Regio- and Stereochemical Control in Substitution Reactions of Cyclophosphazenes

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Contents

Christopher W. Allen was born in 1942 in Waterbury, CT. He received his B.A. degree from the University of Connecticut and his M.S. and Ph.D. degrees (with T. Moeller) from the University of Illinois. He joined the faculty of the University of Vermont in 1967 where he has been a full professor since 1976. His research interests include the synthesis, structure, and spectroscopic properties of inorganic ring systems with emphasis on phosphazenes, borazines, and sulfur-nitrides. He is also actively involved in the study of hybrid organic–inorganic polymers with particular focus on synthesis, quantitative study of monomer reactivity, and reactions of polymers.

1. Introduction

a. Reaction Pathways

One of the major intellectual attractions of organic chemistry is the enormous range of regio- and stereochemical pathways observed in the reactions of organic molecules. Within the domain of inorganic chemistry, this diversity of behavior is matched in the substitution reactions of halocyclophosphazenes (Scheme I). While all six positions in the hexahalocyclotriphosphazene, $N_3P_3X_6$, (the most common case being X = Cl which is commercially available) are equivalent, the remaining five positions in the monosubstituted derivatives, $N_3P_3X_5Y$, are not. Therefore, reactions leading to the disubstituted material, $N_3P_3X_4Y_2$, can result in the formation of regioisomers, i.e. 2,2 vs 2,4 (numbering starts at the nitrogen atom), which are also referred to as geminal and nongeminal isomers. The nongeminal materials can exist in two stereoisomeric forms with groups being disposed in a cis or trans fashion about the average plane of the ring. A careful examination of the *trans*-2,4-$N_3P_3X_4Y_2$ molecule (and of 2,2,4-$N_3P_3X_3Y_3$) will show the absence of the appropriate symmetry elements necessary for superimposable mirror images, consequently the possibility of optical isomerism also exists. Only one resolution of diastereomeric cyclotriphosphazenes has been reported, and these derivatives did not arise from substitution reactions of the parent trimer.[1] Recent advances in identification of chiral entities by NMR and their resolution using HPLC suggest that a reexamination of some of these systems would be profitable. The pattern of regioisomers, stereoisomers, and optical isomers described for the disubstituted derivatives reoccurs in the tri- and tetra-substituted systems ($N_3P_3X_3Y_3$ and $N_3P_3X_2Y_4$, respectively). On going to the halocyclotetraphosphazenes, $N_4P_4X_8$, one observes the structural diversity noted in the trimeric series with the additional complexity of a choice of two sets of nongeminal regioisomers based on substitution at the 2,4 and 2,6 positions. The complexity continues to increase with ring size. Only sporadic interest has been noted for systems larger than tetramers.

The emphasis of this review will be on the examination of well-characterized systems which allow for clarification of the factors controlling the reaction pathways in cyclophosphazene substitution reactions. A comprehensive survey of all reactions and other aspects of phosphazene chemistry is beyond the scope of this review. An older, but valuable, monograph[2] as well as a more recent thorough review of phosphazene chemistry[3] are available and can be used for access to the primary and secondary literature. Yearly summaries of the literature in this area are also available.[4]

b. Electronic Structure

The precise details of the electronic structure of cyclophosphazenes is still a matter of active investigation, and the interested readers is referred to reviews[3–5] and recent ab initio calculations[6,7] for these details. For the purposes of this review, we will focus on simple models which are useful for rationalizing certain aspects of the substitution patterns under discussion. A convenient starting point for a discussion of phosphazene electronic

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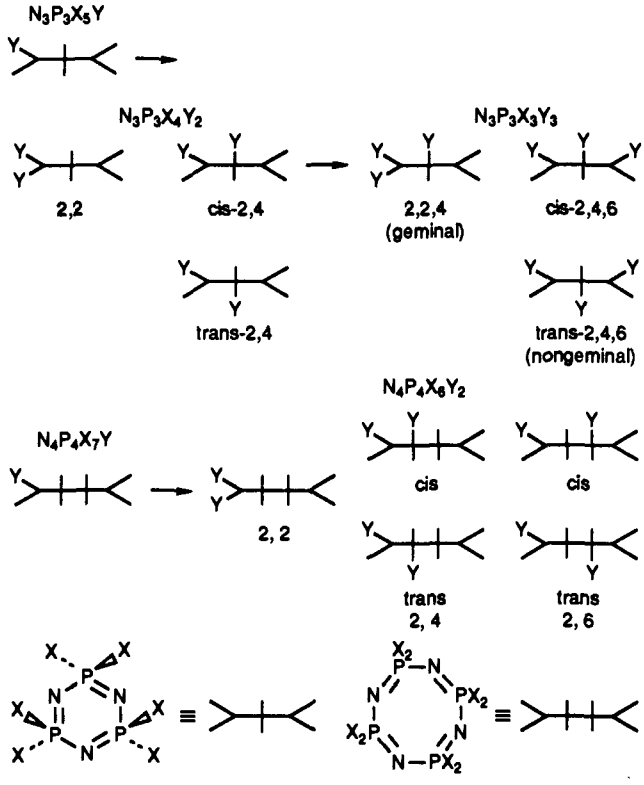
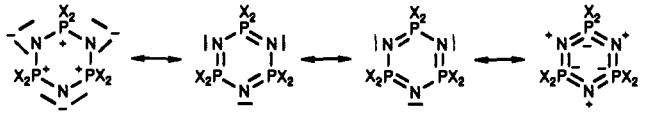
SCHEME I



structure is a consideration of the resonance structures available for the valence electrons. The accumulated



structural[2,3] and calculational data[2,3,6,7] support some degree of multiple PN bonding. The π bonds are strongly polarized toward the nitrogen atoms, resulting in reduced or no π-electron density at the phosphorus atoms. As is suggested in one of the resonance forms above, the possibility of some dative π-electron donation from the remaining nitrogen lone pair to phosphorus acceptor centers can also be considered. This model allows for a simple rationalization of general structural trends in phosphazene derivatives.[3] The persubstituted trimers, $N_3P_3X_6$, are generally planar rings with approximate tetrahedral geometry at the phosphorus atoms. The phosphorus–nitrogen bonds are all equal and approximately 20 pm shorter than the single-bond distance (177 pm). The general trend is toward shorter endocyclic bond lengths with increased substituent electronegativity. Bond-length variations and nonplanarity are observed in mixed substituent phosphazene derivatives. For the molecule 2,2-$N_3P_3X_4Y_2$ where the electron-releasing ability (σ or π) of Y is greater than that of X, the phosphorus–nitrogen bond adjacent to the PY_2 center will be long, the other bond in the Y_2PNPX_2 fragment will be short, and the remaining phosphorus–nitrogen bonds in the X_2PNPX_2 fragment will be essentially equivalent to those found in $N_3P_3X_6$. The magnitude of this effect is demonstrated by a specific example where X = F and Y = C_6H_5.[3] In this system the respective values for the phosphorus–nitrogen distances are 161.7 (5), 153.9 (5), and 155.5 (4). A simplistic way of viewing this phenomena is to suggest that the $\equiv PY_2$ center is less effective in competing for nitrogen lone-pair electron density than is a $\equiv PX_2$ center, thus giving rise to the observed bond-length variation in the Y_2PNPX_2 fragment. The structures for the tetrameric rings are more complex with both planar ($N_4P_4F_8$) and nonplanar ($N_4P_4Cl_8$) persubstituted systems occurring. Mixed substituent tetramers also show systematic bond-length variations.

The other major electronic structure question which impinges on the behavior observed in substitution reactions involves π donation from exocyclic substituents to the phosphorus atom. The π-donor ability of exocyclic nitrogen atoms to endocyclic phosphorus centers in aminocyclophosphazenes has been investigated in detail. Two structural criteria have been of value in establishing exocyclic π donation. The geometry about the nitrogen atom is trigonal planar and the exocyclic phosphorus–nitrogen bond length is significantly shorter (approximately 161 pm) than the accepted single-bond distance.[3] Both theoretical and experimental evidence has been presented supporting the possibility of spirocyclic conjugation with particular reference to those derivatives in which nitrogen atoms are the linking moieties between the phosphazene and exocyclic (spirocyclic) ring.[8] While the phosphazene competes more effectively for exocyclic nitrogen lone-pair electron density than does a trimethylsilyl group,[9] lone-pair delocalization to the phosphazene does not occur if the exocyclic nitrogen atom is part of a delocalized system such as in pyrazoyl[10] or imidazoyl[11] derivatives. The most documented example of localized exocyclic nitrogen lone-pair electrons occurs in aziridine derivatives where, due to the constraints of the three-membered ring, the nitrogen atom assumes a pyramidal, rather than trigonal-planar, configuration thus directing the lone pair away from the phosphorus atom. In these cases, the exocyclic phosphorus–nitrogen bond distance is significantly longer than in the unconstrained cases.[3,12,13] These observations provide additional evidence for lone-pair delocalization in amines with trigonal-planar geometry. Exocyclic lone-pair delocalization has been shown to be significant for carbanionic phosphazenes.[14] In derivatives with two-coordinate exocyclic oxygen atoms, the large electronegativity of the oxygen atom probably precludes significant exocyclic lone-pair delocalization. Recent work has shown that the ability of the vinyl group in (vinyloxy)cyclophosphazenes to accept oxygen lone pair electron density is strongly influenced by the remaining phosphazene substituents.[15] The question of delocalization of π electrons from an exocyclic aryl group is controversial. NMR studies have been interpreted as showing significant phosphorus–aryl mesomeric interaction.[16–18] An alternative model for the NMR data has been suggested[19] and methods as diverse as PE spectroscopy[20] and polymerization reactivity ratios[21] suggests that the effect is small or nonexistent. Similarly, exocyclic vinyl groups do not show any significant delocalization of π electrons to the phosphazene ring.[22]

c. Preliminary Observations

Before examining some specific systems, it is instructive to briefly examine some general expectations of behavior which one might expect to see in cyclophosphazene substitution reactions. Prior to any dis-

cussion of isomeric (regio or stereo) control, it is important to note that stoichiometric control of the degree of substitution is reasonably good. While mixtures containing small amounts of lower and higher degree of substitution than the desired product are often obtained, chromatographic separation is easily accomplished. Separation of isomers remains more problematic. The rates of substitution usually decrease (except in some geminal processes) with each successive replacement of a halogen atom.[23,24] The rates of substitution of tetrameric phosphazenes are significantly greater than those of the trimer,[25-27] so one might expect lower degrees of stereo- and regioselectivity for the tetramer. For a given ring size, the rates of substitution correlate with the ease of phosphorus–halogen bond breaking, i.e. PBr > PCl > PF.[25]

Steric effects are often the most straightforward. The introduction of a sterically demanding substituent should favor nongeminal over geminal structures and 2,6 over 2,4 substitution in the tetrameric series. In addition to the aforementioned regiocontrol, stereoselectivity could also be effected with trans being favored over cis isomers. Electronic effects are potentially very complex. At this stage, it is sufficient to suggest that a possible manifestation of electron release from a substituent to the phosphazene ring would be a preference for nongeminal substitution since the donation of electrons reduces the positive charge on phosphorus at the geminal site.[23,28] This focus on properties of the cyclophosphazenes obviously does not take into account any features of the incoming nucleophile which can be, as will be shown in the next section, of paramount importance in pathway selection in substitution reactions.

