The Effect of Methyl Groups on Nucleophilic Substitution Reactions of Chlorocyclotriphosphazenes

by

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(ABSTRACT)

The reactions of methyl-substituted chlorocyclotriphosphazenes with aryl Grignard reagents and with bifunctional amines, aminoalcohols, and alkoxides were investigated.

The characterization data for the compounds formed in the reactions of monomethylpentachlorocyclotriphosphazene and the Grignard reagents were found to be informative with respect to the extent and nature of the interaction between the phosphazene ring and its exocyclic substituents.

This interaction was found to be responsible for significant effects on the reactions of the phosphazene ring with nucleophiles. The reactions of the bifunctional nucleophiles were found to be useful probes of the reactivity of the phosphazene ring. Specifically, a single methyl group is found to activate the chlorine on the same phosphorus atom, while a pair of geminally substituted methyl groups is found to deactivate the chlorine atoms on a different phosphorus atom. The results allow a new interpretation of the substitution patterns of various nucleophiles on chlorocyclotriphosphazenes.

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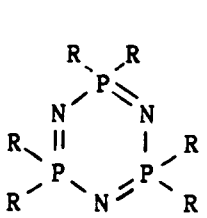
TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

INTRODUCTION

The cyclo or polyphosphazenes, generally known as phosphonitrilic compounds in the earlier literature references, are probably the best known and most intensively studied phosphorus-nitrogen compounds. They are valence unsaturated cyclic or open-chain molecules of alternating P and N atoms, with two substituents on each P and no substituents on N. Typical structures are the cyclic trimer **1**, the cyclic tetramer **2**, and the high polymer **3** shown in Figure 1. The substituent R can be halogen, pseudohalogen, amino, azido, or a wide variety of organic groups such as alkoxy, aryloxy, alkyl- or arylamino, alkyl- or arylthio, alkyl, or aryl.



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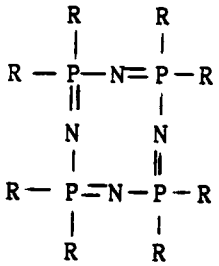

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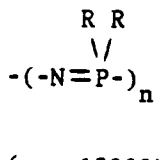

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Figure 1. Examples of phosphazenes

Mixed substitution is also possible. Throughout this dissertation these substituents will sometimes be referred to as ligands. Although this usage of the term is not strictly correct, it is convenient and has found general acceptence in the literature. The cyclic dimer has only recently

been isolated and its formation has been cited as the first evidence of the existence of the monomer[1], :P=N:, which has so far eluded identification. The similarity of the structure of the monomer to that of the cyano compounds or nitriles gave rise to the phosphonitrilic system of nomenclature.

The earliest phosphazenes to be synthesized were the chloro derivatives, $(NPCl_2)_n$, which were formed in the reaction of NH_3 and PCl_5. This reaction was first studied by Liebig and Wohler[2] and by Rose[3] in 1834. The principle reaction product was phospham, $NPNH)_n$, but Liebig and Wohler isolated a small amount of a white crystalline solid that we now know to have been $(NPCl_2)_3$. By 1850 Gerhardt[4] and Laurent[5] showed that the empirical formula was $NPCl_2$. Vapor density measurements were used in the 1860's by Gladstone and Holmes[6] and later by Wichelhaus[7] to show that the molecular formula was $(NPCl_2)_3$. By the end of the ninteenth century pioneering work had been done on the substitution, hydrolysis, and polymerization reactions of the phosphazenes.

Perhaps the most important of this early work was performed by Stokes[8] who, among other things, described the thermal polymerization of phosphazenes to inorganic rubber and suggsted the cyclic structure of the trimer $(NPCl_2)_3$. Schenk and Romer[9] developed an improved synthesis of chlorophosphazenes in 1924. This method, which utilizes NH_4Cl rather than NH_3, with the reaction taking place in refluxing chlorinated hydrocarbon solvents, remains the basis of the commercial production of these materials to this day. The use of dialkyl-trichlorophosphoranes, R_2PCl_3, in

the place of PCl_5, led to the direct synthesis of several organophosphazenes[10] in the 1950's. By 1960 bromophosphazenes[12] had been prepared in an analogous manner to the chloroderivatives, and fluorophosphazenes[12], which cannot be synthesized directly, had been prepared by treatment of bromo- and chlorophosphazenes with inorganic fluorinating agents.

Since the 1950's there has been an almost explosive increase in research on the substitution reactions of phosphazenes, much of it spurred by interest in the inorganic polymer field and by updated analytical techniques. Many phosphazene-based high polymers have been prepared and some of these have found industrial use. The production of these polymers involves first the thermal polymerization of $(NPCl_2)_3$ to form poly(dichlorophosphazene), $(NPCl_2)_n$. Although high molecular weight polymers are obtained by this method, the Cl substituents render the material hydrolytically and thermally unstable. These chlorine atoms are replaceable by nucleophilic substitution reactions, just as the chlorine atoms of the smaller cyclic molecules are. Many of these substituted polyphosphazenes have improved properties compared to the chloropolymer. Currently alkoxy-substituted, and to a lesser extent, amino-substituted polyphosphazenes, have found the greatest commercial market. These polymers are characterized by flame retardance, elasticity at extreme temperatures, and high thermal stability and oil resistance. The increased stability and other desirable properties expected of alkyl-substituted polyphosphazenes has led to current interest in developing methods of synthesizing them. Some of the cyclic molecules have found use as in-

secticides and herbicides and others have been shown to have anti-tumor activity.

From a more academic point of view, the bonding involved in phosphazenes has aroused considerable discussion over the years, and the mechanisms of even simple reactions are unknown. The phosphazenes are typical of many inorganic ring or chain compounds consisting of alternating first row and second row elements, and similarities of bonding and reactivity are bound to exist. Although offering much promise for the future, a great deal of fundamental work still needs to be done in the phosphazene field. The morass of seemingly disparate facts derived from studies of nucleophilic substitution pathways by various alkoxides and amines is ample evidence that the system is not fully understood in terms of its structure, bonding, and reactivity.

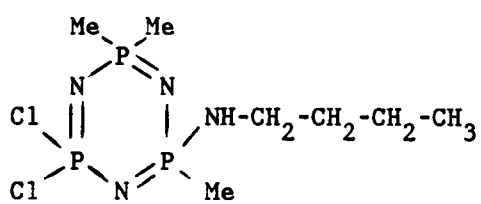
NOMENCLATURE

Historically, several different systems of nomenclature have been employed in the literature. The oldest of these is the phosphonitrilic system. This system is based upon the as yet unisolated, triply bonded compound :P≡N:, isoelectronic with N2, and formally considered an analogue of the triply bonded nitriles, -C≡N:. In this system the hexachlorinated trimer, $(NPCl_2)_3$, is known as phosphonitrilic chloride trimer, or triphosphonitrilic chloride, or chlorophosphonitrilic trimer. The obvious problem with this system is its lack of adaptability in cases of varied substitution.

Another possibility is the use of the standard IUPAC system for heterocyclic compounds. Thus the compound $(NPCl_2)_3$ becomes 2,2,4,4,6,6-hexachloro - 2,2,4,4,6,6 - hexahydro - 1,3,5,2,4,6 - triazatriphosphorine and $(NPPh_2)_4$ becomes 2,2,4,4,6,6,8,8- octaphenyl- 2,2,4,4,6,6,8,8 - octahydro 1,3,5,7,2,4,6,8-tetrazatetraphosphorine. This system has been employed by Chemical Abstracts and some organic oriented journals but is considered unwieldy and has not gained general acceptance. A similar system which has been more commonly employed is based upon a hypothetical substituted cyclohexane. Thus the geminally substituted isomer of $N_3P_3Cl_4Ph_2$ would be named 1,1-diphenyl-3,3,5,5-tetrachloro-1,3,5-triphospha-2,4,6-triazacyclohexane. This system has also been used with the N atoms numbered 1, 3, and 5, and the P atoms numbered 2, 4, and 6. This system allows flexibility in naming molecules containing varied substituents, but is

still considered unwieldy. The most commonly accepted and most often used system is the phosphazene system. The name refers to the phosphorus (phospha) nitrogen (aza) double bond (ene). Thus the same molecule would be called 1,1-diphenyl-3,3,5,5-tetrachlorocyclotriphosphazene with the prefix cyclotri- referring to a ring of three PN units or six atoms overall. Even with this system some workers number the P atoms 1, 3, and 5, while others number the P atoms 2, 4, and 6. Either of these systems allows relatively simple and unambiguous naming of multisubstituted molecules.

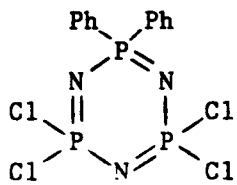
It would seem that the most reasonable system of nomenclature is the phosphazene system. Since the substituents are on P and not N, assigning the P atoms the lowest possible numbers, i.e. 1, 3, and 5 would seem the most consistent with other currently accepted naming systems and will be used exclusively throughout this dissertation. For example then, molecule **4** would be called 1,1,3 trimethyl 3-n butylamino-5,5-dichlorocyclotriphosphazene.



4

Another point regarding nomenclature which should be made explicit concerns the relative positions of substituents on a phosphazene ring. Three isomers of diphenyltetrachlorocyclotriphosphazene exist and are shown in

Figure 2. When both phenyls are substituted on the same P atom as in structure **5** they are referred to as being geminal, or gem, to one another. while phenyls on different P atoms, as in **6** and **7** are referred to as being nongem substituted. Since the P atoms are roughly tetrahedral in geometry the substituents will lie above and below the plane of the ring. This gives rise to cis and trans isomers as shown.



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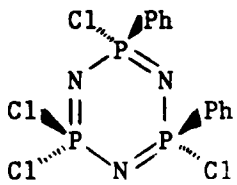

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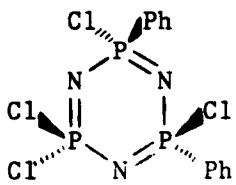

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Figure 2. Isomers of diphenyltetrachlorocyclotriphosphazene

BONDING IN PHOSPHAZENES:

The characteristic bonding present in all phosphazenes consists of a tetracoordinate phosphorus atom bonded to a dicoordinate nitrogen atom. The formation of the σ system leaves one electron on P and three electrons on N left to be accounted for, as shown below for the cyclic trimer.

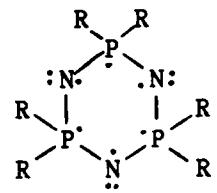


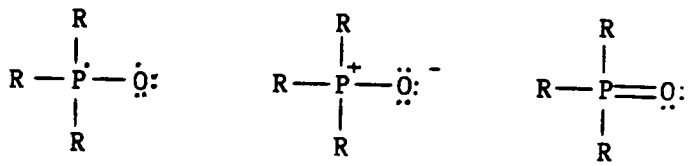
Figure 3. Sigma system of cyclotriphosphazenes

The distribution of these electrons determines the chemistry of the phosphazenes. For a bonding model to be realistic it must explain the physical and chemical properties of these compounds. The various bonding theories will be discussed below. Pertinent data will be introduced here but discussed in more detail in later sections.

First of all it will be seen that the nitrogen atoms of phosphazenes can function as basic or nucleophilic sites. Thus two of the electrons on N are probably in a nonbonding orbital. A reasonable assignment would be an sp2 hybridized nitrogen, with the nonbonding pair in an in-plane sp2 orbital as shown. The third electron would be assigned to an unhybridized p orbital perpendicular to the plane in the same manner as in carbon-ni-

trogen cyclic molecules like pyridine. While the normal P-N-P angle in cyclotriphosphazenes of 120° fits the proposed sp2 hybridization, in larger rings larger angles are observed. This would correspond to an increase in p character of the nonbonding pair, and greater sp character in the bonds to phosphorus with one electron still in the perpendicular p orbital. The variety of angles is evidence of the ease of rehybridization at nitrogen in the phosphazene system.

The orbital description of bonding at phosphorus has drawn considerable discussion. Comparisons to other teracoordinated phosphorus compounds like the phosphine oxides are useful. Ignoring interaction with R it is possible to draw three resonance structure **8**, **9**, and **10**.



