable potential in deprotonation and elimination reactions [156]. By way of comparison, certain of these phosphazenes are 1500 to 10 000 times more basic than DBU [157]. Another novel phosphazene reaction of considerable synthetic utility is the ozonolysis of $R_3PNR'$ which leads to the nitro organic species $R'NO_2$ [158].

The next type of reactions under consideration are those which have more of an "inorganic" emphasis. Nucleophilic displacement reactions of acyclic chlorophosphazenes such as $Cl_2P(O)NPCl_3$, $Cl_2P(O)NPCl_2NPCl_3$ and $Cl_3PNPCl_2NPCl_2NPCl_3{}^+PCl_6{}^-$

have received some attention. Per-substitution with aryloxides [20,159,160], trifluoroethoxide [161] and aniline [20] have been reported for $Cl_2P(O)NPCl_3$ and with aryloxides [20,159,160] and aniline [20] for the longer chain species. Partial substitution of $Cl_2P(O)NPCl_3$ with trifluoroethoxide [161] and mercapto groups [162] to form $(CF_3CH_2O)_{3-n}Cl_nP{=}NP(O)Cl_2$ ($n = 1,2$) and $(RS)_3PNP(O)Cl_2$ has also been reported. Partially substituted materials can be susceptible to rearrangement as shown by the thermal transformation of $CF_3CH_2OCl_2P{=}NP(O)Cl_2$ to $[Cl_2P(O)]_2NCH_2CF_3$ [161]. The $R_3P{=}N$ group can be transferred to other main group functions by reactions of $R_3P{=}NX$ where X can be H, Li or $SiMe_3$. As an example of this process, the reactions of $Ph_3P{=}NLi$ with RCl gives $Ph_3P{=}NR$ where $R = C(O)R$ [163], $CO_2R$ [163], $P(O)Ph_2$ [155] $SO_2C_6H_4Me$ [155] and $SO_2Cl$ [155]. Similarly, $Ph_3PNH$ reacts with silylstannanes to give $(Ph_3P{=}N)_4Sn$ [164] and $Me_3SiN{=}PPh_2N{=}S(O)Me_2$ with $SeOCl_2$ gives $SeCl_2[N{=}PPh_2N{=}S(O)Me_2]_2$ [165]. The formation of transition metal phosphazene derivatives has also been explored in detail in recent years [166]. As mentioned in Section C(ii)(b), bifunctional phosphazenes in combination with transition metal halides lead to metallocyclophosphazenes [166]. While there are a variety of specialized routes to acyclic metallophosphazenes [166], the most general route involves, as in the case of the main group derivatives, monophosphazenes with good leaving groups on the nitrogen atom. Typical reactions are shown below:

$$WF_6 + R_3PNSiMe_3 \longrightarrow WF_{6-n}(NPR_3)_n \; (n = 1, 2) \qquad [167]$$

$$Re_2O_7 + Ph_3PNSiMe_3 \longrightarrow Ph_3PNReO_3 \qquad [168]$$

$$Mo_2Cl_{10} + Ph_3PNSiMe_3 \longrightarrow [MoCl_4(NPPh_3)]_2 \qquad [169]$$

$$Cp_3AnCl + LiNPPh_3 \longrightarrow Cp_3AnNPPh_3 \; (An = U, Th) \qquad [170]$$

The prevalence of high oxidation state complexes should be noted. Electrochemical studies have shown that the $Ph_3PN$ ligand effectively stabilizes high oxidation states, presumably due to its strong electron donating character [171]. Calculations and structural work on the actinide complexes indicate that the anionic phosphazene ligand promotes metal–nitrogen multiple bond interactions [170]. Coordination of the neutral $R_3P{=}NR'$ ligand to metal centers has also been observed particularly in cases where R' is a poor leaving group, e.g. in the formation of $Ph_3PNPh \cdot CuCl$ [172]. An extensive series of $RhL_2Cl(R_3PNR')$ complexes have been prepared [173]. It should be noted that even the trimethylsilyl group may be retained in certain circumstances [122].