2. Reactions with Amines

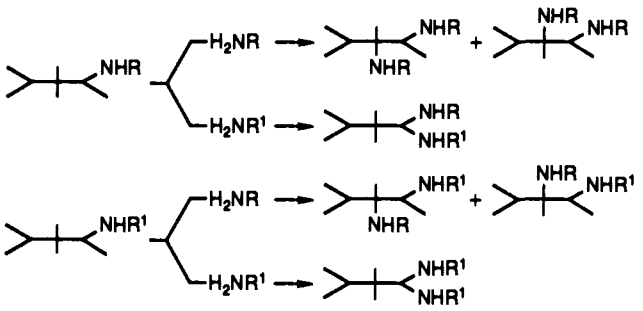
Reactions leading to aminophosphazenes are the most numerous and intensively investigated in cyclophosphazene chemistry.[3,29,30] While several processes, such as reactions with lithio-, stannyl-, or silylamines, deamination, or halogen exchange of preformed aminophosphazenes, are available, the focus of this section will be on reactions of halophosphazenes with amines since this is the source of all the significant mechanistic information. Before examining specific systems, certain complications arising in these reactions need to be explored. Solvent effects have been increasingly recognized as being significant to the point where both the degree of stereo-[31-33] and even regioselectivity[29,34] can be altered by changing solvents. Isomerization reactions have been observed for aminophosphazenes. In the nongeminal series, cis–trans isomerization can be promoted by the amine hydrohalides which are present in the reaction mixture.[35-37] Thermodynamic data is available in certain cases[37,38] and shows that the cis isomer is the thermodynamically favored product.[39] Consequently, if isomeric distributions are used to argue points of stereochemical control in the reaction, care must be taken that the isomer ratio reflects the initial (kinetically controlled) rather than the equilibrated (thermodynamically controlled) product mixture. Solvent-assisted cis–trans isomerization, particularly with solvents which are good nucleophiles such as acetonitrile,[31-33] must also be considered in this regard. Recently, a remarkable geminal to nongeminal isomerization has been observed in the reactions of 2,2-$N_3P_3Cl_4(NH_2)_2$ with certain alkoxide ions.[40] Mechanistic details of this unique process are not as yet available.

TABLE I. Selected Aminolysis Reactions of $N_3P_3Cl_6$[a]

amine	$N_3P_3Cl_{6-n}(NRR^1)_n$ $n = 2$	$n = 3$	$n = 4$	ref
NH_3	g			41, 42
NH_2CH_3	t > c			32, 43
$NH_2C_2H_5$	t > c	tr	g	44
$HN_2C_2H_4Cl$				
(diethyl ether)	g	tr	g	34
(acetonitrile)	g > ng	tr	g	34
$NH_2C_2H_4OCH_3$	ng	tr	g	34
$NH_2CH(CH_3)_2$	t > c, g		g	31, 44
$NH_2CH_2C_6H_5$	g > ng		g	45
$NH_2C_6H_4X$	ng	g ~ ng	g	46
(X = H, CH_3, OCH_3)				
$NH_2CH_2CO_2C_2H_5$	g		g	47
$NH_2C(CH_3)_3$	g		g	48
$NH(CH_3)_2$	t > c	t > c,g	ng	23, 49-51
$NH(C_2H_5)_2$	t > c	t > c,g	t > c,g	33
NHC_2H_4 (aziridine)	g ≃ ng	g ≃ ng	g ≃ ng	52
NHC_5H_{10} (piperidine)	t > c	ng, g	c	53
NHC_4H_8 (pyrrolidine)	t > c	ng, g	c > t	54, 57
NHC_4H_8O (morpholine)	t > c	tr	tr	55, 57
$NH(CH_3)C_6H_5$	t ≃ c	c, g		56
$NH(C_6H_{11})_2$	ng			58
$NH(CH_2C_6H_5)_2$	ng			45

[a] g = geminal; ng = nongeminal; c = cis; t = trans; tr = trace amount.

SCHEME II[a]



[a] R = C_2H_5; R^1 = $C(CH_3)_3$

A summary of the substitution patterns of various amines with $N_3P_3Cl_6$ is provided in Table I. As can be readily appreciated from the information provided above, several possible variants of the results quoted in Table I are possible. The emphasis in the table is on nonisomerized materials in nonparticipating solvents but the possibility of cis–trans isomerization can rarely be ruled out and must be assumed to occur to some degree.

An interesting pattern of regioselectivity is observed in the reactions of ammonia and primary amines. An exclusively geminal, disubstituted product is obtained in the ammonia reaction[41,42] while with primary amines the pathway shifts from nongeminal to geminal disubstitution with increased steric bulk of the amine (a contrasteric result). A crucial insight into this behavior was provided by Shaw who showed that the regiocontrol in the ethyl- and *tert*-butylamine systems was determined by the *incoming* reagents (Scheme II).[59] In addition to this steric effect, an electronic effect has been observed in the reactions of (β-haloethyl)amines. While the reactions of ethylamine lead to nongeminal products, (β-haloethyl)amines exclusively give the

geminal derivative in diethyl ether. In acetonitrile a roughly 2:1 geminal to nongeminal mixture of (β-haloethyl)amino derivatives was obtained.[34] While nongeminal anilino derivatives, 2,4-$N_3P_3Cl_4(NHC_6H_4$-*p*-$R)_2$ (R = H, Me, OMe), are obtained in solvents ranging from diethyl ether to acetonitrile, the corresponding geminal derivatives are obtained when trialkylamines are added to the reaction medium.[46]

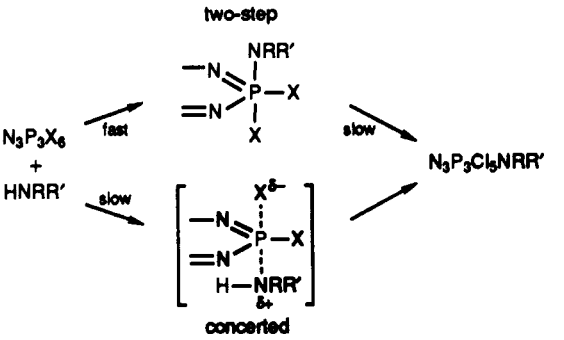
As the reactions of primary amines progress to higher degrees of substitution, the trisubstituted species which are isolated usually follow the same pathway as their disubstituted precursors, however in most cases the trisubstituted derivative is not isolated or is isolated in low yields. By way of contrast, the tetrakis derivatives are generally geminally substituted. When nongeminal bis and tris products are formed, the trans isomer is the kinetically preferred product. The cis isomer, which is often also observed, presumably arises (in part at least) from isomerization processes.

The pathways followed in the reactions of secondary amines with $N_3P_3Cl_6$ show more consistency throughout the amine series than was observed in the reactions of primary amines (Table I). These reactions are generally stereo- and regioselective rather than stereo- and regiospecific, and one observes the trans nongeminal isomer as the major species. The dimethylaminolysis of $N_3P_3Cl_6$ has been widely investigated with the trans nongeminal isomers being the most common bis and tris derivative while both cis and trans nongeminal isomers are observed at the tetrakis stage.[23,49-51] Interestingly, in the reactions of more sterically demanding amines such as diethylamine[33] and *N*-methylaniline[56] the trans preference decreases. Regioselectivity can be affected by the reaction medium as is shown by the fact that the geminal portion of the tris isomers (Scheme I) can be increased by using aromatic solvents.[35] Conversely, the use of acetonitrile promotes the formation of tris nongeminal derivatives[30] except in the case of *N*-methylaniline. For sterically crowded amines, e.g. dicyclohexylamine[58] and dibenzylamine,[45] and strongly electron donating amines, e.g. $HN{=}PPh_3$(a strong σ donor),[60] it is difficult to go beyond the bis stage of substitution. In stark contrast to other secondary amines, reactions of aziridine proceed equally by geminal and nongeminal pathways.[52]

The aminolysis of $N_3P_3X_6$ (X = F, Br) have been less intensively investigated but the general results parallel those found in the corresponding reactions of $N_3P_3Cl_6$. The major factor differentiating the reactions of the various halophosphazenes is the ease of phosphorus–halogen bond cleavage.[25] Thus, while several dimethyl-[61] and ethylamine[62] derivatives of $N_3P_3Br_6$ are obtained, reactions of $N_3P_3F_6$ show a reluctance to proceed to higher degrees of substitution.[63] While exceptions and special cases have been noted above, a few general trends in the aminolysis reactions of cyclotriphosphazenes can be noted. The primary amines show an increased tendency to geminal substitution with increased steric bulk and may exhibit incoming group control of the reaction pathway. Secondary amines give nongeminal products with the trans stereoisomer often being the favored product.

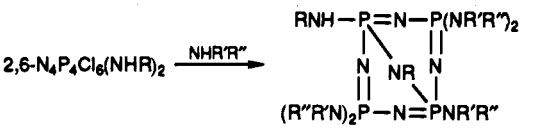
The aminolysis of $N_4P_4Cl_8$ is a complex process for two aforementioned reasons, i.e. the large number of isomeric possibilities and the loss of selectivity due to

SCHEME III



the rapid rate of the reaction (section 1.c). Generally less reactive amines such as *tert*-butylamine,[64] benzylamine,[65] *N*-methylaniline,[66] and aziridine[67] provide 2,4- and 2,6-disubstituted derivatives in comparable quantities. More reactive nucleophiles such as dimethylamine,[68] methylamine,[65] and ethylamine[69] give high relative yields of the 2, trans-6 derivatives. Again note the importance of the bis trans isomer. However at the tris stage of substitution, the 2, cis-4, trans-6 isomers appears most common[64,68] but it is unclear if this is the kinetically or thermodynamically controlled product distribution. The regiochemistry of the mixed ethylamine/*tert*-butylamine system is controlled by the nature of the incoming groups.[64]

There is a reaction pathway, unique for the tetrameric system, which has been recognized in the reactions of primary amines with $N_4P_4Cl_8$ or in the aminolysis of 2,6-primary amino derivatives.[70] The result is a bicyclic



derivative which arises formally from an intramolecular nucleophilic substitution via an attack of the amine substituent at P(2) on P(6).[70]

While the complexities of the interactions of amines with cyclophosphazenes can be explored in more detail by considering reactions of partially substituted phosphazenes, e.g. $N_3P_3Cl_{6-n}X_n$ (X = OR, Ph, other amine substituents),[3] all of the important aspects of regio- and stereochemical control may be found in the systems described above. Thus it becomes appropriate to examine some mechanistic studies. Building on the early work of the groups of Moeller, Shaw, and Goldschmidt, Krishnamurthy has conducted detailed kinetic studies which have led to an understanding of the bewildering array of synthetic observations.

A consideration of the mechanism of formation of the monosubstituted derivatives, $N_3P_3Cl_5NRR^1$ (R = H, alkyl, aryl; R′ = alkyl), without the complications of regio- and stereochemical selectivity will allow for establishment of several important features of the substitution process. The reaction kinetics are bimolecular in polar solvents and show mixed second- and third-order (in amine) rate laws in nonpolar solvents (due to base catalysis). In polar solvents, the solvent assumes the base catalysis function. Activation parameters for several reactions can be found in Table II. Two related pathways can be envisioned for the bimolecular substitution (Scheme III).[24] The difference between these two mechanisms revolves about the intermediacy of a

TABLE II. Selected Activation Parameters for Cyclophosphazene Aminolysis Reactions

		product		
phosphazene[a]	solvent	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J K^{-1} mol^{-1}	ref
$N_3P_3Cl_5NHMe$	thf	2.9 ± 1.7	−205 ± 6	71
$N_3P_3Cl_5NMe_2$	thf	7.1 ± 2.1	−197 ± 8	76
$N_3P_3Cl_5NMe_2$	CH_3CN	20.7 ± 1.2	−128.0 ± 2.3	23
$N_3P_3F_5NMe_2$	CH_3CN	53.1 ± 1.7	−128.7 ± 3.2	23
$N_3P_3Cl_5NC_5H_{10}$	thf	12.1 ± 2.1	−188 ± 6	72
$N_3P_3Cl_5NHCMe_3$	thf	47.6 ± 2.1	−125.9 ± 6.0	73
$N_3P_3Cl_5NHCMe_3$	CH_3CN	20.3 ± 1.7	−205.7 ± 17.3	73
$N_4P_4Cl_7NHCMe_3$	CH_3CN	8.2 ± 2.0	−201.6 ± 42.2	73
$N_3P_3Cl_5NHPh$	CH_3CN	29.1[b]	−203.9[b]	74
$N_3P_3Cl_5NHC_6H_4OMe$	thf	21.9[b]	−261.7[b]	74
$N_3P_3Cl_5NHC_6H_4OMe$	CH_3CN	25.2[b]	−189.5[b]	74
cis-$N_3P_3Cl_4(NMe_2)_2$	thf	8.8 ± 0.5	−238 ± 8	75
trans-$N_3P_3Cl_4(NMe_2)_2$	thf	28.5 ± 1.3	−159 ± 8	75
trans-$N_3P_3Cl_4(NMe_2)_2$	CH_3CN	10.6 ± 1.4	−189.7 ± 3.2	23
2,4-$N_3P_3Cl_4(NHC_6H_4OMe)_2$	thf	29.1[b]	−278.2[b]	74
trans-2,4,6-$N_3P_3Cl_3(NMe_2)_3$	CH_3CN	14.0 ± 1.0	−196.4 ± 3.6	23
cis-2,2,4,6-$N_3P_3Cl_2(NMe_2)_4$	CH_3CN	21.0 ± 1.1	−217.2 ± 4.1	23

[a] Obtained in the reaction of the amine and the parent phosphazene. [b] Error estimated as <5%.