8 **9** **10**

Figure 4. Resonance structures of the phosphine oxides

Of the three, form **8** is undoubtedly an extremely minor contributor to the overall resonance hybrid. There is no evidence of paramagnetism in these compounds and the expectation of a diradical form is contrary to the electronegativities of the two atoms. Structure **9** is reasonable in electronegativity terms and is also attractive due to its similarity to the structure of the isoelectronic amine oxides. It is the importance of structure **10**, which includes the formation of five bonds, supposedly by the use of energetically accesible 3d orbitals by phosphorus, which

has been the most debated. The best argument in favor of the use of d orbitals involves the length of the P-O bond. This bond is found to be shorter than the normal P-O single bond length. This shortening could be caused either by the existence of a d-p pi bond between P and O, or by coulombic attraction of the two atoms due to the charge separation. Experimentally it is found that the presence of electron withdrawing groups on phosphorus has the effect of shortening the P-O bond and that electron donating groups on P lengthen it. The pi bonding argument states that strongly electron withdrawing groups cause a contraction or lowering of energy of the unoccupied 3d orbital, allowing a more favorable overlap with the smaller 2p orbital on O in a situation analogous to back-bonding in transition metal complexes. On the other hand, if the P-O bond were shortened by coulombic attractions of the charged atoms, it would be expected that the greater the induced charge separation the shorter the bond would be. The +P-O- dipole is due to electron drift away from P and towards O. Electron withdrawing groups on P would offset this drift and lead to less charge separation and a longer bond, and not a shorter one as observed experimentally.

In spite of the bond length arguments, it is possible to argue against the use of d orbitals in phosphine oxides and related compounds. It has been suggested that for second row and later elements that any of the higher orbitals may be lowered in energy and lead to situations which are impossible to describe in terms of n orbitals for n bonds. Nevertheless it remains tempting to consider the 3d orbitals as representative of all

the higher orbitals and talk with respect to their degree of involvement in various physical and chemical properties.

With regard to the phosphazenes, it is possible to draw resonance structures analogous to those of the phosphine oxides. As with the phosphine oxides we can

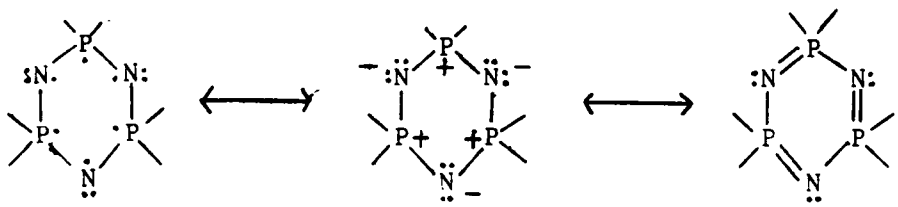


Figure 5. Resonance structures of the cyclotriphosphazene skeleton

disregard the diradical structure **11**. The zwitterionic structure **12** was one of the first structures suggested in an attempt to explain the bonding in phosphazenes.[13] However it fails in at least two respects. First of all the highly polar skeleton implies a high reactivity towards ionic reagents, which is not found experimentally. The second problem with this model involves the assignment of the two nonbonding pairs of electrons to nitrogen. If these pairs were to strongly repel one another the exocyclic angle would be contracted to the extent that it would be energetically untenable.[14] Nevertheless the zwitterion model represents one extreme of the bonding possible in the phosphazenes.

The other bonding extreme is the fully pi-bonded represented by resonance structure **13**. Two different molecular orbital descriptions of the use

of 3d orbitals have been published. The first of these was by Craig and Paddock whose molecular orbital treatment suggested a novel type of aromaticity in the phosphazenes and other alternating first and second row heterocycles.[15,16,17] These authors assumed the use of one of the 3d orbitals of phosphorus to overlap with the 2p orbitals of both adjacent nitrogens. In Figure 6 this overlap is illustrated as seen from above, with only the top lobes of the dyz and pz orbitals shown. This arrangement allows

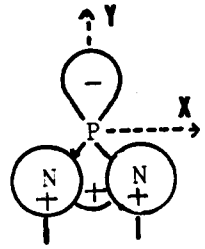


Figure 6. The aromatic model

constructive overlap of the positive and negative lobes of the p orbitals with those of the d orbital. The predicted pi system is fully delocalized, with no nodes in the wave function of the lowest energy molecular orbital, as in the organic aromatic systems. Calculations using this system predicted that the aromatic stability would exist with any even number of electrons, not just the 4n+2 necessary for organic aromaticity. This would explain the similar properties of different sized phosphazene rings, for instance the cyclic trimer and tetramer.

These results were criticized by Dewar, Lucken, and Whitehead[18] however. These workers objected to the use of only the dyz orbital by P with the

exclusion of the symmetrically similar dxz orbital, as illustrated in Figure 7.

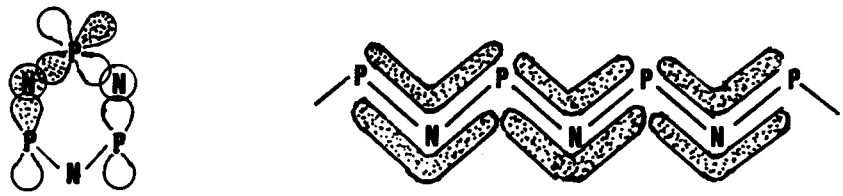


Figure 7. The island model

The interaction of this orbital with the p orbitals of the adjacent nitrogens leads to destructive overlap in one of the two bonds suggesting a node in the wave equation and thus not a fully delocalized system. Ignoring the the argument that the dyz would be lowered in energy to a greater extent than the dxz due to its closer proximity to the electronegative nitrogen atoms, Dewar et. al. proposed a model using both of these d orbitals as shown in Figure 7. This leads to a node at each P atom and constructive overlap over each P-N-P unit. As illustrated, this suggests a bonding system consisting of three-atom islands of delocalization. The island theory is generally accepted today as being more in agreement with experimental data than the fully delocalized model.

The bonding situation is undoubtedly different for all different phosphazenes. Of interest in this dissertation is the degree to which the nature of the bonding controls the chemistry of the system.

STRUCTURE OF PHOSPHAZENES

Although it was known by the 1860's that $(NPCl_2)_3$ was a cyclic molecule little else was known of the details of its structure. In the ensuing years much work was aimed at the detailed structural elucidation of a great number of phosphazenes, along with discussion of the significance of ther structural data as related to the various bonding theories. The most direct method of structural determination comes from X-ray diffraction data and many substituted phosphazenes have been subjected to this technique. Infrared data also give information concerning the P-N bond, and basicity data and complexation results reveal the nature of the non-bonding electrons on nitrogen. These results will be discussed below.

X-RAY DIFFRACTION DATA

As well as confirming the cyclic structure of phosphazene trimers, tetramers, pentamers, and hexamers, and the linear structure of the high polymer, X-ray data also provide accurate bond lengths, bond angles, and molecular conformations. Table I summarizes the results for some representative phosphazenes. These will be discussed below.

Table 1. Structural Data for Selected Phosphazenes

Compound	P-N bond length (A)	N-P-N bond angle (°)	P-N-P bond angle (°)	R-P-R bond angle (°)	Ref.
$NaPO3NH_3$	1.77	-	-	-	19
$(MeNPCl_3)_2$	1.78	81.1	98.9	90	22
$(NPF_2)_3$	1.57	119.4	120.3	<99.9	28
$(NPF_2)_4$	1.51	122.7	147.4	99.9	23
$(NPCl_2)_3$	1.58	118.4	121.4	101.4	29
$(NPCl_2)_4$	1.57	121.2	131.3	102.8	24
$(NP(NMe_2)_2)_4$	1.58	120	133	104	25
$(NPMe_2)_4$	1.60	119.8	131.9	104	26
$1,1\text{-}N_3P_3Cl_4Ph_2$	1.62 1.56	119.7 115.2	122.0 119.2	104.4 100.4	27

Bond Lengths: Although few structural results have been reported which give a length for a P-N single bond, those compounds which have been studied yield similar values. The most frequently quoted value is 1.77A, for sodium phosphoramidate, $NaPO3NH_3$, corresponding to a covalent radius of 1.07A for P and 0.70A for N.[19] These radii are consistent with those results derived from studies of amines[20] and phosphines.[21] A P-N single bond distance of 1.78A is typical for the saturated phosphazanes.[22] Table I shows that the P-N bond lengths in cyclo and polyphosphazenes range from 1.47A to 1.62A, significantly shorter than the single bond lengths. Bond contractions can be caused by either an increase in bond order due to pi bonding or to electrostatic attractions of the two atoms due to charge separation. Evidence favoring the pi-bonding mechanism over the charge separation mechanism can be derived by an examination of the effect of the different exocyclic ligands on the endocyclic PN bond distances. The shortest PN distances are found in molecules,containing the most electron withdrawing substituents such as fluorine, while the longest bonds are associated with molecules containing electron donating substituents such as methyl. For instance in going from $NPF_2)_4$[23] to $(NPCl_2)_4$[24] to $(NP(NMe_2)_2)_4$[25] to $(NPMe_2)_4$[26] the skeletal PN distances increase from 1.51A to 1.56A to 1.58A to 1.60A respectively. If the bond shortening as compared to the single bond distance is assumed to be due to charge separation as shown below (+P-N-) increased electron drift to N would lead to greater charge separation and a shorter bond length. Electron withdrawing substituents on P would be expected to offset this drift and lead to less charge separation and thus a longer bond. In the pi-bonding model on the other hand, electron withdrawal from P would be expected to de-

crease the P-N bond distance by facilitating electron drift from N to P and also by a contraction or lowering of energy of the d orbitals of phosphorus, using similar arguments to those used to explain bond shortening with electron withdrawing substituents in molecules like phosphine oxides. Mixed substituent phosphazenes are also consistent with this pi-bonding model. Consider the molecule 1,1-diphenyltetrachlorocyclotriphosphazene in Figure 8.

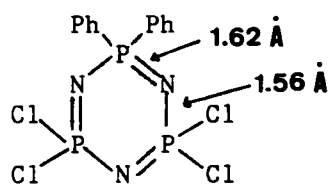


Figure 8. Bond lengths in nonsymmetric cyclophosphazenes

The P-N bonds from the P bearing the electron donating phenyls are the longest in the molecule, while those from the P's bearing the more electron withdrawing chlorines are significantly shorter.[27]

Another feature worthy of note is that all bond distances are equal in symmetrically substituted phosphazenes. This is true even in systems where the ring is puckered such as the cyclic tetramers. This is in contrast with puckered p-p pi systems such as cyclooctatetraene which show distinct long and short bonds. Apparently the d-p pi bonding which leads to the bond shortening can occur in conformations other than planar. This has been ascribed to the variety of d orbitals available for pi bonding

and their spherical distribution, as compared to the single, directional p orbitals used in pi bonding in cyclooctatetraene.

Interestingly the PN bond contraction phenomenon is more noticeable in the cyclic tetamers than in the cyclic trimers. For example in moving from $(NPF_2)_3$[28] to $(NPCl_2)_3$[29] the bond length increases from 1.57A to 1.58A, a change of only 0.01A. In the cyclic tetramers with the same substituents the PN bond lenths are, respectively, 1.51A[23] and 1.56A[24], an increase of 0.05A. This may reflect more steric crowding in the trimer or it may be a consequence of crystal packing forces.

Bond Angles: Examination of the data shows that N-P-N bond angles are very similar in all phosphazenes, regardless of ring size or substituents, always close to 120°. The exocyclic R-P-R angles are smaller, usually about 100° or less. Allcock has described this situation as a distorted tetrahedron. He attributes the relatively large N-P-N angle to repulsive forces between the two nitrogen atoms, and the relatively small exocyclic angle to a scissoring effect.

The P-N-P angles are more variable, and are mainly a factor of ring size. In the six-membered cyclotriphosphazenes P-N-P angles near 120° are normal, while larger angles are found in tetrameric and larger rings.

INFRARED SPECTROSCOPY

The most distinctive feature of the ir spectrum of phosphazenes is the P-N-P asymmetric vibration or degenerate ring stretching mode. This is a very strong absorption in the range of approximately 1200 cm^{-1} to 1400cm^{-1}. A second characteristic band which is sometimes observed is in the 700-950cm^{-1} range and can be considered as a P-N-P symmetric stretch. Cyclic trimers and tetramers will show this band near 885cm^{-1} and 895cm^{-1} respectively, while in the linear polymer the band will appear near 750cm^{-1}. However this is a forbidden transition and is only seen when the selection rules break down, often in the solid or molten state.[30] For this reason the asymmetric stretch has been more commonly reported in the literature. In general only rough trends can be drawn from the data and not detailed comparisons. The presence of electron withdrawing ligands on phosphorus tends to increase the frequency of the P-N vibration. For example vibrational frequencies above 1200cm^{-1} are observed when the substituent is F, Cl, CF_3, NCS, or OR, while frequencies below 1200cm^{-1} are associated with more electron donating substituents such as Br, Me, Ph, or NR_2 groups. These results are consistent with the d-p pi bonding model, in which electron withdrawal increases pi bonding and thus the force constant of the P-N bond and its vibrational frequency.

AVAILABILITY OF NONBONDING ELECTRONS

It was first shown by Bode Butow, and Lieneau[31] in 1938 that cyclophosphazenes form adducts with strong acids such as HCl and $HClO_4$, and later

that weak acids such as acetic acid would also form adducts. It was subsequently shown that these adducts are salts, with the cation a cyclophosphazene protonated at a ring nitrogen.[33] It has been found that the nature of the substituents exerts a strong influence on the basicity of the phosphazene. This basicity data is consistent with the pi bonding model suggested by the x-ray and infrared data.