### *(ii) Cyclophosphazenes*

There are an extraordinarily large number of reactions of cyclophosphazenes which have been reported in the literature. This topic has been reviewed comprehensively [7] and has recently been the subject of a critical review [174]. The range of reaction products which have been observed is a direct consequence of two facts. The first of these being the large number of reagents, mostly nucleophiles, which will displace a halogen atom from the phosphorus center and the second is the regio- and stereochemical complexities of these substitution reactions (Section B(i)(b)). The study of these reactions has reached a sufficient state of maturity that a set of generalized guidelines for predicting, or at least post facto rationalizing, the observed regio- and stereochemistry is available [174]. In the present instance, these guidelines are used as a framework to provide a brief summary of the highlights of cyclophosphazene reactions.

The nature of the substituents on the phosphazene play a dominant role in directing the course of the reaction. The specific interactions that have been recognized are electronic, steric and interactions of ring substituents with incoming reagents. The expectation in the case where the ring substituent is more electron withdrawing than the halogen leaving groups is that the phosphorus atom attached to the electron withdrawing group will exhibit enhanced electrophilic character and geminal substitution will occur. While this situation is not common, it is realized in the geminal pathway followed in the metathetical fluorination of chlorophosphazenes by fluoride transfer agents [175]. Even this simple reaction becomes complicated if antimony fluorides are used in place of simple fluoride salts. In this case, non-geminal substitution occurs [176], the origin of which can be traced to coordination of the antimony reagent to the most basic endocyclic nitrogen atom which happens to be the one most distant from the ≡PFCl center [176,177]. This particular observation shows the feasibility of reactions at the nitrogen center in the cyclophosphazene. A significant amount of work has been devoted to evaluating the relative basicity of various endocyclic sites as a function of the phosphorus substituent [177]. In cases of phosphazenes with strong electron donating groups, the endocyclic basicity is sufficient to be exploited for formation of metal complexes [7,178].

The more common situation with respect to exocyclic electronic effects is that the substituent is electron-donating with respect to the phosphazene ring. In general, this will result in a rate reduction for bimolecular reactions due to the decreased electrophilic nature of the phosphazene. The regio control exercised by the substituent depends on the nature of the electron releasing effect. Systems which are $\pi$ releasing such as amines or hyperconjugatively releasing such as organooxy substituents, will result in electron density enrichment at the substituted phosphorus atom and hence attack at the distant (non-geminal) phosphorus center. Substituents which are $\sigma$ electron releasing such as thiolates or those with a direct phosphorus–carbon bond favor geminal substitution. The origins of the regioselectivity in the amino and organooxy derivatives is the donation of lone pair electron density to phosphorus acceptor orbitals consequently the nucleophile prefers an alternate (non-geminal) site. In the $\sigma$ electron releasing cases, no additional phosphorus orbitals are used and the net result is that endocyclic nitrogen lone pairs are preferentially donated to the non-geminal site (see Section B(ii)(b)). The phosphorus atom bearing the $\sigma$ releasing substituent thus becomes the favored site of attack [174].

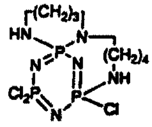
Observed reaction pathways allow one to judge the validity of these models and to identify additional factors of relevance. Secondary amines, with the exception of aziridine, and most oxyanions all tend to follow the expected non-geminal pathway. Primary amines, however. follow both geminal and non-geminal routes depending on steric requirements of amine. In these systems, there are two competing mechanistic pathways with the bimolecular path providing the non-geminal product and a dissociative process giving the geminal product. The dissociative process goes through a three coordinate phosphorus intermediate [179] and hence is favored with sterically demanding amines.