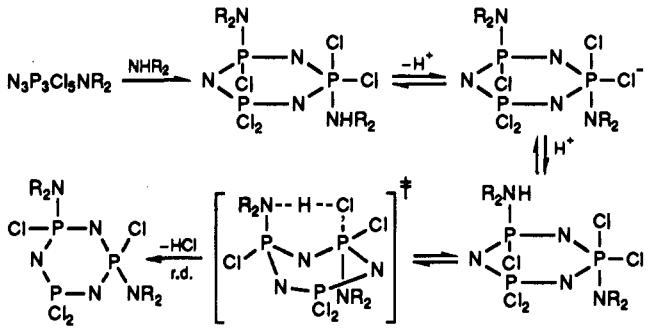
neutral, five-coordinated phosphorus Lewis acid–base adduct of the amine and the phosphazene. If the adduct is formed, a two-step $S_N2(P)$ mechanism is followed, otherwise a one-step, $S_N2(P)$ concerted, processes occurs. The former process is most significant in the synthesis of the monosubstituted derivatives in question. The enthalpy of activation, $\Delta H^{\neq}$, is associated with the formation of the five-coordinate intermediate[72,76] since significant variation in $\Delta H^{\neq}$ with the nature of the amine is observed.[72] For alkylamines the correlation is with size rather than basicity; thus primary amines are more reactive than secondary and α branching leads to rate reduction.[72] The entropy of activation, $\Delta S^{\neq}$, is essentially constant and is the most important contributor to the free energy of activation.[71,76] The lack of a measurable deuterium isotope effect indicates rapid H^+ loss followed by rate-determining loss of X^- from the transition state.[77] The differences in the reactivites of $N_4P_4Cl_8$ or $N_3P_3F_6$ relative to $N_3P_3Cl_6$ are totally due to the $\Delta H^{\neq}$ term (Table II). This has been interpreted in terms of ring flexibility and hence ease of formation of the intermediate adduct.[73] Thus, the flexible tetramer easily adjusts to the new geometry at phosphorus and hence exhibits a low $\Delta H^{\neq}$ while the rigid fluorotrimer is more resistant to structural change and has a higher $\Delta H^{\neq}$.[23,73] The acceptor ability of the phosphorus atom may also play a role in the reactivity of $N_3P_3F_6$. The observation of a shortened phosphorus–nitrogen bond in the fluoro compared to the chloro trimer[3] is suggestive of increased π and lone-pair (π') electron donation from nitrogen which in turn would reduce the acceptor ability of the phosphorus atoms. The variation in rate of chlorine exchange observed for higher cyclic oligomers[78] indicates that additional factors beyond ring flexibility may also be of importance in the reactivity of these molecules.[73,78]

Secondary amines are more regular than primary amines in their reaction patterns for higher degrees of substitution and hence will be considered first. In situations where both geminal and nongeminal paths are available, nongeminal reactions are observed to follow bimolecular kinetics.[3] The regioselectivity can be seen as reflecting both steric and electronic effects. Steric effects dictate that the incoming group in a bimolecular reaction will go to the most accessible phosphorus atom, thus giving the lowest $\Delta H^{\neq}$. However, while large incoming group effects have already been noted in the first stage of substitution (Table II), only relatively small steric effects due to ring substituents have been observed in the reactions of $N_3P_3Cl_5NRR'$ (R = Bu^n, R' = H; R = R' = Bu^n; R = Pr^i, R' = H; R,R' = C_5H_{10}).[81] It is presumed however that very large amines, e.g. dibenzylamine, would exhibit significant substituent steric effects. The steric effect does show up when the steric bulk of the incoming amine is increased.[80]

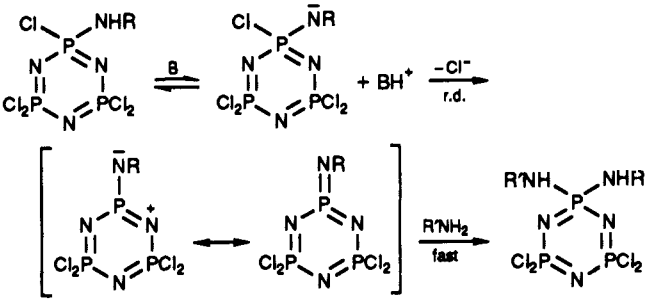
Electron release from the exocyclic amine substituent (see section 1.b) reduces the acceptor ability of the substituted phosphorus atom, thus also promoting nongeminal attack. The electron release is, in part, transmitted throughout the whole ring thus adding to the difficulty (i.e. decreasing the rate) of higher degrees of substitution. The lack of exocyclic lone-pair donation to phosphorus (section 1.b) coupled with the small size of the aziridine moiety results in greater accessibility of the substituted phosphorus atom to adduct formation and hence the loss of nongeminal regioselectivity.[52] There is a subtle mechanistic variation in the formation of $N_3P_3Cl_{6-n}(NMe_2)_n$ (n = 2,3). Goldschmidt has shown that on going from the mono to the disubstituted dimethylamino derivatives in tetrahydrofuran (thf), the $\Delta H^{\neq}$ values increase as one would expect from the arguments presented above.[75] Krishnamuthy has shown that in a polar solvent, acetonitrile, not only are the rates faster but ΔH decreases on going to the disubstituted derivative.[24] He has proposed a mechanistic change wherein on formation of $N_3P_3Cl_4(NMe_2)_2$ in acetonitrile the reaction follows the concerted pathway (Scheme III) which resembles the familiar direct displacement involved in the S_N2 reactions.[24] The polar transition state in the concerted reaction is favored in polar solvents and is reflected in the large negative $\Delta S^{\neq}$ indicating extensive transition-state solvation.[24]

The individual rates of formation of *cis*- and *trans*-$N_3P_3Cl_4(NMe_2)_2$ have been measured.[75] As was observed in the formation of the monosubstituted derivatives, the rates are controlled by $\Delta S^{\neq}$ and the kinetic preference for the trans isomer is solely due to differences in $\Delta S^{\neq}$ between cis and trans isomers (i.e. $\Delta S^{\neq}$, less negative for trans isomer formation). In fact, $\Delta H^{\neq}$ favors the cis isomer ($\Delta H^{\neq}_{cis} < \Delta H^{\neq}_{trans}$), thus paralleling the difference in heats of formation for the neutral molecules. A mechanism based on an intramolecular substituent solvating effect has been proposed to rationalize these data.[79] The mechanism leading to the cis isomer is identical with the mechanism followed in the first step of substitution. In the pathway leading to the trans isomer, the possibility of intramolecular stabilization the H^+Cl^- ion pair in the transition state exists (Scheme IV). A significantly reduced degree of solvation of the departing Cl^- is required, thus leading to a less negative $\Delta S^{\neq}$. This substituent solvating effect would be even more pronounced in a concerted $S_N2(P)$ process, thus leading to the high observed (> 95%) trans stereoselectivity when the reaction occurs in acetonitrile.[23] Additional support for this proposal comes from a comparison of the reactions of piperidine and *N*-deuteriopiperidine with $N_3P_3Cl_5NC_5H_{10}$.[77] A

SCHEME IV



SCHEME V



reduction in the amount of the *trans*-2,4-$N_3P_3Cl_4(NC_5H_{10})_2$ isomer was noted when the deuteriated amine was used, thus adding support for involvement of H(D) in the transition state in the formation of the trans isomer.[77]

Given the information provided above, it is reasonable to suppose that the predominant, and occasionally exclusive, formation of the geminal isomer in the reactions of ammonia or primary amines with cyclotriphosphazenes follows a different mechanistic pathway than that presented for secondary amines. A dissociative route, the conjugate base mechanism, S_N1(CB), shown in Scheme V, is believed to be operative in the formation of geminal isomers.[48] In this process, a base (solvent or amine) abstracts a proton from the mono primary aminophosphazene. This is followed by loss of chloride ion leading to a coordinatively unsaturated transition state. Attack by another mole of amine on the phosphoranimine leads to the observed geminally substituted product. The nongeminal isomers would arise by the routes described previously for secondary amine reactions. Experimental evidence for this mechanism comes from the observation of increased ratios of geminal to nongeminal products with added base for the reactions of primary amines but not for secondary amines.[81]

The observation of first-order (in phosphazene) kinetics for the formation of 2,2-$N_3P_3Cl_4(NHC_6H_4R)_2$ (R = H, *p*-Me, *p*-OMe) from the corresponding monosubstituted derivatives in the presence of tri-*n*-butylamine has been reported.[74] The three-coordinate phosphoranimine intermediate in these reactions has been trapped by reaction with methanol, leading to 2,2′-$N_3P_3Cl_4(OMe)NHC_6H_4R$.[74] In keeping with the expectations based on a dissociative mechanism that the steric effects of an incoming reagent would not be significant, the rates of geminal isomer formation in the reaction of primary amines with $N_3P_3Cl_6$ are roughly equal.[80] The rates of formation of the nongeminal isomers in the same series, however show a large incoming group steric inhibition. Thus, in the reaction of methylamine, the rate of nongeminal isomer formation is greater than the rate of geminal isomer formation and the nongeminal isomer is the major product. The steric problems associated with a bimolecular mechanism involving *tert*-butylamine are such that the rate of nongeminal isomer formation is prohibitively slow compared to geminal isomer formation via the dissociative pathway so the geminal isomer is observed exclusively. Similar arguments allow for the rationalization of the isomers formed in the mixed (ethylamino)- and (*tert*-butylamino)phosphazenes (Scheme II). The slow rate of nongeminal isomer formation, relative to geminal isomer formation, with *tert*-butylamine as a reactant results in geminal isomer formation in the reactions of $N_3P_3Cl_5NHEt$ with *tert*-butylamine. The rapid rate of nongeminal isomer formation by ethylamine results in the production of the nongeminal isomers in the reaction of $N_3P_3Cl_5NHBu^t$ with ethylamine.