The adducts in question have formulas such as $(NPR2)_3 \cdot HX$, where R can be any ligand, with amino, alkoxy, alkyl, aryl, and halo, extensively studied. The hydrochlorides can be prepared by bubbling dry HCl gas through a solution of the phosphazene in benzene, ether, or ethyl acetate. Treatment of these hydrochlorides with $AgClO_4$ precipitates AgCl and leaves the perchlorate salt.

In addition, hydrohalide salts are sometimes isolated from the reactions of phosphazenes with amines. For example reaction of $(NPCl_2)_3$ with n-propyl amine followed by recrystallization from heptane yields the monohydrochloride $(NPNHPr2)_3 \cdot HCl$.[34] Analogous behavior behavior was observed with n-butylamine, and also with $(NPBr_2)_3$.

These adducts can be recrystallized repeatedly with no change in composition, indicating that the hydrogen halide is chemically bonded to the phosphazene rather than physically trapped in the crystal lattice, as for example in a clathrate type structure. The instantaneous precipitation of silver halide upon treatment with $AgClO_4$ indicates the presence of ionic halide and shows that the adducts are salts. The site of protona-

tion is indicated by spectral, x-ray, and reactivity data to be the ring nitrogen. For example the simple fact that adducts can be formed with phosphazenes which have no basic side groups indicates that protonation occurs at ring nitrogen. In addition the adducts show major shifts in the ir P-N skeletal vibrations, and broadened and shifted ^1H nmr spectra compared to the nonprotonated forms. Even when amino ligands are present protonation appears to occur at the ring nitrogen. These results are confirmed by the x-ray structure of $N_3P_3Cl_2(NH^iPr)_4 \cdot HCl$.[33] Large differences in pK_a values for the first and second protonation are also consistent with ring protonation.[35] These data suggest a structure like that shown in Figure 9, page 25.

The pK_a's of a large number of substituted phosphazenes have been measured. While some of these measurements have been done in water, or water with 3% methanol[36], many phosphazenes are insoluble in these media. Feakins, Last, and Shaw, developed a technique for the potentiometric titration of these compounds with perchloric acid in nitrobenzene solution.[37] Most of the basicity values which have been obtained have been done in nitrobenzene solution, and are labelled pK_a' in Table 2 to distinguish them from those values determined in aqueous solution, which are labelled pK_a. It should be noted that these values are actually for the acidity of the protonated form, so a small pK_a refers to a strongly acidic conjugate acid and thus a weakly basic phosphazene.

Table 2: Basicity Values for Selected Phosphazenes

Compound	pK_a	pKa'	reference
$N_3P_3Cl_6$		<-6.0	38
$N_3P_3(CF_3)_6$		<-6.0	36, 38
$N_3P_3(OPh)_6$		-5.8	36
$N_3P_3(OMe)_6$		-1.9	36, 38
$N_3P_3(OEt)_6$		0.2	36
$N_3P_3(O^nBu)_6$		0.1	36, 38
N_3P_3Ph6		1.50	36, 38
N_3P_3Et6	5.85	6.40	36, 38
$N_3P_3(NHMe)_6$	7.80	8.8	35
$N_3P_3(NHEt)_6$	8.65	8.2	35
$N_3P_3(NHPr)_3$		7.9	35

Perhaps the most useful information which arises out of these studies is the effect that various substituents have on the basicity of a phosphazene. Since protonation occurs at one or more of the nitrogen atoms of a phosphazene ring, basicity values give a measure of the electron density at those atoms. The decrease in availability of electron density at ring nitrogen with electron withdrawing ligands could be due to either inductive withdrawal by the ligands or to a greater overlap of the nitrogen lone pair with the in-plane dxy orbital of phophorus, which could be contracted just as the d_{x-z} and d_{y-z} orbitals are thought to be. Both of these effects operate in the same direction and attempts to separate them have not been successful. Nevertheless the basicity measurements give important information concerning the relative electronic effects of various phosphazene ligands.

Referring to Table 2 it can be seen that the Cl[38] and CF_3[36,38] groups act as powerful electron withdrawers, with pK_a' values for the hexasubstituted trimer less than -6.0 Phenoxy groups are also strongly electron withdrawing with the pK_a' for the hexaphenoxy trimer at -5.8.[36] Alkoxy groups are appreciably more electron donating than phenoxy, with pK_a' for the methoxy, ethoxy, and n-butoxy at -1.9, 0.2, and 0.1 respectively.[36,38] Phenyl groups are more electron donating than the alkoxy groups with the pK_a' of the hexaphenyl trimer at 1.50.[36,38] The hexaethyl trimers pK_a' of 6.40[36,38] indicates strong electron donation from the alkyl groups. The most strongly donating groups of all are the aminos, with with the pK_a'values for the hexasubstituted methylamino, ethylamino, and n-propylamino trimers at 8.8, 8.2, and 7.9, respectively.[35] In fact it is found

that the amino phosphazenes are stronger bases than the unsubstituted amines.

The pK_a' values of many mixed-substituent phosphazenes have also been measured. Feakins, Shaw, and coworkers, have shown that the results can be quantified.[39] By calculating a substituent value for each different ligand the basicity of a new phosphazene can be predicted due to the additivity of the substituent values.

Whenever comparing acid-base strengths it should always be remembered that what is being measured is a thermodynamic energy difference between the conjugate base and the conjugate acid, in this case the neutral phosphazene and its positively charged conjugate acid. Changes in structure will affect the stability of these two forms to different extents and thus yield acidities or basicities which are not always directly comparable with another, seemingly similar system. Nevertheless the changes in pK_a' from below -6.0 for the hexachloro trimer to over 8.0 for the amino analogues would seem to be significant enough to reflect the real nature of the system.

The nonbonding electrons on nitrogen allow phosphazenes to act as nucleophiles or Lewis bases, as well as Bronsted bases. Electron donating substituents increase the nucleophilicity of the endocyclic nitrogens just as they increase the Bronsted basicity. Thus, for example, $(NPMe2)_3$, with electron donating methyl ligands, will form complexes with the weakly Lewis acidic $SnCl_4$ and $TiCl_4$, while $(NPCl_2)_3$ with electron withdrawing

Cl ligands will not form complexes with these acids.[40] The donating ability of the methyl groups is also apparent in the formation of complexes of $(NPMe2)_3$ with methyl iodide and ethyl iodide with structures analogous to the protonated phosphazenes discussed above.[41]

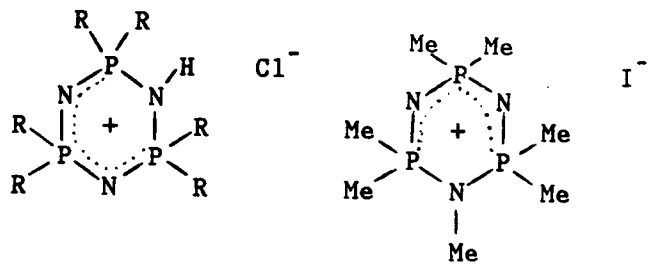


Figure 9. Cyclophosphazenes as Bronsted and Lewis bases

ANALYTICAL TECHNIQUES:

Many of the recent advances in phosphazene chemistry, as well as in chemistry in general, has been spurred by the development of powerful analytical methods. NMR of various nuclei, ir spectroscopy, and mass spectrometry are the techniques which are most commonly used in the indirect determination of the sturucture of new phosphazene molecules, and will be discussed below. X-ray diffraction data are of course extremely important but less routine. Numerous other techniques have been applied in attempts to probe the nature of the phosphazene system. Included among these are UV[42], ESR[43], NQR[44], PES[45], electrical conductance[46], polarography[43], cyclic voltammetry[43], and Raman spectroscopy.[47]

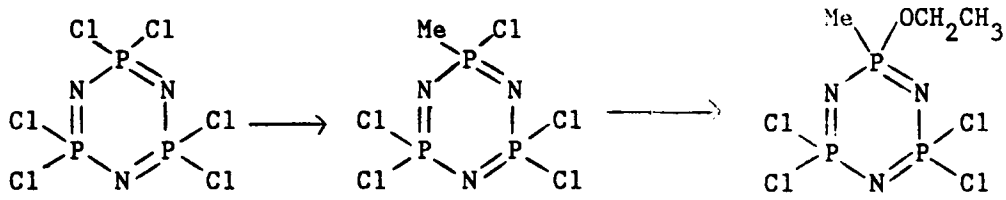
NMR SPECTROSCOPY

NMR spectroscopy is one of the most powerful tools in phosphazene chemistry. The phosphorus nucleus is nmr active with a spin=1/2 and shows coupling to nearby atoms. With ^{31}P, ^{1}H, and ^{13}C, nmr spectra, plus mass spectral data, it is often possible to arrive at an unambiguous structure for a newly synthesized organo-phosphazene.

^{31}P NMR: When the substituents are Cl, alkyl, aryl, alkoxy, or alkyl- or arylamino, the P resonances of a cyclotriphoshazene will invariably be downfield of 85% H_3PO_4, the common reference standard in ^{31}P spectroscopy. These resonances will be assigned positive chemical shift va-

lues. While it is tempting to discuss trends in ^{31}P chemical shifts and coupling constants, it should be borne in mind that numerous factors besides shielding by electrons affect these values. Among the most important of the factors are endo- and exocyclic bond angles and molecular flexibility. Varying substituents on a cyclophosphazene may vary any or all of these factors causing misleading comparisons. However careful comparison of similar molecules does uncover some general trends.

Chemical Shifts: An illustration of typical ^{31}P chemical shifts in phosphazene chemistry is the two step synthesis of 1-methyl-1-ethoxy-tetrachlorocyclotriphosphazene from $(NPCl_2)_3$ as shown in Scheme 1.



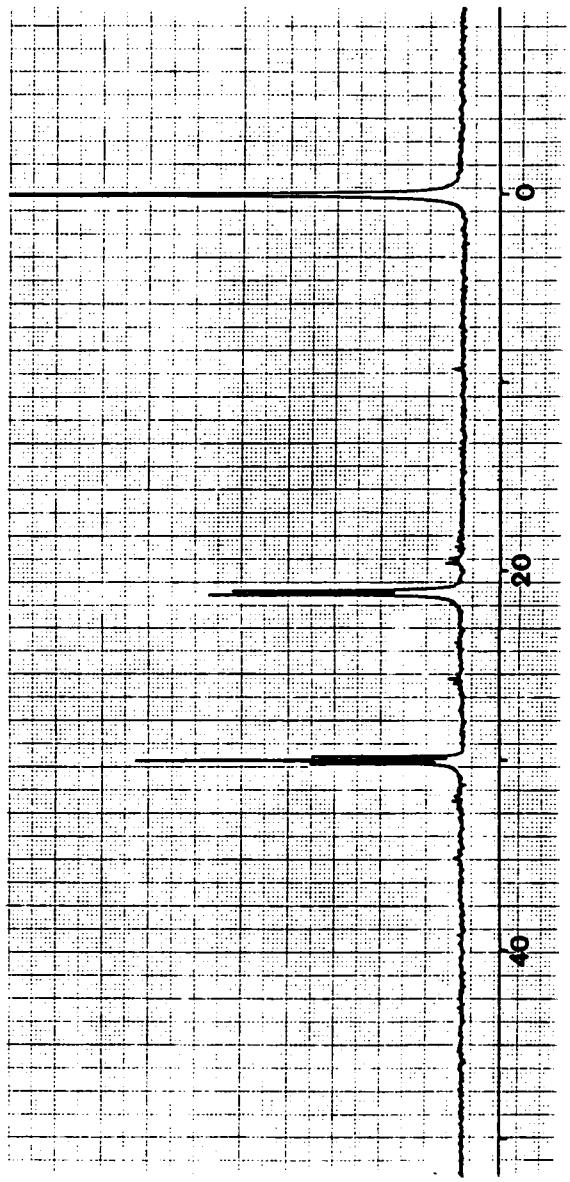
Scheme 1.

In the starting material $(NPCl_2)_3$, all three P atoms are identical and the ^{31}P spectrum consists of a single peak, at 20ppm downfield from 85% H_3PO_4. The immediate precursor to the 1-methyl-1-ethoxy product is the monomethylpentachloro compound. The ^{31}P spectrum of this compound consists of two signals, one for the CH_3-P-Cl phosphorus and one for the PCl_2 groups. Perhaps surprisingly, the effect of the methyl group has been to shift the original PCl_2 resonance at 20ppm well downfield, to 41ppm,

and not upfield as might be expected by simple electron donation from the methyl group. Replacement of the chlorine of the CH_3-P-Cl unit with the ethoxy group shifts the resonance back upfield, to 30ppm. Other groups besides ethoxy have this effect to a lesser or greater degree. Upon amino substition the CH_3-P-N unit will fall near 25ppm. A CH_3-P-O unit will also be found near 25 ppm and the chemical shift of a CH_3-P-CH_3 group is about 36ppm. While the exact reasons for these shifts are not clear, the magnitude of the changes with shifts in structure are large and quite useful in the analysis of reaction products.