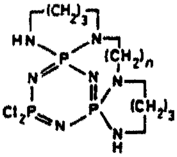
$$N_3P_3Cl_5NHR \xrightarrow{B} N_3P_3Cl_4NR + BH^+Cl^- \xrightarrow{R'NH_2} N_3P_3Cl_4(NHR)(NHR')$$

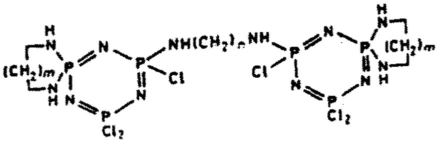
On going from tri- to tetra-substituted secondary amine derivatives, a shift to geminal isomer formation is observed which has been ascribed to a mechanistic change over to a dissociative process [174]. The geminal pathway observed in the reactions bulky aryl oxide anions has also been proposed to be the result of a dissociative mechanism [160]. In the case of the $\sigma$ releasing substituents, the geminal pathway is uniformly followed by thiolates even in the case of the reactions of the less familiar 10-membered ring, $(NPCl_2)_5$ [180]. The reactions of organometallic reagents with phosphazenes is a much more complicated story [174,178]. The reactions of $(NPF_2)_3$ with small carbanionic reagents follow the predicted geminal path but steric demands can result in the formation of non-geminal derivatives for bulky alkyl [181], aryl [182] and substituted alkynl [183] systems. The reactions of $(NPCl_2)_3$ are more complex with a balance of the bimolecular substitution mechanism and a halide abstraction mechanism wherein the organometallic reagent abstracts a chlorine atom leaving a reactive phosphazene anion [178]. The anionic intermediate can then go on to form a variety of products [178]. Another low coordinate intermediate leading to a geminal product is encountered in the Friedel–Crafts reaction. In this case, a chloride ion is abstracted by a Lewis acid, such as aluminum chloride, leaving a phosphonium ion which rapidly reacts with nucleophiles [174].

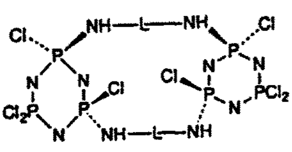
Stereoselectivity is observed in addition to regioselectivity in the non-geminal pathways. The a priori expectation for stereoselectivity is that steric requirements will favor a *trans* disposition of bulky groups in a non-geminal structure. In the reactions of secondary amines with $(NPCl_2)_3$, the di-substituted product is indeed predominantly *trans* with the *cis* product arising totally or in part from isomerization [174]. Detailed kinetic analyses, however, have shown that the *trans* preference arises from the entropy of activation. A model involving intramolecular substituent assistance in chloride displacement has been proposed to fit the kinetic data [184]. The stereospecific formation of *trans*-$N_3P_3F_4(CMe_3)_2$ appears to be an authentic example of steric control of stereochemistry [181]. Suprisingly few stereochemical studies of oxyanion substitution reactions are available. In the cases where the *trans* isomer has been established as the dominant product, i.e. $OC_4H_9$ and $OCH_2CF_3$ [185], the steric model is sufficient to rationalize the data. Activation parameters would be of interest in order to test this hypothesis. A surprising number of reactions following a non-geminal pathway yield the *cis* isomer as being competitive or dominant with respect to the *trans* isomer. This contrasteric result is restricted to carbanionic and oxyanion reagents which contain $\pi$ electrons in the organic moiety, e.g. NaOAr [186], $LiOCH{=}CH_2$ [187], ArLi [182] and $RC{\equiv}CLi$ [183]. It has been proposed [174,182,187] that the electron rich incoming reagent associates with the ring substituent which is relatively electron poor due to the strong electron-withdrawing effect of the phosphazene. This association leads to preferential *cis* attack on the phosphazene.