The previous argument suggest that only the steric effect of the entering amine is significant but the range of basicity is extended when (2-haloethyl)amines are considered; e.g. $pK_b(BrCH_2CH_2NH_2)$ = 8.9 vs, pK_b-$(HCH_2CH_2NH_2)$ = 10.6.[82] Thus, the weaker entering nucleophile (assuming nucleophilicity follows basicity) would have a higher activation energy so the alternative (dissociative) mechanism would be dominant, leading to the geminal product. As one goes to more polar solvents, the rates of associative reactions of amines with $N_3P_3Cl_6$ increase, hence, the appearance of the nongeminal product. The basicity of (2-methoxyethyl)amine (pK_b = 9.44) is greater than that of the (haloethyl)amines, and hence, the formation of the nongeminal product is observed.[34] The possibility of β-halogen atom intramolecular assistance in displacement of the geminal chlorine atom has also been suggested.[34]

As higher degrees of substitution are obtained, the primary amines all give geminally substituted 2,2,4,4-$N_3P_3Cl_2(NHR)_4$ derivatives. It is reasonable to suppose that this reflects the dominance of the S_N1(CB) mechanism since the nongeminal (bimolecular) rates become progressively lower with increased substitution. The low yields of tris isomers can be traced to the presumed rapid dissociative reaction of each nongeminal site in the nongeminal bis or geminal tris derivatives. The formation of the trissubstituted secondary amino derivatives follows the same mechanistic pathway as described for the disubstituted derivatives.[23] A significant change over in mechanism occurs when *trans*-2,4,6-$N_3P_3Cl_3(NMe_2)_3$ is converted to the tetrasubstituted derivative. This reaction follows first-order kinetics. In addition to steric effects, the combined electron-releasing ability of three dimethylamino groups weakens the remaining phosphorus–chlorine bonds.[23] The formation of the cis isomer of $N_3P_3Cl_2(NMe_2)_4$ has been shown[23] to correlate nicely with the expectation of the dissociative mechanism in that the longest phosphorus–chlorine bond[83] in the precursor molecule, *trans*-$N_3P_3Cl_3(NMe_2)_3$, is the one which is replaced upon dimethylaminolysis. It is conceivable that the low yields of geminal derivatives in the early stage of substitution by secondary amines also results from a competing dissociative pathway which only becomes dominant when the rate of the associative (bimolecular) reaction

has become prohibitively low, i.e. at high degrees of substitution.

Few mechanistic studies, separate from product distribution, have been reported for the reactions of amines with $N_4P_4Cl_8$. The formation of $N_4P_4Cl_7NHCMe_3$ from $N_4P_4Cl_8$ and *tert*-butylamine follows a bimolecular, $S_N2(P)$, kinetics with a five-coordinate phosphorus intermediate or transition state.[73] As in the case of the trimeric series, $\Delta H^{\ddagger}$ is associated with the formation of the intermediate and $\Delta S^{\ddagger}$ is associated with formation of the ionic (H^+, Cl^-) products from the transition state and hence is rate controlling. As previously discussed, the rates of reaction of the tetramer are significantly faster than those of the trimer. Therefore, the dissociative processes, $S_N1(CB)$ and phosphorus–chlorine bond ionization, will be of less importance, particularly in the early stages of substitution, so nongeminal isomers will predominate. A new question of regiocontrol arises with the tetramer i.e. 2,4 vs 2,6 substitution. Statistically, 2,4 substitution is favored but electron release from amines which are good lone-pair donors will deactivate adjacent phosphorus centers and thus favor 2,6 substitution.[66] Thus strong donors will promote 2,6 substitution while weak donors such as *N*-methylaniline[66] and aziridine[67] will give both 2,4- and 2,6-disubstituted derivatives.

The $S_N1(CB)$ mechanism has been proposed to become significant in formation of the bicyclic species (vide supra) derived from cyclotetraphosphazenes.[70,84] On the basis of product studies and precedents from cyclotriphosphazene reactivity patterns, it has been proposed that 2,6-$N_4P_4Cl_6(NHR)_2$ derivatives can undergo a double dehydrohalogenation. The addition of an incoming primary amine to one of the two phosphoranimine moieties would be followed by a transannular attack of a $\equiv$PNHR group on the other phosphoranimine leading to the bridging $\equiv$PNRP$\equiv$ functionality. The formation of the 2,6 rather than a 2,4 bridge is ascribed to strain which would be inherent in the four-member ring resulting from 2,4 attack.[70]

In summary, the mechanistic models which have been developed for the reactions of amines with cyclophosphazenes allow for a reasonable level of understanding of the regio- and stereochemical control operative in these reactions. These models are summarized along with the results from other systems in section 8. The concepts developed in these studies have been applied to the aminolysis of substituted phosphazenes and will allow for modeling of reactions with other nucleophiles. In recent years, increased interest has also been shown in the reactions of multifunctional reagents such as diamines, polyamines, amino alcohols, and diols with cyclophosphazenes.[3,4] While a detailed discussion of these systems is beyond the scope of this review, the basic mechanistic pathways observed in these reactions may be expected to follow the models developed above (and in section 4) for the first of the sites of the multifunctional reagent to undergo reaction. The stereo- and regiochemical pathways exhibited by reactions of the remaining sites will be constrained by the geometry of the multifunctional reagent.

3. Metathetical Halogen and Pseudohalogen Exchange

The simplest of all phosphazene substitution reactions is the exchange of labeled chloride ion for bound chlorine atoms in $(NPCl_2)_n$ (n = 3–6) which has been examined by Sowerby. The reactions are bimolecular and as previously mentioned rate variations with ring size were noted with the activation energy for $(NPCl_2)_5$ being greater than those of $(NPCl_2)_{4,6}$.[78] Most methathetical reactions of interest involve fluorination reactions, and this is a major route to these derivatives.[3] Three fluorinating systems have been used to effect these transformations: alkali metal fluorides, potassium fluorosulfite (KSO_2F), and antimony trifluoride either alone or with catalytic amounts of antimony pentachloride. While differences in reactivity might be expected, there is a surprising variation in regiospecificity. Fluorination reactions of $(NPCl_2)_{3-5}$ with anionic reagents (NaF for the trimer[85] and KSO_2F for the tetramer[85] and pentamer)[86] all follow a geminal pathway. In the tetramer, 2,2,4 rather than 2,2,6 substitution is observed[85] while in the pentamer equal amounts of each show up.[86] Approximate rate studies show that the rate of fluorination of a $\equiv$PFCl center is greater than that of a $\equiv PCl_2$ center by a factor of 9 for the trimer,[85] 7 for the pentamer,[86] and 100 for the tetramer.[85] Fluorination of $(NPCl_2)_{3-6}$ with the $SbF_3/SbCl_5$ mixture,[87] which produces SbF_3Cl_2 as the active fluorinating species,[88] gives nongeminal derivatives. In reactions of $N_3P_3Cl_5NMe_2$ with NaF or KSO_2F substitution occurs at the $\equiv PCl_2$ center and proceeds in a geminal fashion with the chlorine atom geminal to the dimethylamino group as the most difficult halogen atom to exchange.[89] If $SbF_3/SbCl_5$ is used as the fluorinating agent, then the $\equiv P(NMe_2)Cl$ halogen is the first to be replaced.[89] A similar pattern of behavior is observed in the conversion of 2,4-$N_3P_3Cl_4(NMe_2)_2$ to $N_3P_3Cl_2F_2(NMe_2)_2$ where KSO_2F effects substitution at the $\equiv PCl_2$ centers and SbF_3 at the $\equiv P(NMe_2)Cl$ site.[90] The reaction of SbF_3 with all of the $N_3P_3Cl_3(NMe_2)_3$ isomers also occurs initially at the $\equiv P(NMe_2)Cl$ centers.[91]

A different behavior is noted when *cis*- and *trans*-2,4-$N_3P_3Cl_4(NHMe)_2$ are allowed to react with KSO_2F. Initial attack is at the $\equiv P(NMe_2)Cl$ centers and is accompanied by isomerization. Sequential reactions occur at the remaining ($\equiv PCl_2$) sites.[92] It should be noted that numerous mixed chlorofluoro derivatives have been obtained by deamination of aminocyclophosphazenes[3] but they will not be considered here.

While some pseudohalogen derivatives have been prepared by metathesis, the reaction pathway has only been examined for the isothiocyanate system. At the stage of disubstitution, the geminal chloro trimer, 2,2-$N_3P_3Cl_4(NCS)_2$,[93] is obtained while in the tetrameric case tentative evidence suggests the formation of a nongeminal sequence.[94]

The observations summarized above, in part, follow some of our simple expectations (section 1.c) but also suggest some new complexities. The geminal pathway followed in fluorination reactions using simple fluoride salts (e.g. NaF) and the rate acceleration on going from a reaction at a $\equiv PCl_2$ center to the one at a $\equiv$PFCl center are understandable on an electrostatic basis. The presence of the highly electronegative fluorine atom increases the positive charge on the phosphorus atom, thus favoring nucleophilic attack.[85] In the tetrameric series, a $\equiv PF_2$ center will compete effectively for lone-pair electron density on an adjacent nitrogen atom

relative to an adjacent $\equiv PCl_2$ (section 1.b), thus increasing the positive charge on the $\equiv PCl_2$ center and favoring fluorination at that center i.e. 2,2,4-regioisomer formation. The reason for the equal distribution of 2,2,4- and 2,2,6-regioisomers in the pentamer is unclear. In fact, since the rate of reaction of the pentamer is lower than the trimer,[86] the regioselectivity should be greater not less. As in the reactions of secondary amines (section 2), the electron-donating ability of the amine promotes reaction at a distant phosphorus atom so anionic fluorination occurs at a $\equiv PCl_2$ rather than $\equiv P(NMe_2)Cl$ center. Once the $\equiv PFCl$ group is formed then, as discussed above, it will be converted to a $\equiv PF_2$ center.

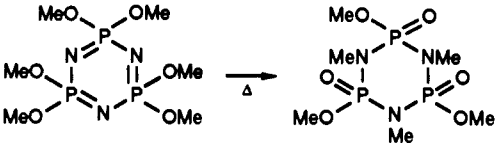
The nongeminal pathway followed by the antimony reagents has been proposed to be the result of coordination of the antimony compound, a Lewis acid, to the most basic nitrogen atom in the ring.[90] Extensive evidence exists that Lewis acids such as MX_3 (M = Sb, X = F, Cl;[95] M = Al, X = Br[96]) and SbF_5[97] can coordinate directly[95,96] to endocyclic nitrogen or possibly form halogen-bridged[97] structures. Alternatively, ionic structures involving MX_6^- ions have been proposed[98] with other MX_5($SbCl_5$, $TaCl_5$) type Lewis acids. The work of Shaw on basicity measurements has resulted in quantitative information, in the form of substituent constants, which allow for the prediction of the most basic endocyclic sites.[29,99,100] In order to understand the phosphazene–Lewis acid interaction, by which ever route it takes, with respect to fluorination, one must first explore the effect of a fluorine atom on various regions of the molecule. The electron-withdrawing effect of the fluorine atom will draw electron density from an adjacent nitrogen atom making the distant nitrogen atom the more basic site. A second effect will be a shortening of the phosphorus–chlorine bond in a $\equiv PFCl$ vs a $\equiv PCl_2$ center; an effect which has been observed in structural studies.[101] Thus an incoming Lewis acid will interact with the phosphazene at a site distant from $\equiv PFCl$ center. If the interaction is with an endocyclic nitrogen, it is the distant nitrogen center which is most basic. If the interaction is halogen-bridging abstraction, the distant chlorine atoms exhibit more charge separation than the chlorine atom in a $\equiv PFCl$ center. The fluorination agent is thus positioned to deliver the fluorine atom to the nongeminal site. Conversely when a strong donor is attached to the phosphorus atom, all effects are reversed. Since the phosphorus–chlorine bond in a $\equiv P(NMe_2)Cl$ center is weakened,[83] it will preferentially undergo metathesis.

In a simple (Hückel) MO model, endocyclic nitrogen lone-pair delocalization varies with ring size to give π-charge densities at phosphorus atoms in $(NPCl_2)_n$ in the order $n = 3 > 5 \gg 4$ which correlates with the approximate activation energies of fluorination of these systems (i.e. easiest for $n = 4$).[86] However, recent ab initio calculations on $(NPCl_2)_{3,4}$[6,7] emphasize the localization of charge on ring atoms. It would be of interest to see if calculations on $(NPCl_2)_5$ reproduce the reactivity order suggested by the Hückel approach.