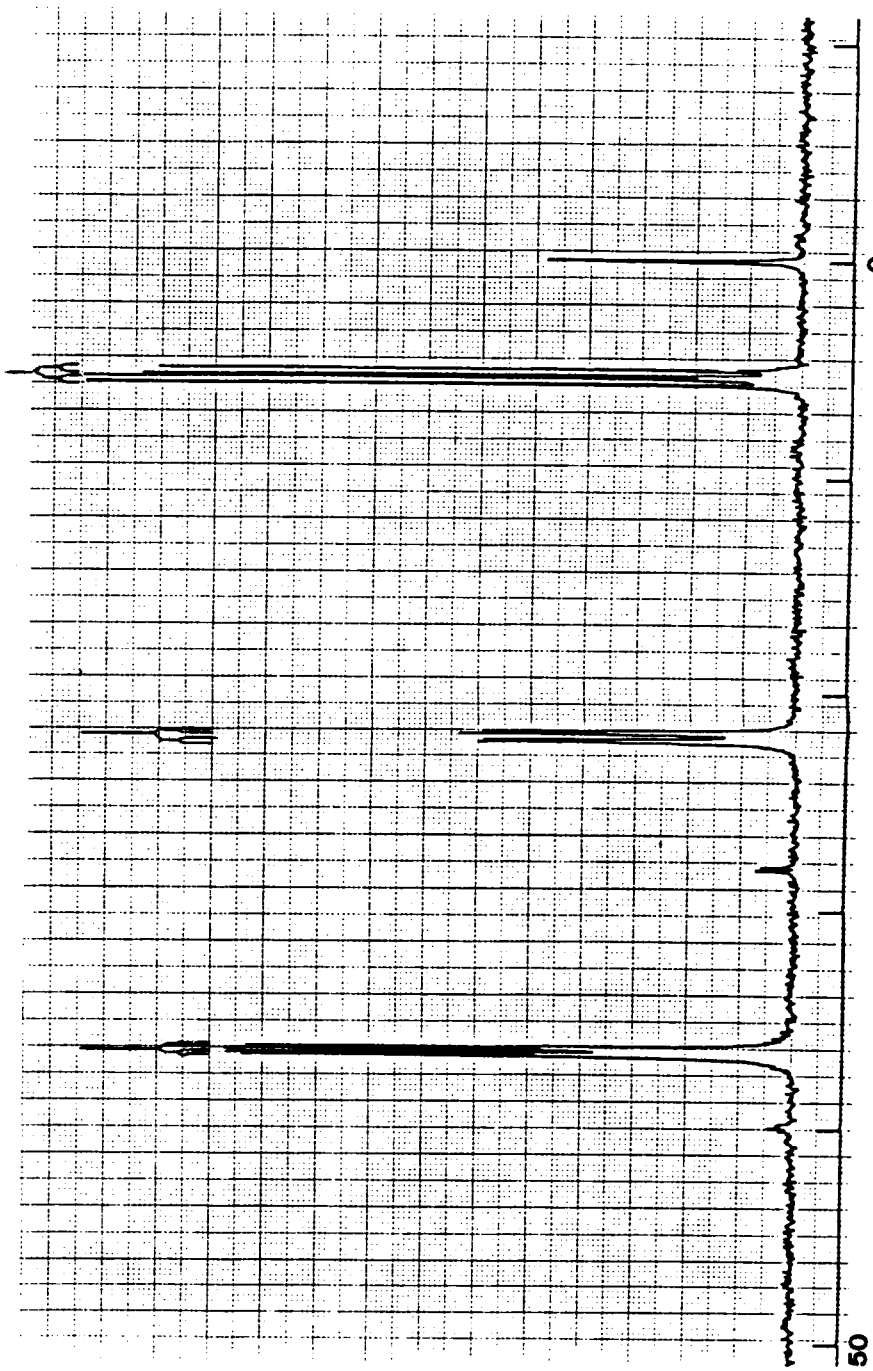
P-P Coupling: In cyclotriphosphazenes a few coupling patterns are the most commonly encountered, and these often are extremely helpful in the identification of a new compound. When the phosphazene is symmetrically substituted of course there is only a single resonance in the ^{31}P spectrum. The other most common structural possibilities are when one P atom is different from two other, identical P atoms, and when all three P atoms are different from each other. A simple example of the first is the 1-methyl-1-ethoxy compound in Scheme 1. Designating the methyl-ethoxy substituted phosphorus atom P_A and the chloro-substituted phosphorus P_X, and assuming first order behavior, the proton decoupled ^{31}P spectrum is described as an AX_2 spin system (Fig. 10). This system would be expected to show up as a triplet for P_A and a doublet for the P_X's, with identical coupling constants J_{AX}, which is what is observed. A molecule with three different phosphorus atoms is **46**, which is discussed in more detail later. If the chemical shifts are sufficiently different to allow first order behavior the proton decoupled ^{31}P spectrum would be described as an AMX

spin system. In such a case each P resonance would be expected to show up as a doublet of doublets, with three different coupling constants, J_{AM}, J_{AX}, and J_{MX}, as observed. Figure 11 shows the proton decoupled ^{31}P spectrum of this molecule, along with an analysis of the coupling. Examination of the proton coupled spectrum is useful in the assignment of the resonances to the various P atoms in the molecule. In Figure 12 it can be seen that the resonance for the PCl_2 group is unchanged by coupling to protons, but the $P(CH_3)_2$ and the spiro-P signals broaden significantly.



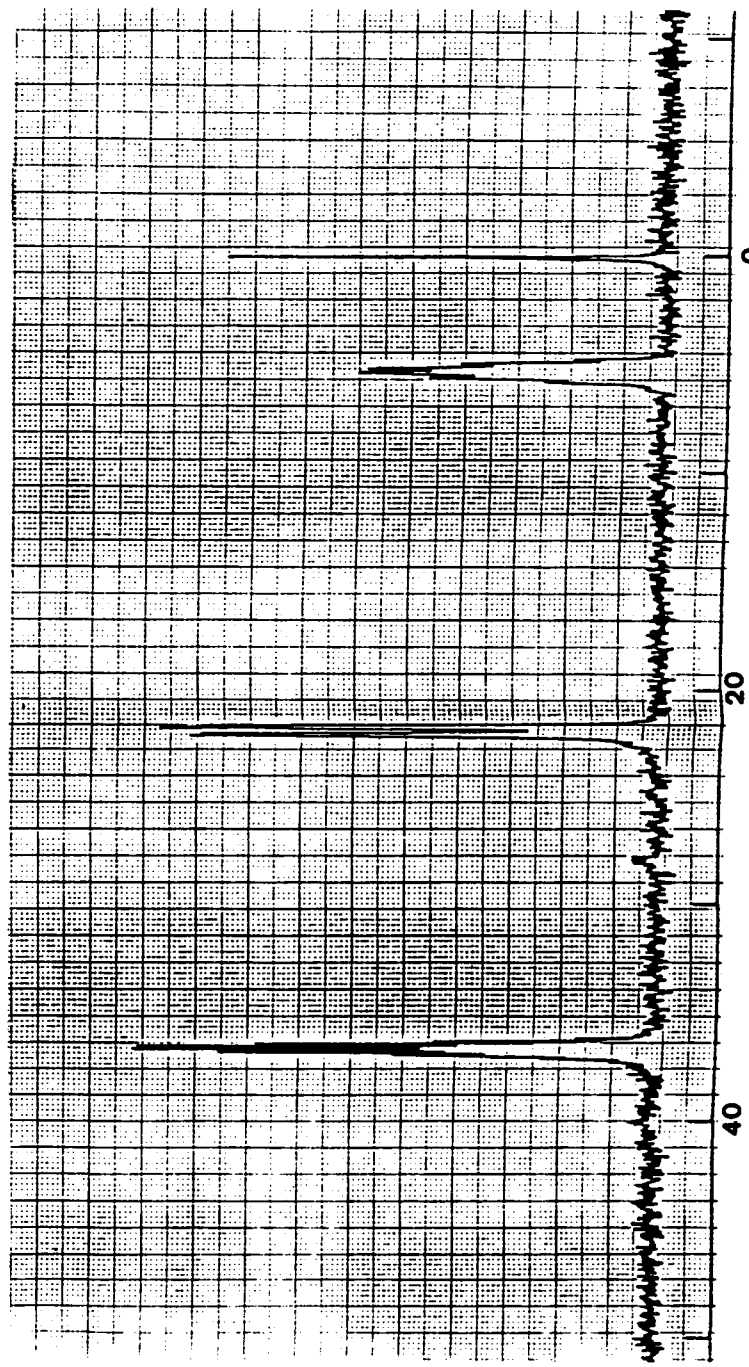
270 MHz ^{31}P NMR spectrum (proton decoupled) of the 1-methyl-1-ethoxy compound (Scheme 1).

Figure 10. An AX_2 spin system



270 MHz ^{31}P NMR spectrum (proton decoupled) of compound 46.

Figure 11. A proton decoupled AMX spin system.