Three other types of reactions of cyclophosphazene deserve brief attention. The first is a thermally driven rearrangement process wherein a N=P(OR)$_2$ unit undergoes tautomerization to a N(R)P(O)(OR) moiety [188]. This process can be complex if a mixed substituent phosphazene, e.g. $N_3P_3(OMe)_{6-n}(OC_6H_4Me)_n$ ($n = 1$–$3$), undergoes this phosphazene–phosphazane rearrangement [189]. The facile rearrangement for the hydroxy derivatives allows for a complex hydrolysis reaction of the cyclophosphazenes [190]. Another general class of reactions which are of interest are those of polyfunctional reagents. The simplest potentially difunctional reagent is a primary amine and this property is shown in the formation of cyclotetraphosphazenes in which a NR group bridges the ring between the 2 and 6 positions [191]. Difunctional reagents with short spacing, e.g. two carbon units, between the reactive centers have been studied in detail. The reactions of $(NPCl_2)_3$ with dinucleophiles including diamines, diols and amino alcohols gives spirocyclic phosphazenes wherein both nucleophilic centers are attached to the same phosphorus atom [7]. If a rigid difunctional reagent such as hydroquinone is employed, the two nucleophilic centers cannot bind to the same phosphorus atom and alternatively two phosphazene rings can be linked through the bridging reagent [192]. This pathway can also lead to cyclolinear polymer formation [5,192]. Considerable interest has been shown in the reactions of long chain flexible polyamines [193,194] and polyols [195,196] with chlorocyclophosphazenes. The large separation between nucleophilic sites allows for considerable structural diversity with often small variations in preparation conditions leading to different structure types [194]. Spirocycle formation is commonly observed and with long chain reagents macrospirocyclic entities are obtained. The added flexibility also allows for the possibility of binding non-geminal positions (ansa structures). Linking of two phosphazene rings (bino structures) with one, two or three long chain diamines has been observed. When more than two nucleophilic sites are available, structures which combine these structural types are obtained. Typical species are shown below. Recent work with polyols shows that in, addition to structures analogous to those exhibited by the polyamines, derivatives containing a free hydroxyl unit remaining on the polyol can be obtained [197].



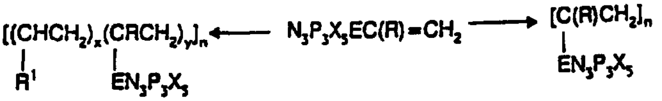






Dilithiometallocenes [178] and 1,1'-dichalcogenato ferrocene anions, $Fe(C_5H_4ELi)_2$ (E = S, Se) [198] give ansa and spirocyclic derivatives respectively.

Reactions at the exocyclic group of a substituted cyclophosphazene have become a major synthetic methodology for producing new phosphazene derivatives. Basic sites on the substituent can bind with Lewis acids, typically metal complexes [7,178]. Several "organic" type reactions on substituents have been explored. In many cases, the reactions on the cyclophosphazene were used to model reactions applied to poly(phosphazenes) [199] and certain of these will be briefly discussed in the next section. Polymers containing cyclophosphazenes may also be obtained from exocyclic group reactions. Cyclolinear and cyclomatrix phosphazene polymers may be successfully prepared using this approach. Typically, *para*-aminophenoxy derivatives, $N_3P_3(OPh)_{6-n}(OC_6H_4NH_2)_n$, serve as precursors. Reactions of the aminophenoxyphosphazenes with maleic anhydride gives maleamic acids which upon heating provide maleimides which can be thermally cured [200]. Other curing applications of aminophenoxy derivatives such as with epoxides have been explored [201]. An extensive body of work has developed around the addition polymerization of cyclophosphazenes with vinyl groups as, or as part of, the substituent [202].

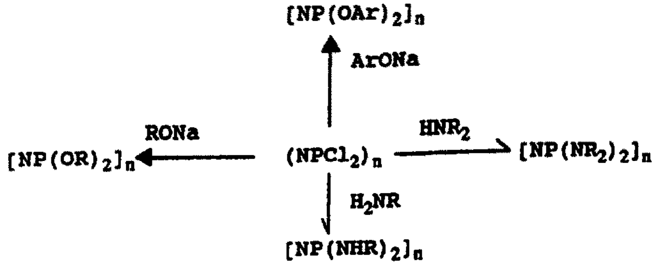


$$[(\underset{R^1}{CHCH_2})_x(\underset{EN_3P_3X_5}{CRCH_2})_y]_n \longleftarrow N_3P_3X_5EC(R){=}CH_2 \longrightarrow [\underset{EN_3P_3X_5}{C(R)CH_2}]_n$$

Thus homopolymerization, or copolymerization with organic olefins, of these monomers produces carbon chain polymers with the phosphazene as a substituent. The phosphazene may be directly bonded to the chain or linked through some substituent (E). Traditional inorganic polymers such as siloxanes and poly(phosphazenes) have an inorganic backbone surrounded by organic substituents while in this case the opposite situation is obtained. The cyclophosphazene substituent can undergo reactions with nucleophiles in a fashion analogous to the small molecule cyclophosphazenes [202]. The presence of several olefin substituents on the same ring allow for conversion to cyclomatrix materials as shown by the formation of hard films by the polymerization of $N_3P_3[OCH_2CH_2OC(O)C(CH_3){=}CH_2]_6$ [203].