Finally, factors operating in the isothiocyanato system are unclear. The formation of the geminal trimer derivative may be due to the effectiveness of the NCS group to function as a σ donor but not a π donor. This concept will be examined in detail for the reactions of main-group organometallics with $N_3P_3F_6$ (section 5). The nongeminal tetrameric derivatives must then be due to loss of regioselectivity as a result of rapid rates of reaction. The paucity of data on these systems is such that speculations of this type are of questionable value.

4. Reactions of Oxyanions and Thiolates

In spite of the fact that a large number of reactions of oxygen bases (as neutral species or more commonly as oxyanions) with halocyclophosphazenes have been examined, the number of systems where isomeric composition has been established or kinetic data has been obtained is surprisingly small. The reasons for this state of affairs can be traced, but not limited, to the variety of factors discussed below. Most reactions have been carried out to complete substitution in order to obtain materials of technological interest.[3] Alkoxy and aryloxy derivatives tend to be oils and isomeric separation, either by classical or chromatographic methods, is more difficult than in the case of aminophosphazenes. The possibility of a thermally induced tautomeric phosphazene–phosphazene rearrangement, illustrated in eq 1 for $N_3P_3(OMe)_6$,[3,29,99,102,103] also adds to the complexity of dealing with these systems. Degradative transfor-

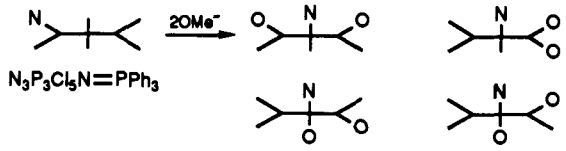


(1)

mations can also occur. For example, in the reaction of $N_3P_3Cl_6$ with benzyl alcohol, benzyl chloride formation and phosphazene decomposition are observed in addition to formation of the expected derivatives.[104] The degradation pathway is believed to proceed through formation of a hydroxyphosphazene which undergoes a facile phosphazene–phosphazene tautomerization of the type shown above with a hydrogen atom in place of the methyl group. A more general degradative pathway is the dehydration of tertiary alcohols; thus tert-butyl alcohol or its sodium salt is converted to isobutylene on reaction with $N_3P_3Cl_6$.[105] Other complications arise from the possibility of dealkylation of a $\equiv P(X)OR$ unit by strong bases.[106] The resulting oxyanonic species, $\equiv PX(O)^-$, can either abstract a proton to generate the hydroxy derivative which undergoes tautomerization or can couple with another phosphazene to give an oxo-bridged dimer.[107]

The reaction with the simplest oxygen base, water, or the hydroxide ion, was one of the first cyclophosphazene reactions to be examined.[2,3] The ultimate products, phosphate and ammonia, arise from trimetaphosphimic acid, $[NHP(O)OH]_3$, which in turn is the phosphazane obtained from tautomerization of $N_3P_3(OH)_6$. The early stages of the reaction have not received much attention. The reaction of water with $N_3P_3Cl_6$ in ether is reported to give the geminal, tautomerized material, $(NPCl_2)_2NHP(O)OH$.[108] On the other hand, a careful study of the reaction of $[Ph_4As]Cl{\cdot}H_2O$ with $N_3P_3Cl_6$ in acetonitrile shows the formation of the anionic species, $[NPCl_2NPCl(O)NHPCl(O)]^-$.[109] A reasonable hypothesis for the ethereal hydrolysis is formation of $N_3P_3Cl_5OH$ followed by rapid tautomerization. The phosphorus atom in the $\equiv P(O)Cl$

SCHEME VI[a]



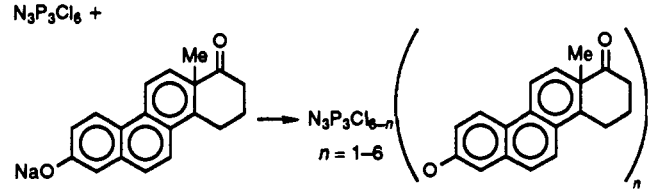
[a] N = $NPPh_3$; O = OMe.

center carries a large positive charge, hence is the site of the second nucleophilic attack. In the presence of the tetraphenylarsonium ion and a polar solvent, deprotonation to give $N_3P_3Cl_5O^-$ occurs and the strongly electron donating oxo substituent directs substitution to the nongeminal site.

Surprisingly few investigations involving the preparation of partially substituted alkoxyphosphazenes have been reported. A nongeminal pathway has been observed in the formation of $N_3P_3Cl_2(OR)_3$ (R = Me,[110] Pr,[111] CH_2CH_2Ph[111]) and $N_3P_3Cl_{6-n}(OCH_2Ph)_n$ (n = 2–4).[111,112] A fully characterized series of trifluoroethoxy derivatives, $N_3P_3Cl_{6-n}(OHC_2CF_3)_n$ (n = 1–6),[113] has been reported. The reaction pathway is basically the same as that observed in the corresponding reactions of dialkylamines, with the trans nongeminal isomers predominating for n = 2,3 and small amounts of cis and geminal isomers also being observed. The cis isomer becomes predominant in the tetrakis system. The trans isomer has also been suggested to be the most important species in the $N_3P_3Cl_{6-n}[OCH_2(CF_2)_mH]_n$ systems.[114] A trans nongeminal sequence is followed in the formation of $N_3P_3Cl_{6-n}(O\text{-}n\text{-}C_4H_9)_n$ (n = 1–4).[115] In contrast to the systems noted above, the highly reactive compound $N_3P_3Cl_4(OCH_2CH_2Cl)_2$ has been assigned a geminal configuration.[34] Information on fluorophosphazenes is even more limited, but a nongeminal species, $N_3P_3F_3(OCH_2C_3F_7)_3$ has been reported.[116] The reaction of the trifluoroethoxide ion with $N_4P_4Cl_8$ provides the series $N_4P_4Cl_{8-n}(OCH_2CF_3)_n$. The surprising lability of these molecules prevented detailed characterization but 2,4- and 2,6-disubstituted derivatives were detected and geminal products were observed for n = 3 and 4.[117]

A detailed study of the reactions of $N_3P_3X_5N{=}PPh_3$ (X = Cl, F) with the methoxide ion has been reported.[118] The presence of two different substituents allows for a multiplicity of products but for $N_3P_3Cl_4(NPPh_3)OMe$, the cis nongeminal derivative is favored. The cis/trans ratio decreases with decreasing solvent polarity. In acetonitrile, four products of the stoichiometry $N_3P_3Cl_3(NPPh_3)(OMe)_2$ are obtained (Scheme VI), indicating reaction at all phosphorus–chlorine sites ($\equiv PCl_2$, $\equiv P(NPPh_3)Cl$, $\equiv P(OMe)Cl$) whereas in benzene the two isomers which arise from attack at the $\equiv P(NPPh_3)Cl$ center predominate. The major tris product is 2,2,4,4-$N_3P_3Cl_2(NPPh_3)(OMe)_3$, indicating preference for substitution geminal to both of the substituents is followed at this stage. The corresponding reactions of the fluorinated analogue, $N_3P_3F_5NPPh_3$, present an interesting contrast. Substitution at the $\equiv P(NPPh_3)F$ center is the last reaction to occur. Equal amounts of the nongeminal, $N_3P_3F_4(NPPh_3)OMe$ isomers are observed. Similarly, comparable amounts of the three nongeminal $N_3P_3F_3(NPPh_3)(OMe)_2$ and the two nongeminal $N_3P_3F_2(NPPh_3)(OMe)_3$ isomers are obtained.[118]

The reactions of oxyanions derived from unsaturated organic moieties have been explored in some detail. The reactions of the phenoxide[119,120,121,122] and p-cresoxide[121] ion with $N_3P_3Cl_6$ give rise to the complete series of derivatives, $N_3P_3Cl_{6-n}(OC_6H_4\text{-}p\text{-}R)_n$ (n = 1–6; R = H, Me). The major pathway is nongeminal but



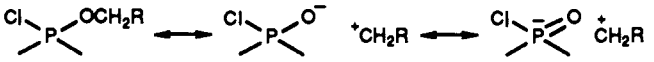
a small amount of the geminal products are also obtained. A cis preference is observed at the stage of disubstitution but does not continue for the tris (trans > cis) and tetrakis (trans ≃ cis) derivatives. Other p-phenoxides (R = Br,[123] NO_2[124]) follow a nongeminal pathway. An interesting study involves steriodal derivatives in which a nongeminal pathway is observed and equal amounts of cis and trans isomers are observed.[105] The reaction of sodium phenoxide with $N_4P_4Cl_8$ gives rise to an extensive series, $N_4P_4Cl_{8-n}(OPh)_n$ (n = 1–8), of nongeminal isomers. Comparable amounts of the 2,4 and 2,6 derivatives are found at the disubstituted stage.[125]

An extensive series of (vinyloxy)cyclophosphazene derivatives has been prepared from reaction of the halophosphazene with the lithium enolate of acetaldehyde.[15,126–128] The reaction leading to the chlorotrimer derivatives, $N_3P_3Cl_{6-n}(OCH{=}CH_2)_n$ (n = 1–6) follows a predominant, but not exclusive, nongeminal pathway with a cis preference being observed in the di-[126] and trisubstituted[128] products.[126] The corresponding reaction of the fluoro trimer gives rise to the series $N_3P_3F_{6-n}(OCH{=}CH_2)_n$ (n = 1–5) which is exclusively nongeminal.[127] The tetrameric derivatives $N_4P_4Cl_{8-n}(OCH{=}CH_2)_n$ (n = 1,2) have been prepared and at the stage of disubstitution, all isomers are obtained but the major component is the 2,4 derivative with the cis isomer predominating.[128] Preferential formation of the 2,4 regioisomer is unique in reactions of $N_4P_4Cl_8$.

Unfortunately, few kinetic studies of the reactions of oxyanions with cylcophosphazenes are available however it has been shown that the reaction of the n-butoxide ion with $N_3P_3Cl_6$ is second order through the tetrakis stage.[115] A dissociative (first-order) pathway has been observed for the reaction of $N_3P_3(OPh)_5Cl$ with dimethylamine.[24]

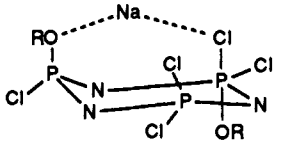
If one contrasts the behavior of oxyanions with that of nitrogen bases (section 2) significant parallels and some differences are noted. Certain of these observations can be related to nature of the exocyclic groups. The regioselectivity is strongly nongeminal with geminal products being very rare and always in low yield. It has been suggested that this reflects the steric demands of the reagent.[113] However, since small groups such as methoxide[110] and the vinyloxy moiety[126–128] all preferentially give nongeminal derivatives, other factors are clearly involved. Electronegativity arguments suggest that the alkyl(aryl)oxy substituents would be electron withdrawing relative to chlorine. Basicity results do indicate that these substituents are poorer electron donors toward the phosphazene[29] than amines. How-

ever, if the alkyl(aryl)oxy groups were electron withdrawing, geminal substitution would be an important pathway (section 3). Therefore it is reasonable to conclude that they are weakly electron donating. This suggestion is consistent with the dissociative pathway observed in the reactions of $N_3P_3(OPh)_5Cl$.[24] The origin of the electron-donating effect is seen in the facility of the phosphazene–phosphazane rearrangement (vida supra) which suggests partial positive charge on the carbon atom α to the oxo unit. The partial positive charge can be ascribed to a hyperconjugative interaction of the phosphorus oxygen and carbon oxygen bonds which results in increased electron release from oxygen to phosphorus. The formation of benzyl chloride from

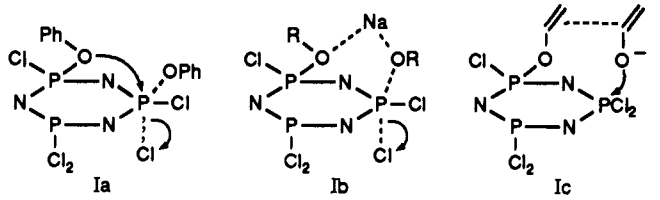


the benzyloxy derivatives[104] is consistent with this proposal. The basic electrostatic effect would then favor nongeminal substitution. Since the alkoxy(aryloxy) groups are poorer electron donors toward the phosphazene than the amino functions,[29] dissociative processes will be less important and consequently fewer geminal derivatives will be obtained.[118] The absence of the conjugate base pathway also decreases the probability of geminal isomer formation.