270 MHz ^{31}P NMR spectrum (proton coupled) of compound 46.

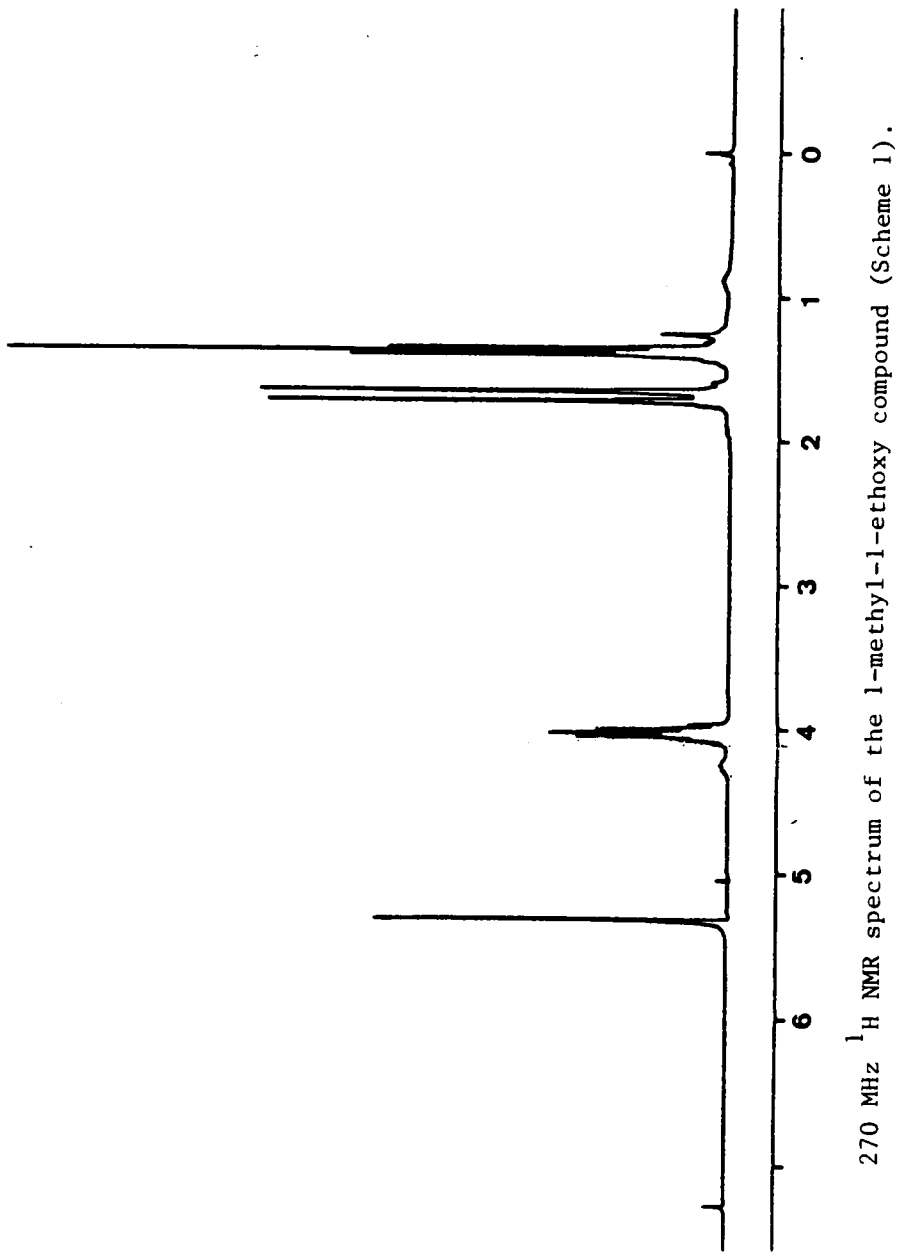
Figure 12. A proton coupled AMX system

^{1}H NMR: ^{1}H nmr can give supporting or additional evidence to the ^{31}P spectrum. A useful example is the substitution of $N_3P_3Cl_5Me$ by CH_3CH_2OH (Scheme 1). In the starting pentachlorophosphazene the methyl protons appear as a doublet of triplets (J=18Hz, and J=3Hz) centered at 2.14d. The large splitting is due to coupling to the closest P atom (J_{PCH}) and the smaller splitting is due to coupling to the two remote P atoms (J_{PNPCH}). The ^{1}H spectrum of ethanol shows the methyl group at 1.3d and the methylene group at 3.6d. In the spectrum of the ethoxy substituted product both the $P\text{-}CH_3$ and the $O\text{-}CH_2$ proton signals have shifted (Fig.13). The $P\text{-}CH_3$ signal still appears as a doublet of triplets but has moved upfield to 1.7d. This upfield shift is also present upon conversion of a $CH_3\text{-}P\text{-}Cl$ unit to $CH_3\text{-}P\text{-}NHR$, $CH_3\text{-}P\text{-}R$ or $CH_3\text{-}P\text{-}Ar$ units, thus providing ready evidence of substitution of the geminal chlorine atom. This supports the ^{31}P data which shows different AX_2 patterns before and after reaction. Further evidence of substitution can be seen in the signal for the $O\text{-}CH_2$ protons. The two changes which occur are both due to the proximity of the P atom. The first is a downfield shift, to 4.1ppm, from 3.6ppm in ethanol, due to electron withdrawal by P. The second is the appearance of $P\text{-}O\text{-}CH_2$ splitting. Ideally this signal would become a doublet of triplets and while overlap reduces the number of lines, the signal is clearly more highly coupled than the corresponding signal in ethanol. The methyl protons of the ethoxy group are too far away from the P atom to show coupling and shift downfield only slightly. ^{13}C spectra act in an analogous manner to the ^{1}H spectra. Substitution on P tends to move the signals downfield and induce splitting. Only the

nearest P atoms and not remote ones, show coupling to C atoms of an organic ligand when an N or O atom intervenes.

MASS SPECTROMETRY

The next most important analytical tool in phosphazene chemistry is mass spectrometry. The spectra are usually relatively simple to interpret due to the presence of distinctive Cl isotope patterns and simple fragmentation pathways. For example, in the ethoxy substitution reaction discussed above one sees for the starting phosphazene a Cl_5 isotope pattern, a molecular ion at 325 amu, and sequential loss Cl atoms. The ms of the final product shows a Cl_4 pattern, indicating the substitution of only one chlorine atom, a molecular ion at 335 amu and the loss of the organic ligand as well as chlorine. Skeletal breakdown fragments carry only a minor fraction of the total ion current.



270 MHz ^{1}H NMR spectrum of the 1-methyl-1-ethoxy compound (Scheme 1).

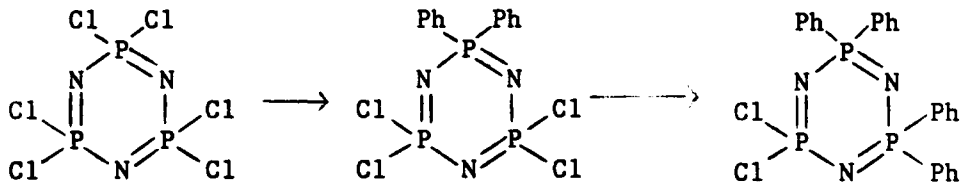
Figure 13. ^{1}H nmr in phosphazene chemistry

ARYL-SUBSTITUTED PHOSPHAZENES: INTRODUCTION

Arylphosphazenes were the first phosphazenes to be synthesized which contained a phosphorus to carbon bond. These compounds have long been considered theortically interesting, particularly with regard to the electronic nature of the interaction between the aromatic system of the benzene ring and the phosphazene moiety. The first phase of our work entailed the synthesis of a series of 1-methyl-1-aryl-3,3,5,5-tetrachlorocyclotriphosphazenes and an examination of their characterization data for evidence of interaction between the phosphazene ring and the benzene ring. The study of these interactions is important in the determination of the nature of the effect of phenyl substuents in particular and all first row substituents in general on the chemistry of the phosphazene system. The following sections will review the synthetic methods which have historically been used to prepare these molecules and the results of various studies regarding the nature of the phosphazene-benzene interaction.

SYNTHESIS OF ARYLPHOSPHAZENES: HISTORICAL

One method by which these compounds can be synthesized is by a Friedel-Crafts reaction between a halophosphazene and an aromatic hydrocarbon in the presence of a Lewis Acid, usually $AlCl_3$. By reacting $(NPCl_2)_3$ with benzene under these conditions, Acock, Shaw, and Wells, prepared the geminally substituted diphenyl and tetraphenyl derivatives (Scheme 2).[48]



Scheme 2.

Refluxing the phosphazene in benzene without $AlCl_3$ led to the recovery of the starting material, indicating the necessity of using the catalyst. Mono, tri, penta, and hexa-substituted products were looked for but were not found, nor were any nongeminal di-, or tetra-substituted products. The authors favored a mechanism involving a monopositive phosphonium ion such as $N_3P_3Cl_5^+$, not a dipositive ion as suggested by Bode and Bach.[49] The reaction was very slow, with three days needed for the formation of the diphenyl molecule, and six weeks for the tetraphenyl product, both in about 40% yield. The authors attributed the long reaction times to the extra stability of the phosphonium ion derived from electron donation from nitrogen, either intra- or intermolecularly. The increasing difficulty of progressive replacement of chlorines was attributed to the increased donor properties of the nitrogens as phenyl substitution takes place, thus stabilizing the cation even more. The geminal substitution pathway was attributed stabilization of the cation by the phenyl group.

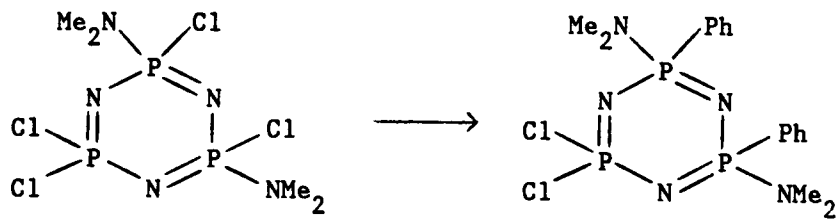
Attempted extensions of the Friedel-Crafts synthesis to other aryl groups, for instance tolyl, met with only limited success. Reaction times were still long, with 80 hours necessary to maximize the yield of the bis-tolyl product. Since the tolyl group can be bonded to phosphorus at different positions on the benzene ring several different isomers were formed. However a geminal substitution pathway was followed as in the reaction with benzene.

Bis- and tetrakis-xylyl derivatives were also prepared, but no reaction was observed with mesitylene, biphenyl, anisole, thiophene, or furan.

Chlorobenzene does react with $(NPCl_2)_3$ in the presence of $AlCl_3$, yielding a monosubstituted product and and two isomeric bis- derivatives.[48] After eleven days of reaction a tetrakis and the hexakis derivative were formed. Thus the Friedel-Crafts reaction with chlorobenzene does not proceed in an exclusively geminal manner as do the reactions with benzene and toluene. This is probably due to the destabilizing effect of the electron withdrawal by chlorine on the phosphorus cation. This electron withdrawal also explains the presence of the monosubstituted product in the reaction mixture. The high reaction temperatures, to which the authors attributed the relatively short reaction times, may also be important in the reaction pathway.

The influence of dimethylamino groups on the Friedel-Crafts reaction has also been investigated.[50] Reaction of the 1,3-bisdimethylamino compound **14** with benzene in the presence of $AlCl_3$ led to the formation of the

1,3-diphenyl-1,3-bisdimethylamino compound **15**, in which the amino groups have directed arylation geminal to themselves while no reaction occurs at the PCl_2 units. This is to be expected since the NMe2 group acts as an electron donor to the phosphazene ring and stabilizes the positive charge caused by the loss of the chloride ion. Acock, Shaw and Wells

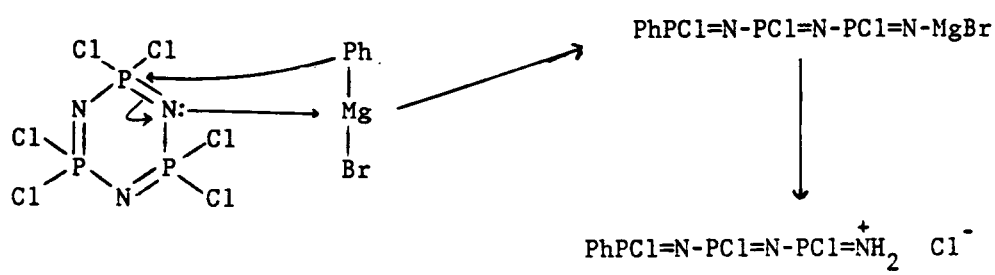


Scheme 3.

stressed the fact that in none of their reactions could a mass balance be obtained for all the phosphazene used. This is evidence that the mechanism is more complicated than the simple one given in Scheme 2.

Fluorophosphazenes can also be arylated under Friedel-Crafts conditions. For instance Allen and Moeller refluxed $N_3P_3F_5Ph$ with benzene in the presence of $AlCl_3$ and triethylamine and obtained the geminal diphenyl compound.[51] Reaction of the nongem diphenyl molecule under similar conditions led to the formation of the geminal tetraphenyl derivative. Thus the Friedel-Crafts phenylation of fluorocyclotriphosphazenes follows the same substitution pathway as it does with chlorocyclotriphosphazenes.

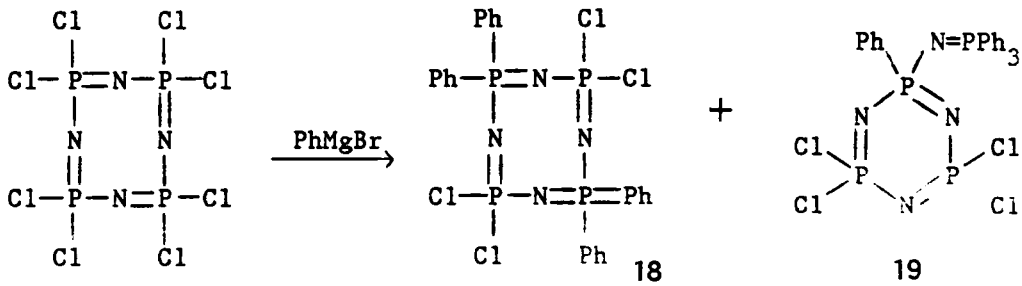
The other synthetic approach to arylphosphazenes involves nucleophilic substitution reactions by organometallic reagents, especially Grignard reagents and organolithiums. Reaction of $(NPCl_2)_3$ with these reagents has been shown to lead to products other than the desired arylphosphazenes. For instance Shaw and Biddlestone examined the reaction of $(NPCl_2)_3$ with phenylmagnesium bromide.[52] While the hexaphenyl derivative was produced, yields were very low, about 5%, and the evidence suggests a mechanism other than direct substitution. For example the only products which retained the cyclic structure were $(NPCl_2)_3$ and $(NPPh_2)_3$. No partially substituted products were detected. The major products were open chain phosphazenes such as **16**. Treatment of these products with aqueous NH_4Cl gave species with end groups such as **17**, and treatment of these species with $AgClO_4$ exchanged the chloride ion with ClO_4^-. These perchlorate salts corresponded to derivatives reported earlier by Bode and Bach.[49] Treatment of cyclic $(NPPh_2)_3$ with additional PhMgBr did not lead to ring opening. On the basis of these facts the authors suggested the following mechanism (Scheme 4), in which the first attack by PhMgBr leads to substitution by phenyl and ring opening in a slow step. This linear species



Scheme 4.

undergoes rapid substitution by phenyl, presumably facilitated by the greater flexibilty of the linear species than the cyclic molecule. The fully substituted cyclic compound would arise via a recyclization step.

Further evidence for this ring-opening mechanism is provided by the reaction of PhMgBr with $(NPCl_2)_4$.[53] Two major products were isolated (Scheme 5), the 1,1,5,5-tetraphenyl cyclic tetramer **18** and the cyclic trimer **19**, plus smaller amounts of different tetraphenyl derivatives and the octasubstituted compound. The cyclic trimer was the major product, isolated in yields up to 93%. A ring opening step analogous to the one with $(NPCl_2)_3$ was proposed, followed eventually by recyclization to the six membered ring. Feldt and Moeller synthesized the same cyclic trimer by treatment of the fully chlorinated analogue with PhMgBr.[54] It is noteworthy that the only chorines replaced by phenyl in this reaction are the ones on the acyclic P atom and the one geminal to the acyclic $N{=}PPh_3$ group.