### *(iii) Poly(phosphazenes)*

The study of poly(phosphazene) reactions is a highly active area of research and in many ways represents a unique type of polymer chemistry. [5,7,9,10,147,199,204–206] The availability of the high polymer $(NPCl_2)_n$ allows for application of the broad spectrum of reactions which have been developed in cyclophosphazenes chemistry. This results in a wide array of different polymers being prepared from a common polymeric precursor. This approach to polymer synthesis is different from the standard methodology wherein chemical changes leading to new polymers are most commonly done on the monomer which then undergoes a polymerization reaction. Typical general reactions of $(NPCl_2)_n$ are indicated below.



The physical properties of the resulting polymers vary extensively with the nature of the substituents. Typically, large changes in glass transition temperature, crystallinity and polymer solubility can be effected in this way. Sequential reactions with more than one nucleophile have also been examined in detail. This mixed substituent approach is of value in that it allows transformation of microcrystalline materials, typically per-substituted polymers, to elastomeric polymers, some of which are of commercial interest [207]. The other major reason for sequential reactions is to remove remaining reactive phosphorus–chlorine bonds if the first nucleophile cannot (or is not allowed to) derivatize all reactant sites. The nucleophile of choice, due to its high reactivity in the chlorophosphazene system is the trifluoroethoxide anion. Complete substitution of the phosphorus–chlorine bonds normally results in the hydrolytically unstable polymer, $(NPCl_2)_i$, being transformed into polymers that are resistant even to concentrated acid or bases. In select cases, it is desirable to build in instability, usually by the use of amino acid ester substituents. In these systems, bioactive co-substituents may be employed and the resulting materials are viable controlled drug release systems [199,205,208]. The focus of more recent direct substitution reactions is to utilize more complex substituents which lead to the development of liquid crystalline materials [205,209] and polymers exhibiting non-linear optical properties [210].

As suggested in the section on cyclophosphazenes reactions, exploitation of reactive sites of phosphazene substituents allows for synthesis of numerous materials that are inaccessible by direct substitution [199]. The entire range of these reactions is beyond the scope of an introductory review but they are noted in yearly literature surveys [10]. Some selected examples of interest are noted below. Polyphosphazenes with diacetone-D-glucose substituents have been prepared and subjected to hydrolysis to yield the glucose derivatized polymers [211]. Polypeptide side chains can be built up from deprotection of amino acid side chains followed by amidation [212]. The hydrolysis of the ester functions in $[NP(OC_6H_4CO_2R)_n$ leaves the carboxylic acid substituted polymers, which exhibit hydrogel behavior [203]. Reduction of nitroaryloxy derivatives followed by diazonium salt formation gives a reactive center which can couple with biologically active amines such as dopamine [214]. Aminophenoxy side chains can also be coupled to enzymes such as trypsin to provide polymers in which the enzymatic activity is maintained [215]. Another useful approach is deprotonation of the methyl group in $[NP(Me)Ph]_n$ followed by reactions of the resulting anion. This allows for the synthesis of a number of diverse substituents or the anion can serve as a site for graft copolymerization [216]. Finally, it is important to note the coordination of salts such as lithium perchlorate to the oxygen atoms in the side chain of the polyether derivative MEEP, $\{NP[O(CH_2)_2O(CH_2)_2OMe]_2\}_n$. These materials exhibit significant solid state ionic conductivity and are of interest as solid electrolytes [217]. The activity in synthesis of new polyphosphazenes is so extensive that by mid-1991 over 300 different types of these materials have been prepared and investigated [206].

In summary, it is clear that the behavior of molecules which contain one of the classical inorganic bond types, the $\equiv P=N-$ or phosphazene unit, is of interest across the entire spectrum of chemistry subdisciplines. Significant current work in theory, structure, organic synthesis, inorganic (both non-metal and transition metal) synthesis, polymer and biochemistry involves phosphazene derivatives.

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