An interesting situation arises when the question of stereoselectivity is considered. As in the case of secondary amines, the alkoxy and fluoroalkoxy systems exhibit a predominance of trans isomer formation. While this result may be exclusively due to steric effects, the possibility of a "substituent-solvating effect" (shown below) analogous to that found for secondary amines should be considered. Definitive evidence for this proposal must await careful kinetic studies including activation parameters.



A significant change in stereoselectivity is observed when the organic entity affixed to the exocyclic oxygen atom is an unsaturated (aryl or vinyl) unit. In these cases, a definite cis preference is noted. This is a contrasteric effect and even occurs when the organic groups are very sterically demanding such as the steroid derivatives.[105] Three similar models have been proposed to account for these observations. An internal displacement mechanism wherein oxygen lone-pair electron density is donated to d orbitals on an adjacent phosphorus atom has been proposed to be operative in phosphonium ion chemistry.[129] This concept has been applied to the phenoxide system (Ia)[118,121] as well as the highly basic exocyclic nitrogen in the reactions of the methoxide ion with $N_3P_3Cl_5N{=}PPh_3$.[118] An alternative approach involves substituent stabilization of the highly polar methoxide salt (Ib), thus favoring entry at the cis position.[118] Finally, a variant of the reagent stabilization model involves an electrostatic or charge-transfer interaction of the unsaturated moiety attached to the strongly electron withdrawing phosphazene and the incoming electron-rich oxyanion (Ic), again lining up the incoming reagent for cis substitution.[26,128] While each



Ia Ib Ic

of these models is sufficient to rationalize the cis stereoselectivity observed in the aryl- and vinyloxy reactions, if Ia or Ib were operative, the alkoxy derivatives would also be expected to exhibit cis stereoselectivity, particularly since in the butoxide case, the basicity of the oxygen atom would be greater than that in vinyl- and aryloxy derivatives. In the ligand–ligand intraction model, the processes leading to cis alignment are restricted to π-electron-containing systems. The exceptionally strong σ-electron-donating ability of the exocyclic Ph_3PN[29,118] group would allow for the operation of Ia and Ib and extensive competition of $S_N1(P)$ and $S_N2(P)$ mechanisms in the reactions of $N_3P_3Cl_5NPPh_3$.[118] The occurrence of $\equiv P(OMe)NPPh_3$ centers at the stage of bis substitution is consistent with a $S_N1(P)$ process and the fact that 2,2,4,4-$N_3P_3(NPPh_3)(OMe)_3Cl_2$ is the major product at the tris stage suggests a nearly complete changeover to the $S_N1(P)$ route at this stage.[118]

The equal cis/trans ratio observed in the methoxylation reaction for $N_3P_3F_5NPPh_3$ has been nicely rationalized by a sequence involving initial formation of a five-coordinate intermediate with the fluorine atoms located in the energetically favorable axial positions. The departure of F^- from the axial sites gives rise to the cis or trans isomer.[118] The success of this approach indicates than an analysis of bimolecular intermediates and/or transition states in cyclophosphazene substitution reactions based on the elegant work on pseudorotation and site preferences in phosphoranes may be a profitable area for future work. The high phosphorus–fluorine bond strength restricts the occurrence of the $S_N1(P)$ processes as shown by the difficulty in replacing fluorine atom in the $\equiv P(NPPh_3)F$ center.[118] Finally, one is left with the anomaly of geminal disubstitution in $N_3P_3Cl_4(OCH_2CH_2Cl)_2$. It has been suggested that the β-chlorine atom (on the alkoxide) aids in displacement of the geminal chlorine atom[34] but like many of the proposals in this section, the absence of detailed kinetic studies severly hampers the ability to make definitive mechanistic proposals.

Relatively few investigations of thioalcoholysis reactions have been reported and in all cases the regiocontrol is the same with only geminal isomers being observed. The following geminal trimeric derivatives are known: $N_3P_3X_{6-n}(SR)_n$ (X = Cl, R = Me, n = 2,4,6;[130] X = Cl, R = Et, n = 1–6;[131] X = Cl, R = Ph, n = 2,4,6;[132] X = F, R = Et, n = 1–5).[133] In the tetrameric series, 2,2,6,6-$N_4P_4Cl_4(SR)_4$ (R = Et, Pr^n, Bu^n, Ph, p-MeC_6H_4, p-ClC_6H_4)[134] as well as $N_4P_4Cl_{8-n}(SEt)_n$ with two geminal isomers being observed for n = 3–5 are known.[131] The exclusive formation of geminal isomers extends to the rarely investigated 10-membered ring in the formation of $N_5P_5Cl_{10-n}(SR)_n$ (R = Et, Ph; n = 1–4).[135]

Unfortunately, no kinetic studies are available in the thioalcoholysis reactions. The donor ability of a thiolate function to the phosphazene ring, as reflected in basicity

TABLE III. Selected Syntheses of Disubstituted Organocyclotriphosphazenes, $N_3P_3X_4R_2$ (X = F, Cl)

phosphazene	organometallic	products[a]	ref
$N_3P_3F_6$	CH_3Li	g	138
	n-C_4H_9Li	g	139
	t-C_4H_9Li	t	139
	$CH_3CH{=}CHLi$	g	140
	$CH_2{=}C(OC_2H_5)Li$	g	141
	C_6H_5Li	c > t > g	142
	3,5-$C_6H_3D_2Li$	c > t > g	143
	C_6H_5MgBr	g	144
	o-$CH_3C_6H_4Li$	c, t	142
	p-$NMe_2C_6H_4Li$	c ~ t	145
	p-$NMe_2C_6H_4MgBr$	c ~ t ≫ d	145
	p-$CH_2{=}C(CH_3)C_6H_4Li$	c > t > g	19
	m-$CH_2{=}C(CH_3)C_6H_4Li$	c > t > g	19
	$C_6H_5C{\equiv}CLi$	g >>> c, t	146, 147
	$(CH_3)_3SiC{\equiv}CLi$	g ~ c, t	147
	n-$C_4H_9C{\equiv}CLi$	g ~ c, t	148
$N_3P_3Cl_6$	$(CH_3)_3Al$	g > c, t	149
	CH_3Li	an > d > g	150
	t-C_4H_9Li	an	150
	CH_3MgCl/CH_3I	g	152
	n-C_4H_9MgCl/CH_3I	g (CH_3/C_4H_9)	151
	i-C_3H_7MgCl/CH_3I	g (CH_3/C_3H_7)	151
	t-C_4H_9MgCl/CH_3I	g (CH_3/C_4H_9)	151
	C_6H_5MgCl/CH_3I	g (CH_3/C_6H_5)	151
	$(CH_3)_3SiCH_2MgCl$	g	152
	$(CH_3)_3SiOSi(CH_3)_2CH_2MgCl$	g	152
	O-$[Si(CH_3)_2O]_3Si(CH_3)CH_2MgCl$	g	152

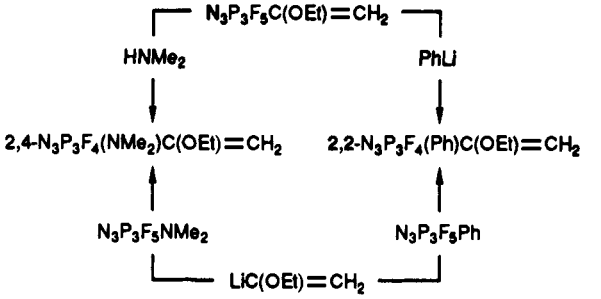
[a] g = geminal; c = cis; t = trans; d = dimer (see text); an = anions (see text).

measurements,[29] is approximately the same as the analogous oxy derivatives. Since the σ-donor ability (as measured by relative electronegativity values) of the thiolate will be greater than that of the oxy derivative, the π-donor ability of the thiolate must be lower. Since the overall electron-releasing ability of the thiolate is approximately the same as the oxy derivative, the $S_N1(P)$ pathway is probably not operative until the last stages of the reaction (vida supra). Consequently, the geminal pathway must result from the low π-donor ability of the exocyclic sulfur atom. In a partially substituted phosphazene, the nitrogen lone-pair electron density will be preferentially shifted to the $\equiv PX_2$ (X = F,Cl) center (section 1.b), thus leaving a more electropositive site and more acceptor orbitals at the $\equiv$ PCl(SR) site which favors the formation of the geminal derivative. If the substituent is a π donor (OR, NR_2), then these orbitals are occupied and substitution occurs at the nongeminal site.

5. Reactions with Main-Group Organometallics

Some of the most interesting and complex substitution processes of cyclophosphazenes are observed in reactions with organometallic reagents.[136,137] A summary of disubstituted products obtained from the reactions of main-group organometallic reagents with cyclotriphosphazenes can be found in Table III. In contrast to other phosphazene derivatives, the organofluorophosphazenes rather than the chloro analogues have, until recently, received most of the attention.[137] While the reactions of $N_3P_3F_6$ with methyl-[138] and n-butyllithium[139] lead to low yields of the disubstituted geminal derivatives, reactions with *tert*-butyllithium give good yields of the *trans*-$N_3P_3F_{6-n}(t\text{-}C_4H_9)_n$ (n = 2,3) derivatives.[139] The later reaction is the only known regio- and stereospecific cyclophosphazene reaction.

SCHEME VII

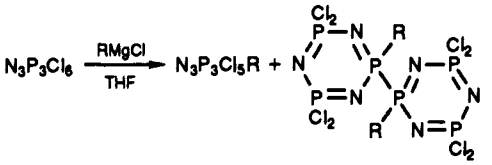


The low yields of the primary alkyl derivatives are a result of formation of α-stabilized carbanions by deprotonation of the alkyl group.[139,153] The geminal pathway is exclusively followed by alkenyllithium reagents.[140,141] Aryllithium and Grignard reagents present a more complicated picture. Phenyllithium yields all three disubstituted isomers with the cis nongeminal species predominating by a significant amount.[142,143] The isomer distribution can be perturbed by varying the substituents on the aryl group. The presence of an o-methyl group blocks the formation of the geminal derivative.[142] The cis/trans ratio is decreased (relative to the phenyl derivative) in the p-(*N*,*N*-dimethylamino)phenyl derivatives[145] or if a α-methethenyl function is in the meta rather than the para position.[19] The nature of the metal is also important as demonstrated by the fact that only the geminal derivative is obtained in the reaction with phenylmagnesium bromide.[144] The question of incoming group or substituent-based regiocontrol is more complex than in the case of primary amines (section 2). The reaction of $N_3P_3F_5C_6H_5$ with 1-propenyllithium gives a geminal product demonstrating incoming group control.[140] However, in reactions involving 1-ethoxyvinyl derivatives (Scheme VII), incoming group control is observed in reactions of $N_3P_3F_5C(OEt){=}CH_2$ where a geminal product obtained in the reaction with phenyllithium and nongeminal products result from the reaction with dimethylamine. Substituent control is demonstrated by the fact that a common reagent, LiC(OEt)=CH_2, follows different pathways in reactions with $N_3P_3F_5NMe_2$ and $N_3P_3F_5Ph$.[141]

Alkynyllithium reagents show a shift from geminal to mixed geminal/nongeminal pathways on going from phenyl-[146,147] to n-butyl-[148] or trimethylsilyl-[147] substituted acetylenes. Reactions of larger fluorocyclophosphazenes have been examined[3] but in only one case has the question of isomeric preference been addressed. The reaction of methyllithium with $N_4P_4F_8$ yields $N_4P_4F_{8-n}Me_n$ [n = 2 (all five isomers), 3 (two geminal isomers), and 4 (one geminal isomer)].[154] The 2,6-geminal isomers are favored over the 2,4-geminal species.