18 19

Scheme 5.

The presence of dimethylamino groups apparently aids substitution and hinders ring opening. Thus reaction of the 1,3,5-trisdimethylamino molecule with MeMgI leads to good yields of the trimethyl substituted product.[55] This suggests that substitution of the ring phenyl group in **19** may take place after cyclization, aided by activation by the $-N=PPh_3$ group.

In contrast to the chlorocyclotriphosphazenes the fluoro-cyclotriphospazenes will undergo substitution reactions with Grignard reagents. Allen has shown that $(NPF_2)_3$ undergoes stepwise replacement of fluorine when treated with PhMgBr in refluxing tetrahydrofuran (THF).[56] The reaction was shown to follow a geminal substitution pathway. The lack of ring degradation has been attributed to enhanced stability of the ring skeleton bonds due to electron withdrawal by flourine.

The other organometallic reagents which have mainly been studied are the organolithiums. It was thought until recently that chloro- cyclophosphazenes underwent ring cleavage upon treatment with organolithium reagents. However Van de Grampel and coworkers have found evidence of a metal halogen exchange mechanism with retention of the phosphazene ring.[57]

The fluorcyclophosphazenes will undergo smooth substitution with organolithium reagents. Allen and Moeller have investigated the reaction of $(NPF_2)_3$ with PhLi.[58] They found that the degree of substitution could be controlled by the stoichiometry, and that the substitution pathway was

mainly, but not exclusively, nongeminal. Through reaction of $(NPF_2)_3$ with PhLi, followed by Friedel-Crafts phenylation, geminal diphenyl- and tetraphenylflourocyclotriphosphazenes could be prepared.[59]

While these reactions have been well studied, none of the methods discussed above posess the general synthetic utility to prepare a wide variety of similar aryl-phosphazenes that would allow for direct comparison of physical properties.

CONJUGATION IN ARYL PHOSPHAZENES: HISTORICAL

Historically, interest has been shown in aryl-substituted phosphazenes with regard to the nature of the electronic interaction, if any, between the benzene ring and the phosphazene. Many experimental data, such as the reactivity of chlorobenzene towards phosphazenes in the Fiedel-Crafts reaction, and the basicity of hexa(p-chlorophenyl)cyclotriphosphazene, suggest that electronic effects are transmitted from phenyl to phosphorus. Workers have used a wide variety of techniques probing this interaction and have come to many different conclusions regarding the mechanism of its operation. The answer to this question is important in explaining much of the chemistry of the phosphazene system.

A brief review of the work done on quantitating the electron donation or withdrawal of substituent groups will be helpful. In the 1930's Louis Hammett studied the effect of various substituents on the acidity of benzoic acids.[60] The presence of electron wihdrawing groups such as nitro

increase the acidity of a substituted benzoic acid, mainly by stabilization of the negatively charged conjugate base. Conversely, electron donating groups such as methyl decrease the acidity. Hammett related the acidities of the substituted acids (K_X) to the acidity of benzoic acid itself (K_H), and defined the term $\log K_X/K_H$ as the substituent or σ constant for the group X. Positive values indicate electron withdrawing groups and negative values indicate electron donating groups. Although sometimes criticized for lack of theoretical basis, a tremendous number of chemical rates and equilibria were found to correlate well with the Hammett sigma values. Many of the reactions or substituents which did not correlate involved systems in which the substituent came into direct conjugation with the reaction center, such as the ionization of anilines and phenols, a situation which is impossible in the benzoic acids. For these reactions and substituents new substituent constants were established which gave good correlations with other, similar reactions.[61,62] Physical data, particularly ^{1}H and ^{13}C chemical shifts were also found to be linearly related to some of these substituent constants.[63] The culmination of this area of research was the separation of the substituent constants into inductive and resonance components.

The inductive effect, sometimes referred to as the polar or field effect is electron donation or withdrwal through space or through σ bonds. Resonance, otherwise known as the mesomeric effect operates through p orbitals or pi bonds. Separation of these effects is in theory possible due to the fact that resonance effects in benzeene rings are felt much more strongly in the ortho and para positions than in the positions meta

to the substituent inducing the effect. For instance the $-NH_2$ group is a much stronger donor in the ortho and para positions than in the meta position, since the ortho and para positions allow direct conjugation with electron withdrawing substituents, while the meta position does not. The methoxy and hydroxy substituents are donors in the ortho and para positions, but electron withdrawers in the meta position due to this same effect. Taft suggested a method which allowed for the separation of the electronic effects of a group into resonance and inductive parameters.[64] The new substituent constants were called σ_I and σ_R. Taft showed that these values could be empirically related to the ^{19}F nmr chemical shifts of substituted benzenes bearing F atoms meta and para to a given substituent.[65] These equations were the cause of much research and debate in the literature, much of it concerned with the exact causes of ^{19}F chemical shifts in these molecules.[66],[67] Debate has since died down and ^{19}F shifts are still commonly used to determine σ_I and σ_R values.

Much of the work with aryl-phosphazenes has concerned the assignment of a substituent constant to a phosphazene as a substituent on a benzene ring. For example Allen and White prepared a series of phenyl and deuterophenyl fluorophosphazenes and studied their ^1H nmr spectra. They found that the fluorophosphazene group was a powerful electron withdrawer, similar to a nitro group, and assigned a σ value of 0.74.[68] They also found that increased phenyl substitution led to a decrease in the electron withdrawing ability of the phosphazene ring. This is consistent with the effect that phenyl groups have on the bond lengths, basiscity, and susceptibility to nucleophilic substitution of phosphazenes. Due to

the correlation of para-proton chemical shifts with calculated pi-electron density[69,70], and the similarity of these shifts to those induced by the nitro group, the authors suggested that the mechanism of electron withdrawal was mesomeric, through the pi-system of the benzene ring. This suggests resonance structures like those shown in Figure 14.

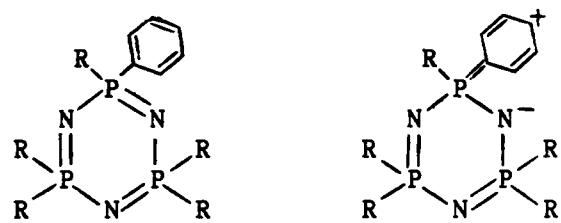


Figure 14. Resonance interaction of phenyl and phosphazene rings

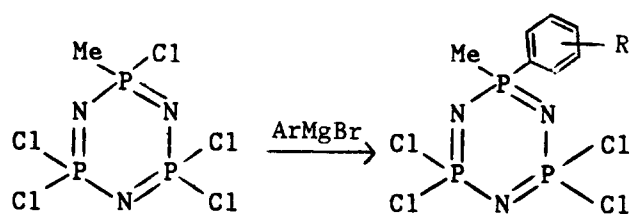
Chivers and Paddock prepared a series of m- and p-fluoro- phenylphosphazenes of varying ring sizes and examined their ^{19}F nmr spectra.[71] They also found that the phosphazene acts as a strong electron withdrawer from the phenyl groups. They estimated a σ_I of 0.55 and a σ_R of 0.24 for the $N_3P_3F_5$ group. This σ_R value is similar to those of PF_2, CN, and NO_2 as determinmed by the same method, but less than those of BF_2 and PF_4.

Other techniques have been applied to probe the phosphazene-phenyl interaction with varying interpretations of the results For instance Whitehead interpreted the results of NQR studies in terms of strong resonance withdrawal by phosphazene[44], while Letcher and Van Wazer saw little evidence of resonance interactions in other P(V) compounds in their study

of ^{31}P data.[72] Allcock and Birdsall studied the electrolytic reduction of a number of phosphazenes bearing organic side groups, including phenyl, and concluded that the exocyclic side group was the primary point of reduction, and that no strong resonance effects were operating in these reductions.[43]

1-METHYL-1-ARYL CYCLOPHOSPHAZENES: RESULTS

The 1-**methyl-1-aryl**-3,3,5,5-tetrachlorocyclotriphosphazenes were all prepared by the same method, treatment of monomethylpentachlorocyclotriphosphazene with the appropriate Grignard reagent as shown in Scheme 6. These reactions proceeded in moderate yields as indicated in table 3. In all, thirteen different aryl compounds were prepared. This synthetic approach is the first to allow the controlled substitution of a wide variety of aryl groups onto the phosphazene skeleton, without the limitations described in the historical section. Thus this series of molecules is particularly useful in the study of the interaction of a phosphazene ring with phenyl substituents specifically and with all first row substituents in general.



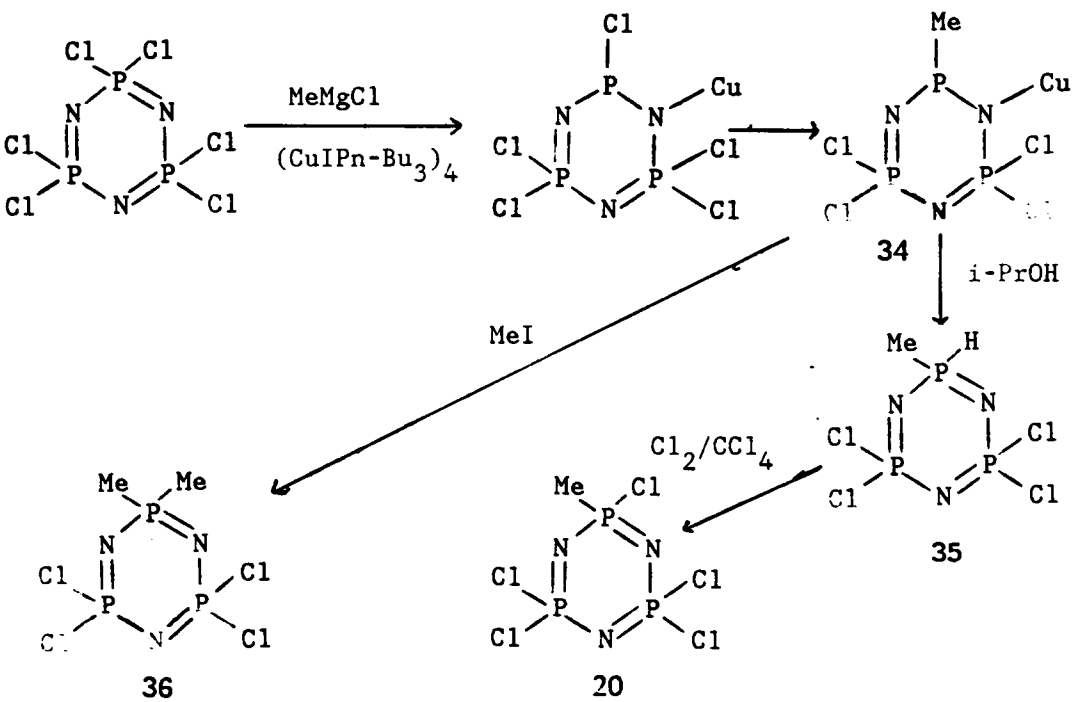
20

R = H, p-NMe_2, m-NMe_2, p-NEt_2, p-OMe, m-OMe, p-F, m-F, Me, t-C_4H_9, Ph, Cl, CF_3.

Scheme 6.

The monomethylpentachloro **20** compound is important not only because it is the immediate precursor to the 1-methyl-1-aryl compounds, but also as

a substrate for the amine and alkoxide substitutions to be discussed later. Its synthesis is shown in Scheme 7. Treatment of $(NPCl_2)_3$ with methyl magnesium chloride in the presence of cuprous ions, present as $(CuIPn\text{-}Bu_3)_4$, leads to the formation of of the phosphazene anion **34** by a metal-halogen exchange step, with the loss of CH_3Cl. This anion can be protonated with isopropyl alcohol to yield the 1-methyl-1-hydrido compound **35** This compound can be isolated by sublimation and chlorinated with Cl_2 in CCl_4 to yield the monomethylpentachloro compound. Alternately, the anion may be quenched with methyl iodide to yield the 1,1-dimethyl compound **36**. The reactions of both 1-methyl-1-hydrido compound and the 1,1-dimethyl compound with bifunctional nucleophiles were also investigated and will be discussed in later sections.



Scheme 7.

The structure of the 1-methyl-1-aryl compounds were determined by the use of a combination of ^{1}H and ^{31}P NMR, infrared and ultraviolet spectroscopy, mass spectrometry, and in representative cases, elemental microanalysis. General characterization data for all new compounds are listed in table 3. ^{31}P nmr data are given in table 4. Ultraviolet and mass spectral data are given in Table 5.