The reactions of $N_3P_3Cl_6$ present an interesting contrast to those of the fluoro analogues. The reactions with trimethylaluminum[150] are straightforward as are those of certain silylmethyl Grignard reagents,[152] leading to $N_3P_3Cl_{6-n}Me_n$ [n = 2 (gem, nongem), 3 (gem), 4 (gem)] and 2,2-$N_3P_3Cl_4R_2$ (Table III), respectively. The reactions of typical Grignards with $N_3P_3Cl_6$ were unclear for a long time. Earlier work showed ring degradation and recyclization as the dominant modes of behavior.[155,156] With the correct choice of solvent, ring substitution can be observed in high yields.[151] At the

first stage of substitution two products may be obtained these being the expected monosubstituted derivative and a phosphorus–phosphorus bonded dimer. The



ratio of $N_3P_3Cl_5R$ to $(N_3P_3Cl_4R)_2$ increases with the size of the alkyl group but the dimer is exclusively formed with phenylmagnesium chloride.[151] Low yields of the analogous dimer are also reported in the reaction of *p*-$NMe_2C_6H_4MgBr$ with $N_3P_3F_6$.[145] If the reaction of $N_3P_3Cl_6$ with RMgCl is run in the presence of methyl iodide a geminal, mixed substituent derivative, 2,2′-$N_3P_3Cl_4(Me)R$ is obtained.[151] The reaction of $N_4P_4Cl_8$ with Grignard reagents provides small amounts of geminal (2,2 and 2,2,6,6) derivatives which are formed, with materials arising from ring contraction, 2,2′-$N_3P_3Cl_4(R)N{=}PR_3$, being the major cyclic products.[157,158]

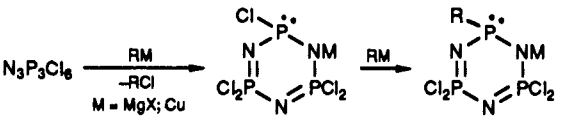
The results of reactions of $N_3P_3Cl_6$ with Grignard reagents in the presence of a copper(I) complex, $[(n\text{-}C_4H_9)_3PCuI]_4$, which, formally, should be considered with transition-metal organometallic reagents (section 7), shed considerable light on the results quoted above.[159–163] The product initially formed in these reactions is a phosphazene anion, $[N_3P_3Cl_4R{\cdot}Cu]^-MgCl^+$,[159] which can be quenched with alcohols to give the geminal hydridophosphazene, 2,2′-$N_3P_3Cl_4(R)H$, or with alkyl halides (R′X) to give 2,2′-$N_3P_3Cl_4(R')R$.[161–163] The reactions of $N_3P_3Cl_6$ with alkyllithium reagents have been shown to go through similar anionic intermediates[150] while the corresponding reaction with $N_4P_4Cl_8$ gives phosphorus–phosphorus bridge dimers of the tetramer.[164]

There have not been any serious kinetic studies of the reactions of organolithium or Grignard reagents with cyclophosphazenes. This is not particularly surprising since the mechanisms of the analogous reactions with simple organic substrates are still in the process of being sorted out.[165] Consequently, all the phosphazene mechanistic models are based on product studies. An examination of Table III shows a strong preference for geminal substitution. A reasonable model for this behavior is identical with the one employed for geminal thiolato derivatives (section 4). In fact, this model was first proposed to account for the formation of geminal organophosphazene derivatives.[140,141] If the substituent in a partially substituted phosphazene is not a π donor to phosphorus, then the transfer of endocyclic lone pair electron density to the ${=}PX_2$ (X = F, Cl) center (section 1.b) will leave the ${=}P(R)X$ center more susceptible to attack. The origins of this susceptibility can be orbital or electrostatically based. Alkyl groups are not π donors, and it has been shown that with alkenyl and aryl derivatives substituent π donation is poor to nonexistant (section 1.b). It has also been suggested that the coordination of the lithium ion to an endocyclic atom is an important factor in the geminal directing effect (section 7). On the other hand, strong π donors such as the dimethylamino groups in $N_3P_3F_5NMe_2$ will favor nongeminal substitution (section 2), thus allowing for the different regioselectivity shown in a comparison of the reactions of $N_3P_3F_5R$ (R = Ph, NMe_2).

If the preferred pathway to organofluorophosphazenes leads to the geminal derivative(s), then the occurrence of other isomers suggests the operation of additional factors. The most obvious of these is steric effects. As the steric demands of the substituent, or incoming group increases, the nongeminal species will be favored over the geminal isomer. Within the nongeminal series, steric considerations favor the trans isomer. Experimental verification of these suggestions is found in the regio- and stereospecific formation of *tert*-butylfluorophosphazenes,[139] the nongeminal preference in reactions of aryllithium reagents[19,142,143,145] and the increase in the trans to cis isomer ratio with increasing steric demands of the aryl ligand.[19] In the aryl derivatives, the steric effect is, in part, associated with the incoming reagent as shown by the fact that phenylmagnesium bromide gives a geminal derivative while phenyllithium favors nongeminal products.[144] Under the conditions employed in these reactions, the Grignard reagent is monomeric[166] and phenyllithium is a dimer[167] and the more sterically demanding dimer favors nongeminal attack. The changes from geminal to mixed geminal nongeminal isomers on going from (phenyllithio)- to (alkyl(or silyl)lithio)acetylenes can also be viewed as a manifestation of steric demands. The structure of 2,2-$N_3P_3F_4(C{\equiv}CPh)_2$ shows the two organic substituents with the aryl rings facing each other[168] whereas in the alkyl and silyl cases the conformation and steric demands of the alkyne substitutions would require more space.

Since steric demands favor the trans nongeminal isomer, formation of the cis isomer as the major component in aryl lithium reactions indicates the operation of an additional selectivity factor. Similar isomer distributions were noted in the reactions of $N_3P_3Cl_6$ with aryloxide anions (section 4), and it is reasonable to suggest a common cause for the observed stereoselectivity. The aryl substituent is subjected to a significant electron-withdrawing influence by the phosphazene[19,20] while the incoming reagent is electron rich. An electrostatic, or charge transfer, interaction between the ring substituent and the incoming reagent results in introduction of the second aryl group cis to the first aryl group.[19] The decrease in cis stereoselectivity in the *p*-(*N*,*N*′-dimethylamino) derivatives can be attributed to the strong electron-donor capability of the amine function which reduces the electropositive nature of the aryl substituent and consequently reduces the magnitude of the electrostatic interaction.[19,145]

Allcock and co-workers have shown that the majority of the chlorophosphazene reactions go via a different pathway.[159–162] In these reactions a halogen–metal exchange process occurs, leading to a low-coordinate phosphazene intermediate, with the metal ion coordinated to a endocyclic nitrogen atom.[159,169] The recognition of the formation of the $N_3P_3Cl_4R^-$ species has allowed for the design of a variety of useful syntheses[137,160–163,170] and rationalization of the products formed in the chlorophosphazene reactions described in Table III. Once the low-coordinate species is formed it can



be trapped in a variety of ways. Thus, in the case of the organocopper or organolithium reactions, addition of an alcohol leads to the phosphazene hydride. The formation of $N_3P_3Cl_5R$ can also occur and upon a subsequent Grignard reaction the predicted (vida supra) geminal disubstituted derivative is obtained. Trapping of the $N_3P_3Cl_4R^-$ anion with methyl iodide (Table III) provides 2,2'-$N_3P_3Cl_4(Me)R$ and coupling with $N_3P_3Cl_5R$ provides the phosphorus–phosphorus-bridged dimer. The observation of an analogous aryl-substituted dimer in the fluoro series, $[N_3P_3F_5C_6H_4NMe_2]_2$, indicates the occurrence of a halogen–metal exchange.[145] The extremely low yield is consistent with the expectation (due to high phosphorus–fluorine bond energy) that halogen–metal exchange is not as significant in reactions of $N_3P_3F_6$.

6. The Friedel–Crafts Reaction

The Friedel–Crafts reaction presents an alternative route for the introduction of an aryl group to a cyclophosphazene.[2,3] In the case of $N_3P_3Cl_6$ only the geminally substituted phenyl derivatives are formed.[171] The

$$N_3P_3Cl_6 \xrightarrow[AlCl_3,\ NEt_3]{PhH} N_3P_3Cl_{6-n}Ph_n \quad (n = 2,4,6)$$

corresponding reaction of $N_4P_4Cl_8$ leads only to low yields of products primarily resulting from ring contraction.[172] Phenylation of certain partially substituted chlorophosphazenes is also successful, e.g. the series $N_3P_3Ph_nCl_{6-2n}(NMe_2)_n$ (n = 1–3) is available from the dimethylamino precursors.[173,174] The reaction in this case occurs at the $\equiv P(NMe_2)Cl$ rather than the $\equiv PCl_2$ site. Similarly, $\equiv P(R)Cl$ (R = NC_5H_{10},[174,175] NHMe,[174] N=PPh_3[176]) centers can be phenylated. In branched-chain primary-amino and highly dimethylaminated derivatives, alternate routes involving amine degradation occur.[174]

In the fluorophosphazene series, the parent trimer does not undergo the Friedel–Crafts reaction but partially substituted derivatives can be phenylated at the $\equiv P(R)F$ site. The reactions of the aryl derivatives, $N_3P_3F_5C_6H_4$-p-X (X = H,[177] NMe_2,[145] Cl, F, OMe, Me[178]) and 2,4-$N_3P_3F_4(C_6H_4$-p-$X)_2$ (X = H,[177] NMe_2[145]), have been studied in detail. Nonarylated species, $N_3P_3F_5R$ (R = NMe_2, n-C_4H_9, t-C_4H_9) also undergo phenylation exclusively at the $\equiv P(R)F$ position.[179]

In spite of the synthetic utility of this reaction, little is known about the mechanism. The first step of the reaction is often assumed to be the formation of a phosphonium ion arising from halide abstraction by the Lewis acid:

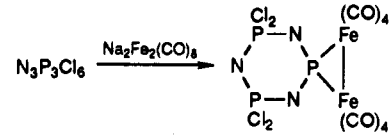
$$\equiv PRCl + AlCl_3 \rightleftharpoons \equiv PR^+AlCl_4^- \xrightarrow{C_6H_6} \equiv PRPh$$

Definitive evidence on this point has yet to become available. The reactions of Lewis acids with cyclophosphazenes can lead to halide abstraction (phosphonium ion formation)[98] or endocyclic coordination[95-97] (section 3). In either case, the formal positive charge at phosphorus increases. Once the phosphonium ion (or complex) forms, attack on the solvent (benzene) could lead to a cationic σ complex and deprotonation to the observed arylphosphazene. The assumption is made that the facility of the Friedel–Crafts reaction at a $\equiv PXR$ (R = aryl, amino; X = F, Cl) center is due to stabilization of the positive charge (or developing positive charge) on the phosphorus atom by the electron-donating substituent, R. Manifestations of a developing positive charge in the reactant for substituted phosphazenes are seen in the long phosphorus–chlorine bonds in $\equiv P(NMe_2)Cl$ center[180-183] and an increased ionic character as demonstrated by NQR studies.[184] The fact that the alkylphosphazenes undergo the phenylation reaction unambiguously demonstrates that π donation from the exocyclic function is not a necessary prerequisite for this reaction to be effective.[179] The significantly higher yield in the reaction of *tert*-butyl vs the *n*-butyl phosphazene[179] suggests the operation of a mechanism wherein the phosphorus atom undergoing substitution goes to a lower coordinate intermediate (or transition state). This process would be more favorable for the *tert*-butyl derivative, where the maximum relief of steric strain can be obtained. A reasonable model for the Friedel–Crafts phenylation reaction of substituted phosphazenes is one in which the substituted phosphorus atom goes through a three-coordinate phosphorus(V) intermediate which is stabilized by the σ-electron-releasing nature of the substituent.[179] It is possible that, in the phenyl and dialkylamino systems, the σ-electron-releasing effect may be supplemented by a π effect, but conclusive evidence of this has yet to be presented.

7. Reactions with Transition-Metal Organometallics

In recent years the Allcock group has reported an exciting array of phosphazenes with organometallic substituents.[4,137] In this review, only the question of regio- and stereoselectivity followed in the organometallic reactions is of interest. A more comprehensive discussion (reactions, structure, properties) of these systems can be found elsewhere.[137] There are two general types of organometallic reagents which have been examined, transition-metal anions and lithiated metallocenes.

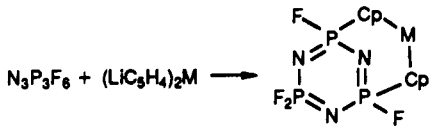
Simple metal carbonyl anions will react with chlorophosphazenes. Specifically, the major product derived from disodium octacarbonyldiferrate and $N_3P_3Cl_6$ is a geminal spirocyclic material[185] which can serve as an entry point to metal carbonyl phosphazene cluster chemistry.[185,186] Similar reactions have been reported



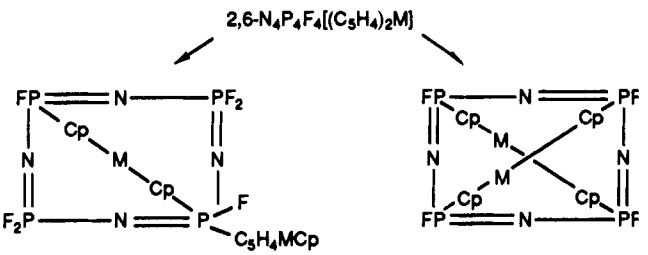
for $N_4P_4Cl_8$.[185] The reactivity of η^5-cyclopentadienyl metal carbonyl anion, $CpM(CO)_2^-$ (Cp = η^5-C_5H_5; M = Fe, Ru), toward cyclophosphazenes has been explored.[187,188] A geminal derivative, 2,2-$N_3P_3F_4$ [$FeCp(CO)_2]_2$, has been prepared.[187] Interestingly, the mixed ruthenium/iron analogue can be obtained from the reaction $N_3P_3F_5RuCp(CO)_2$ with $CpFe(CO)_2^-$ but not by the reaction in which the roles of the metals are exchanged.[188] The reaction of $N_3P_3Cl_6$ with $CpM(CO)_3^-$ (M = Cr, Mo, W) anions yields the monosubstituted product in the case of M = Cr but not with M = W, Mo

where metal–halogen exchange occurs giving 2,2′-$N_3P_3Cl_4(\eta^1\text{-}C_5H_5)M(CO)_3Cp$.[189] The intermediate phosphazene anion can be trapped with methyl iodide to give 2,2′-$N_3P_3Cl_4(Me)W(CO)_3Cp$.[189]

The reactions of lithiometallocenes resemble the main-group organolithium reactions of cyclophosphazenes (section 5) in that reactions of the fluorophosphazenes proceed by direct substitution while the corresponding chlorophosphazene reactions often follow metal–halogen exchange routes. The interactions of lithioferrocences with $(NPF_2)_{3,4}$ lead to the nongeminal 2,4-$N_3P_{34}[C_5H_4FeCp]_2$ and 2,6-$N_4P_4F_6[C_5H_4FeCp]_2$ derivatives, respectively.[190] In the trimeric system, the trans isomer prodominates. Dilithiometallocene, $(LiC_5H_4)_2M$ (M = Fe,Ru), gives rise to unique, transannular, nongeminal derivatives. Thus, the reaction with $N_3P_3F_6$ gives rise to 2,4-$N_3P_3F_4[(C_5H_4)_2M]$ and a small amount of the bridging product, $N_3P_3F_5C_5H_4MC_5H_4P_3N_3F_5$.[190] A similar transannular bridge is obtained in the reaction of bis(lithiobenzene)chromium with $N_3P_3F_6$.[191] The reaction of $N_3P_3F_5Ph$ with $(LiC_5H_4)_2Fe$ occurs at the nongeminal sites, leading to 2,4,6-$N_3P_3F_3(Ph)[(C_5H_4)_2Fe]$, while the reaction of methyllithium with $N_3P_3F_4[(C_5H_4)_2Fe]$ occurs at a geminal site, providing 2,2′,4-$N_3P_3F_3(Me)$-$[(C_5H_4)_2Fe]$.[192] Transannular derivatives are also ob-



tained in the reactions of $N_4P_4F_8$. Bridging of both 2,4 and 2,6 positions can occur as indicated by the formation of 2,4-$N_4P_4F_6[(C_5H_4)_2M]$ and 2,6-$N_4P_4F_6$-$[(C_5H_4)_2M]$.[190] The 2,6-ruthenium derivative can react with another dithiometallocene to give a doubly bridged derivative.[192] The 2,6 derivative can also undergo reactions in which only one of the remaining $\equiv PF_2$ centers has undergone reaction.[192]



The reactions of $N_3P_3Cl_6$ with LiC_5H_4MCp (M = Fe, Ru) are reminiscent of the analogous reactions with traditional Grignard reagents (section 5) giving both the monosubstituted derivatives and the phosphorus–phosphorus-bridged dimers.[190,193] The corresponding reactions with dilithiometallocenes show both substitution and metal–halogen exchange behavior involving the same substrate thus providing $N_3P_3Cl_5$-$(C_5H_4MC_5H_4Cl)$. The addition of tetramethylethylene diamine to the reaction mixture gives rise to a variety of phosphorus–phosphorus-bridged dimers.[193] Ring contraction occurs in the reaction of $N_4P_4Cl_8$ with LiC_5H_4FeCp.[194]

The observed pathways in the reactions of transition-metal organometallic reagents with cyclophosphazenes suggest that the factors exerting regiocontrol are similar to those discussed for reactions of main-group organometallic reagents. In direct substitution reaction, transition-metal anions follow a geminal pathway[185,187] although metal–halogen exchange can also occur with certain nucleophiles.[189] The observation of a geminal substitution pathway suggests that the metal is σ-electron-releasing with respect to phosphorus. This is consistent with the low electronegativity of the metals and with structural data showing significant perturbations of the phosphorus–nitrogen ring.[187,188] Definitive information of the presence or absence of metal to phosphorus π interactions is not available at this stage. The monolithiometallocene reactions of the fluorophosphazenes are reminiscent of the corresponding aryllithium reactions. It is reasonable to assume that the steric factors associated with both the substituent and the incoming reagent are sufficient to overcome the tendency to geminal substitution. It has been proposed that geminal substitution is promoted by coordination of a lithium ion to an endocyclic nitrogen atom adjacent to the substituted phosphorus atom. Evidence for metal–endocyclic nitrogen coordination is available and this process will further decrease endocyclic lone-pair electron donation to the $\equiv P(R)F$ center,[90,192] hence enhancing the basic geminal substitution mechanism previously discussed (section 5).[19,141] A significant difference in stereoselectivity between aryllithium and lithiometallocene reactions is shown by the predominance of the trans isomer of $N_3P_3F_4(C_5H_4MCp)_2$.[190] The charge-transfer interaction which was involved to rationalize the contrasteric, preferential formation of the cis diaryl species requires an alignment, or reasonable close approach, of the incoming and substituent groups.[19] This geometric requirement can be met in the aryl derivatives but not with the more sterically demanding metallocenes. Further evidence for the absence of an incoming and substituent group interaction is the formation of the formation of the 2,6-dimetallocene derivative of the tetramer.[190] In the vinyloxy derivatives (section 4), the associative interaction leads to the 2,4-disubstituted isomers as the major product.[128] Thus, the stereoselectivity in the lithiometallocene reactions is controlled by steric effects and in that regard resembles the behavior observed in reactions of *tert*-butyllithium.[139] The dilithiometallocenes and bis(dilithiobenzene)chromium reagents also give rise to nongeminal products but the transanular bridge necessitates a cis configuration. The steric effect of the metallocene is again noted in the fact that the nongeminal (4,6) positions undergo substitution in the reaction $N_3P_3F_5Ph$ while the electronically more favorable geminal site undergoes substitution in the reaction of $N_3P_3F_4[(C_5H_4)_2Fe]$ with the less sterically demanding methyllithium.[192] The reactions of chlorophosphazenes with lithiometallocenes show a similar balance between substitution and halogen–metal exchange as observed in the main-group organometallic reactions.[193,194]

8. Summary and Conclusions

The major factors responsible for regio- and stereoselectivity in substitution reactions of cyclophosphazenes are charge distribution and steric and mechanistic effects. These factors have been discussed individually and in depth in the previous, relevant sections, and the regio- and stereochemical manifestations of these effects are summarized below. The first,

and in many ways the most important, consideration is the nature of the interaction of the exocyclic group with the phosphazene. If the group is electron withdrawing with respect to the remaining halogen atoms, as in the case of substitution by the fluoride ion (section 3), the substituted phosphorus atom will carry a significant positive charge and geminal substitution will occur. The vast majority of substituents are electron donating with respect to the phosphazene and can be further subdivided into two groups. Those substituents which are electron donating primarily through σ bonds such as organic moieties (sections 5 and 7) and thiolates (section 4) will direct endocyclic lone pairs toward the nongeminal centers (section 1.c) and hence also follow a geminal path. Substituents which act as π donors through lone-pair delocalization such as amines (section 2) or by a hyperconjugative electron release such as oxyanions (section 4) will direct incoming nucleophiles to nongeminal sites.

Superimposed on the charge distributions effects resulting from the basic electronic structure of the phosphazene are steric effects of the ring substituents and/or incoming reagents. The steric demands will promote trans nongeminal substitution. Steric effects can be sufficient to overcome the geminal directing influence of σ-donating substituents as noted with large organic or organometallic substituents. Steric effects work in conjunction with charge distribution in species derived from oxygen and nitrogen bases leading the trans nongeminal species being the most commonly obtained products.

Significant perturbations of these expectations can arise when mechanistic complications or alternate pathways arise. The trans stereoselectivity can be reversed in systems where π-electron-rich species such as aryl, aryloxy, and vinyloxy moieties are involved. In these cases, interactions between the incoming and substituent groups result in an increase or even predominance of the cis isomer. The most complex yet best understood mechanistic complexities occur in the chemistry of aminophosphazenes. For dialkylamino derivatives, mechanistic effects work in conjunction with steric expectations producing trans stereoselectivity (section 2). In derivatives of primary amines, a proton abstraction process leading to a three-coordinate phosphorus center occurs. The coordinatively unsaturated site is trapped by an incoming nucleophile, giving rise to a geminal product. The balance between geminal (dissociative) and nongeminal (associative) pathways in three systems is controlled by the steric demands of the incoming reagent, i.e. the larger the nucleophile, the more difficult it is to form an associative transition state so the dissociative process becomes favorable. Dissociative routes, in general, lead to geminal products and may be expected in certain other types of reactions. The first of these are cases where several π-electron-donating substituents are present on the phosphazene, e.g. highly aminated derivatives. In these cases, some phosphorus–halogen bond weakening is present in the ground state and hence the dissociative process may be favored if the rate of the bimolecular process is slow. Reactions in which a halide abstraction occurs such as the Friedel–Crafts process (section 6) and reactions of chlorophosphazenes with organometallic reagents (sections 5 and 7) which go through a three-coordinate intermediate follow a geminal path.

The generalizations provided above give a general framework for rationalizing and predicting the regio- and stereochemical course in reactions of cyclophosphazenes. The fundamental mechanistic data (rates and activation parameters) are only widely available for aminophosphazenes and consequently there is a significant opportunity in many of these systems for serious mechanistic analysis in order to verify (or disprove) the models presented in this review.

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