The retention of the phosphazene ring in these compounds was confirmed by both ir and ^{31}P nmr data. The infrared spectra showed intense absorbances between 1100 and 1300cm-1, characteristic of the PN skeleton in cyclotriphosphazenes. The AX_2 coupling patterns are also consistent with cyclotriphosphazene structures. The geminal substitution pattern was confirmed by both ^{1}H and ^{31}P nmr spectra. The ^{1}H nmr spectrum always showed the resonance for the P-CH_3 group as a doublet of triplets centered at about 1.8ppm. This is shifted upfield from the resonance for the methyl- pentachloro starting phosphazene, which is found at 2.1d. The proton decoupled ^{31}P nmr spectrum in all cases was interpreted as an AX_2 spin system, which would not have been the case for nongem substitution. The PCl_2 resonances occurred close to 18.5ppm in all of the compounds, and the CH_3-P-Ar resonance appeared as a triplet, centered between 30.0 and 27.7ppm. This resonance broadened significantly upon ^{1}H coupling. The ultraviolet spectra of these compounds were found to be significantly different from those of the aryl substituents unbonded to the phosphazene ring. The mass spectra of all of the compounds were found to be very similar, with the majority of the total ion current carried by only two fragments, the molecular ion, and this fragment minus a CH_3 group.

Table 3. Characterization Data of 1-methyl-1-aryl compounds

compound	% yield	mp or bp (mm), °°C
$N_3P_3Cl_4(CH_3)(C_6H_5)$, **21**	76	76-78
$N_3P_3Cl_4(CH_3)(p\text{-}C_6H_4NMe_2)$, **22**	35	130
$N_3P_3Cl_4(CH_3)(m\text{-}C_6H_4NMe_2)$, **23**	21	150(0.1)
$N_3P_3Cl_4(CH_3)(p\text{-}C_6H_4NEt_2)$, **24**	26	96-98
$N_3P_3Cl_4(CH_3)(p\text{-}C_6H_4OCH_3)$, **25**	46	72
$N_3P_3Cl_4(CH_3)(m\text{-}C_6H_4OCH_3)$, **26**	18	145(0.1)
$N_3P_3Cl_4(CH_3)(p\text{-}C_6H_4F)$, **27**	24	58-60
$N_3P_3Cl_4(CH_3)(m\text{-}C_6H_4F)$, **28**	18	61
$N_3P_3Cl_4(CH_3)(p\text{-}C_6H_4CH_3)$, **29**	50	66-69
$N_3P_3Cl_4(CH_3)(p\text{-}C_6H_4\text{-}t\text{-}C_4H_9)$, **30**	58	141
$N_3P_3Cl_4(CH_3)(p\text{-}C_6H_4C_6H_5)$, **31**	17	81-83
$N_3P_3Cl_4(CH_3)(p\text{-}C_6H_4Cl_4)$, **32**	20	70-75
$N_3P_3Cl_4(CH_3)(p\text{-}C_6H_4CF_3)$, **33**	32	98

Table 4. Ultraviolet and Mass Spetral Data of the Methyl-Aryl Compounds

Compound	max(log ε) CH_3OH	max(log ε) n-C6H14	Mass spec. Found	Mass spec. Calcd.
21	260sh(3.00)		367(Cl_4)	367(Cl_4)
22	281(4.42)	275(4.49)	410(Cl_4)	410(Cl_4)
23	264(4.26)	332(3.41)	410(Cl_4)	410(Cl_4)
24	286(4.44) 219(3.93)		438(Cl_4)	438(Cl_4)
25	260(3.93) 237(4.10)	262(3.82)	397(Cl_4)	397(Cl_4)
26	252(3.55)	251(3.78)	397(Cl_4)	397(Cl_4)
27	259(2.84)	256(3.71)	385(Cl_4)	385(Cl_4)
28	268(3.37)	275(3.90)	385(Cl_4)	385(Cl_4)
29	258(3.07)		381(Cl_4)	381(Cl_4)
30	227(4.29)		423(Cl_4)	423(Cl_4)
31	260(4.31)		443(Cl_4)	443(Cl_4)
32	229(4.28)		401(Cl_4)	401(Cl_4)
33	274(3.14) 267(3.18)		435(Cl_4)	435(Cl_4)

Table 5. ^{31}P NMR Data for Methyl-Aryl Compounds

Compound	CH_3-P-Ar,t	Cl-P-Cl,d	J_{PNP}
21	29.0	18.6	11.0
22	30.0	18.3	8.8
23	30.6	18.1	7.3
24	30.0	18.2	9.7
25	29.3	18.6	8.8
26	29.4	18.5	9.8
27	28.4	18.7	10.3
28	27.7	18.7	11.7
29	29.4	18.7	9.8
30	29.2	18.3	9.8
31	29.1	18.8	10.3
32	28.3	19.0	11.0
33	27.7	19.1	11.7

1-METHYL-1-ARYL CYCLOPHOSPHAZENES: DISCUSSION

Some of the characterization data of the 1-methyl-1-aryl- tetrachlorocyclotriphosphazenes were found to give insight into the nature of the interaction between the benzene and phosphazene rings. These data are discussed in the follwowing section.

^{1}H AND ^{13}C NMR

Chemical shifts in nmr spectroscopy have historically been related to relative shielding or deshielding by electron density surrounding the resonating nucleus. The Hammett substituent constants, σ, for many functional groups have been correlated with chemical shifts in both ^{1}H and ^{13}C nmr. Electron withdrawing groups such as nitro and cyano induce downfield shifts in the resonance for the para carbon, compared with unsubstituted benzene while electron donating groups like methyl or dimethylamino induce upfield shifts. Inspection of the ^{13}C nmr spectrum of 1-methyl-1-phenyl-tetrachlorocyclotriphosphazene **21** allows easy identification of the resonance corresponding to the para carbon by its smaller coupling constant to P than that of the meta, ortho, and ipso carbons. Simple interpolation gives a normal σ constant for the chlorophosphazene ring, as a functional group bonded to the benzene ring. This value is 0.61, indicating a moderately strong electron withdrawal from the benzene ring by the phosphazene ring. A similar process can be followed in the ^{1}H nmr and yields a value of 0.65, well in agreement with

the value obtained from the ^{13}C data. These values can be compared with the normal σ constant for the cyano group, which is about 0.64. These values are also in good qualitative agreement with the σ values estimated for the fluorocyclotriphosphazene group.[73] The chlorophosphazene group is found to be a weaker electron withdrawer than the fluorophosphazene group as would be predicted from the greater electronegativity of F than Cl.

^{19}F NMR

The normal σ constants obtained from ^{1}H and ^{13}C nmr data give information regarding the overall electron withdrawing ability of the phosphazene ring. In an attempt to separate this withdrawal into resonance and inductive components the para and meta fluorophenyl derivatives **27** and **28** were synthesized and their ^{19}F nmr spectra recorded. As expected, the para compound gave the further downfield resonance, presumably due to the direct conjugative interaction which does not occur in the meta compound. The differences in chemical shift between the fluorophenylphosphazenes and fluorobenzene were calculated and the values inserted into the empirically derived equations (1) and (2).[71,74]

$$\sigma_I = 0.1409(0.6 - J_H^{m-X}) \qquad (1)$$

$$\sigma_R = 0.0339(J_{p-X}^{m-X} - J_H^{p-X}) \qquad (2)$$

The equations yielded a $\sigma_I = 0.48$ and a $\sigma_R = 0.16$. The total of 0.64 agrees well with the overall σ value derived from ^{1}H and ^{13}C data, and serves

as an internal check of consistency. The σ_I and σ_R values suggest that approximately 25% of the phosphazenes electron withdrawal takes place via a resonance mechanism and 75% occurs via an inductive mechanism. This can be compared to the cyano group which has an overall σ value about the same as that of the phosphazene but a greater percentage by the resonance mechanism.

ULTRAVIOLET SPECTROSCOPY

Absorption spectroscopy is another technique which has classically been used to demonstrate resonance interactions in benzenes and other conjugated systems. Doub and Vandenbelt recorded the ultraviolet spectra of numerous disubstituted benzenes.[75,76] They showed that the presence of a resonance donor-acceptor pair para, and sometimes ortho, to one another induces a shift to longer wavelegths and an increase in molar absorptivity of the principle pi-pi star absorption compared to the meta isomer. These shifts can be dramatic in the case of strong donors and acceptors like NH_2 and NO_2, and are smaller with weaker donor-acceptor pairs.

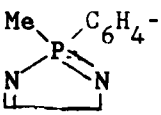
Among the various 1-aryl-1-alkylcyclotriphosphazenes synthesized were three pairs of isomers differing only in the meta or para relationship of the phosphazene and the other substituent. The pairs were p- and m-$N(CH_3)_2$, **22** and **23**, p- and m-OCH_3, **25** and **26** and p- and m-F, **27** and **28**. The uv spectra of these compounds were recorded in methanol or hexane solution. Their extinction coefficients were obtained by standard dilution techniques. All gave correlation coefficients to Beers Law of at

least 0.99 over the concentration range of 10^{-4}M to 10^{-8}M. The data are summarized in Table 6. along with the reported literature data for the corresponding cyano compounds for comparison.[77,78] In comparing the meta and para dimethylamino- substituted phosphazenes there is a shift of 17nm to longer wavelength in going from the meta to the para isomer, and an increase in log ε of 0.16. In the corresponding cyano compounds the increase in wavelength is 25nm and in log ε is 0.2. These numbers seem in good qualitative agreement with the greater resonance withdrawal of the cyano group discussed earlier. Moving to the methoxy-substituted case,the cyano compounds still show substantial shifts, with increases of 25nm in wavelenth and 0.4 in log ε, as one goes from meta to para substitution. In the phosphazene case however, the increase in λ_{max} is only 8nm, while the increase in log ε is 0.28. It is notable that in both the cyano and phosphazene cases the increase in log ε is larger with methoxy substitution than with dimethylamino substitution. The methoxy data are also in qualitative agreement with a greater resonance withdrawal by the cyano group.

The m- and p-fluoro cases provide an interesting comparison. In the cyano compounds the shift upon going from meta to para substitution is actually to shorter wavelengths, the opposite of the methoxy and dimethylamino induced shifts. The extinction coefficients parallel the λ_{max} values with the meta substituted product having a slightly larger log ε. The phosphazene case takes this trend further. The meta-fluoro compound has the longer λ_{max} by 9nm and a larger log ε by a substantial amount. Whatever the effect is that has caused the meta-para switch in the cyano compounds

can be seen to be larger in the phosphazenes. This again can be taken as qualitative agreement with the lesser resonance withdrawal by the phosphazene than the cyano group.

Table 6. UV Data Compared to Cyano Compounds

	 (logε)	$N\equiv C\text{-}C_6H_4\text{-}R$ (logε)
R= p-NMe_2	281(4.42)	290(4.4)
m-NMe_2	264(4.26)	265(4.2)
p-OMe	260(3.93)	255(4.3)
m-OMe	252(3.65)	230(3.9)
p-F	259(2.59)	231(3.95)
m-F	268(3.37)	229(3.99)

REACTIONS WITH BIFUNCTIONAL NUCLEOPHILES: INTRODUCTION

In the second phase of this work, the reactions of methyl-susbstituted cyclotriphosphazenes with simple aliphatic bifunctional amines and alkoxides were investigated. These reactions are of interest for several reasons. Historically, interest has been shown in the use of bifunctional nucleophiles as crosslinking agents for polychlorophosphazenes and for the synthesis of cyclomatrix polymers. Our work in this area was initiated in the hope of synthesizing a molecule in which an atom or group of atoms was suspended over the phosphazene ring. It was hoped that the question of aromaticity could be conclusively answered by the presence or absence of a magnetically induced ring current as indicated by nmr spectroscopy. While no evidence of aromaticity was expected, and the bridged molecules prepared in this study show no significant shifts attributable to magnetic anisotropy, the evidence is inconclusive since these molecules still do not have a atoms suspended directly over the ring. In the course of the study however, several observations suggested that these reactions provided a useful probe of the reactivity of methyl containing phosphazenes towards nitrogen and oxygen nucleophiles. It was found that the presence of methyl groups and also of amino and alkoxy groups, had a significant effect on the reactivity of the remaining chlorines towards nucleophiles. Perhaps the major emphasis in phosphazene chemistry today is the synthesis of new and useful polymers, and probably the most desirable of these would contain methyl substituents and combinations of methyl and alkoxy or amino substituents. While a

controlled synthesis of methyl-containing phosphazene polymers has yet to be discovered, it is still worth investigating their potential chemistry. Since most of the useful syntheses of phosphazene polymers have derived from studies using cyclophosphazenes as models, it is likely that the chemistry discovered here will operate to some extent in the polymer as well. In addition, the research group of Labarre and Lahanna in Tolouse, France who performed the X-ray analysis discussed herein have expressed interest in the ansa molecules as precursors to potential anti-tumor drugs. They have synthesized several biologically active cyclophosphazenes bearing aziridine side groups. Studies have shown that the activity is related to the ability of the phosphazene to deliver the aziridine group to the tumor site. Labarre and coworkers hope that the ring strain indicated by the X-ray structure of the ansa molecule **54**, discussed in more detail later, will aid in delivery of the aziridine residue.

The following sections will review the chemistry of mono and bifunctional amines and alcohols with phosphazenes, with emphasis on the effect of the substituents on the reactivity of the remaining chlorines towards nucleophilic substitution.

AMINOPHOSPHAZENES: HISTORICAL REVIEW

Among the most intensively studied chemistry of the chlorocyclophosphazenes are the reactions with primary and secondary amines and ammonia. These reactions form amino-substituted cyclophosphazenes with the loss of hydrogen chloride. The reactions may yield fully or partially substituted products depending on stoichiometry and other factors. A generalized reaction is shown below. Most simple primary and secondary amines have been studied.

$$N_3P_3Cl_6 + 6HNR_2 \longrightarrow N_3P_3(NR2)_6 + 6HCl \qquad (3)$$

Although well studied the mechanism of the reaction is not well understood. One aspect of the reaction which has received considerable discussion is the substitution pattern as the various chloride ions are replaced stepwise en-route to the fully aminated product. Consider the substitution by the second amine molecule in the reaction above. This group may end up substituted either geminally or nongeminally to the first one. Most information concerning substitution pathways comes from the analysis of incomplete reaction mixtures. The facts derived from these studies are sometimes confusing, and no theory has been proposed which explains them all. The most important factors in determining the substitution pathway have been found to be the specific amine doing the substituting, and the substituents already present on the phosphazene ring. The following discussions will focus on these factors.

INFLUENCE OF THE AMINE ON SUBSTITUTION

This section will discuss the reactions of chlorocyclophosphazenes with various structural categories of amines. For each amine the discussion will center upon two factors. The first of these factors is the ease and degree of halogen replacement. Simple steric arguments are reasonably effective in explaining the observed facts. The second factor discussed will be the preferred substitution pathway followed by the different amines.

Ammonia: Hexachlorocyclotriphosphazene will react with ammonia to give the fully substituted product. The reaction is reasonably facile and complete chlorine replacement takes place in 5 hours at -40°C in diethyl ether-liquid ammonia solution.[79] Reaction of an ether solution of $(NPCl_2)_3$ with aqueous NH_4OH for 1 hr, or if NH_3 gas is bubbled through the solution, a diamminotetrachloro derivative is formed.[80] The diammino compound was treated with PCl_5 to convert the NH_2 groups into $N{=}PCl_3$ substituents. The ^{31}P nmr spectrum of this product was an AX_2C_2 spin system, consistent with a geminal, rather than nongeminal arrangement of the NH_2 groups.[81,82]

Unbranched Primary Amines: These amines will also fully substitute $(NPCl_2)_3$, although under somewhat less mild conditions.[83] For example methylamine will fully substitute all six chlorines below room temperature, while n-butylamine requires refluxing ether or benzene.[84] If the conditions are mild enough, or if the phosphazene is present in excess,

partly substituted products can be isolated. The pattern of halogen replacement has been examined for the reactions with methylamine and ethylamine. ^{31}P nmr[85] and dipole moment[86] data indicates that the reaction of ethereal $(NPCl_2)_3$ with aqueous methylamine proceeds by both geminal and nongeminal pathways. Thus three isomers of $N_3P_3Cl_4(NHCH_3)_2$ have been isolated. Ethylamine was shown to yield exclusively nongeminal disubstitution products upon reaction with $(NPCl_2)_3$ in ether.[87]

Branched Primary Amines: Replacement of all six chlorines of the cyclic trimer with isopropylamine, isobutylamine, sec-butylamine, cyclohexylamine requires appreciably more stringent conditions than the straight chain primary amines or ammonia.[83] Tert-butylamine will not proceed past the tetrasubstituted stage without drastic conditions.[83] The pattern of substitution with these amines is not clear cut. Isopropylamine gives both geminal and nongeminal products.[83] It is tempting to attribute the nongem products to the steric bulk of the isopropyl group, but it has been shown that the even bulkier t-butyl amine reacts by an exclusively geminal pathway[88], yielding one isomer each of the mono-, di-, and tetra-substituted products. No trisubstituted products were found.

Aromatic Amines: Aniline has been shown to react with $(NPCl_2)_3$ by a geminal reaction pathway.[89] This is not changed by the introduction of electron donating groups like p-methyl and p-methoxy or electron withdrawing groups like p-Cl, m-Cl, or m-CF_3.

Secondary Amines: The reaction of dimethylamine with $(NPCl_2)_3$ proceeds mainly by a nongeminal pathway. In ether solution or in a two-phase reaction in benzene with aqueous amine the trans nongem product predominates. The substitution patteren of the third amine appears to be solvent related. In ether the mixture of trisubstituted products is about half gem and half nongem.[90] With the two-phase reaction, the nongem trans was the major product.[91] Complete substitution of the chlorotrimer can be effected in refluxing xylene.[90]

Diethylamine will react with the chlorotrimer to form fully or partially substituted products. However the reaction with diethylamine is significantly slower than the reaction with dimethylamine. For example complete replacement of all six chlorines in the cyclic trimer requires 24hr at 150°C.[83,87] If di-sec-butylamine is used, over 95% of the starting phosphazene can be recovered, even under drastic reaction conditions.[83] The differences in dimethyl- and diethylamine can also be seen in their reactivities toward poly(dichlorophosphazene). While complete replacement of the chlorines with dimethylamine is easily accomplished[92], with diethylamine a maximum of 50% of the chlorines, one on each phosphorus, can be replaced.[93]

Cyclic Secondary Amines: The simplest cyclic amine is ethylene imine or aziridine C_2H_4NH. The reaction of this compound with $(NPCl_2)_3$ has been heavily investigated.[94,95,96] The reaction has been carried out in two-phase aquous systems or in aromatic or chlorinated hydrocarbon solvnts. All degrees of substitution from mono- to hexa- have been reported. The

bis-, tris-, and tetrakis-, substituted products have been shown to be exclusively geminal, by ^{31}P and ^{1}H nmr of the products themselves and their fully substituted dimethylamino derivatives.[95,96]

In the reaction of $(NPCl_2)_3$ with pyrrolidine (C_4H_8NH) in ether, a nongeminal pathway is followed. The cis and trans non-gem isomers are formed, with the cis isomer predominating by about 6 to 1.[97] Morpholine (OC_4H_8NH), reacts under the same conditions to give non-gem products in a similar ratio.[98] However, piperidine, $C_5H_{10}NH$), under the same conditions, yields the two non-gem isomers, with the trans predominating in a 34 to 1 ratio.[99] When the polymer reacts with piperidine, all of the chlorines may be replaced, in contrast to the behavior of diethylamine noted earlier.

Substitution by Diamines: The reaction products of $(NPCl_2)_3$ with simple aliphatic amines have been the subject of some controversy. Several types of products are possible from these reactions. Intramolecular substitution of both ends of the bifunctional nucleophile leads to the formation of spiro or ansa compounds as shown in Figure 15. Intermolecular substitution of both functionalities leads initially to the formation of a bino structure, or, if the reaction continues, to cyclolinear polymers. Original workers reported ansa type structures in which cyclization occurred between two phosphorus atoms of the same phosphazene ring.[100,101] More recently however, these compounds have been subjected to x-ray crystallography. It has been shown that the reaction with propanediamine yields only a spiro product[102] and that reaction with butanediamine yields

a mixture of a spiro molecule and a bino molecule, in which the same diamine joins two phosphazene rings.[103,104] Spiro molecules are also formed in the reaction of $(NPCl_2)_3$ witrh o-phenylenediamine, and with aminoalcohols such as ehtanolamine and N-methylethanolamine.[105]

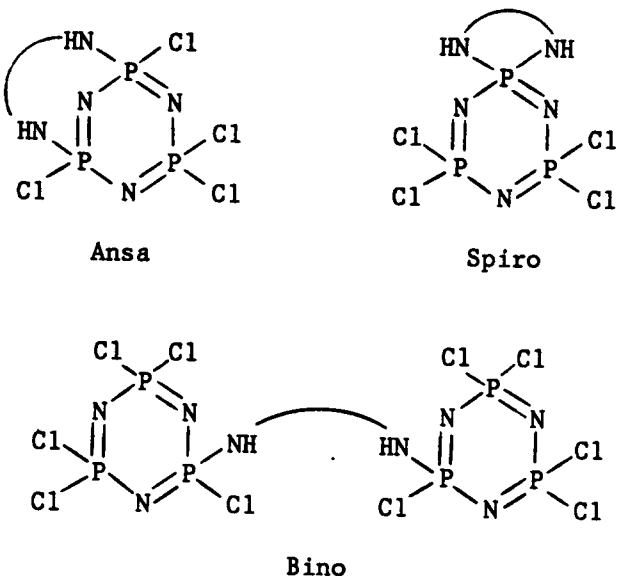


Figure 15. Possible products with bifunctional amines

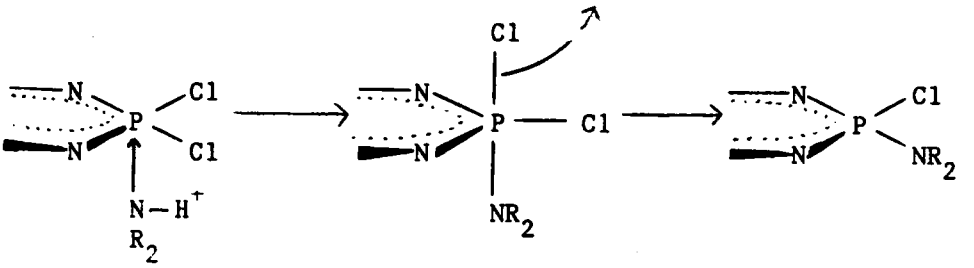
EFFECT OF PHOSPHORUS SUBSTITUENTS

Shaw and coworkers studied the effect of geminal- phenyl gruops on the reactivity of the remaining chlorines toward aminolysis. It was found that the reactivity toward a given amine decreased significantly in the order hexachloro > diphenyltetrachloro > tetraphenyldichloro.[106] The presence of gem-diphenyls did not change the geminal substitution pathway of ammonia.[121] Amino substituents also decrease the reactivity of the

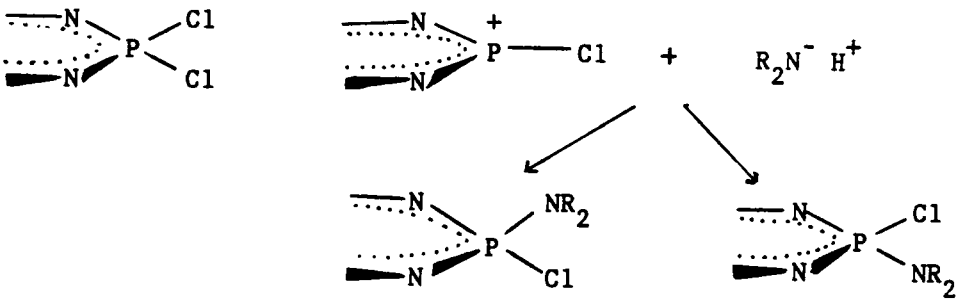
adjacent chlorine atoms. Shaw and coworkers showed that the monopiperidino derivative of the chlorotrimer underwent nongeminal substitution with a molecule of piperidine fifty times slower than $(NPCl_2)_3$, and that the dipiperidino derivative reacted 500 times slower than $(NPCl_2)_3$.[99]

POSSIBLE REACTION MECHANISMS

The two simplest mechanisms which may be followed in the aminolysis of cyclophosphazenes are a bimolecular, S_N2 type mechanism (Scheme 8), or an S_N1, self ionization mechanism involving a positively charged phosphorus, followed by rapid attack of the amine (Scheme 9). The pentavalent species formed in Scheme 8 may be either a transition state with more or less concerted bond making and breaking, or an actual trigonally bonded intermediate. It is likely that the pi system or the nonbonding pair of nitrogen would also be involved in the mechanism. As HCl is formed, protonation of the phospahazene may become important. The evidence favoring each of these mechanisms will be discussed below.



Scheme 8. The S_N2 mechanism



Scheme 9. The S_N1 mechanism

Evidence in favor of an S_N2 type mechanism can be derived from the Friedel-Crafts reaction of $(NPCl_2)_3$ and benzene with $AlCl_3$. This reaction is well established as an electrophilic substitution reaction, and is very likely an S_N1 reaction from the point of view of the phosphazene, with a phosphorus cation being formed. Multisubstitution by phenyl groups follows a geminal reaction pathway, with a phenyl group apparently stabilizing the adjacent phosphorus cation.[48] Ford and coworkers have shown that the Friedel-Crafts phenylation of 1,3 bisdimethylaminocyclotriphosphazene substitutes the chlorines geminal to the amino substituents.[50] If the Friedel-Crafts reaction follows an S_N1 mechanism, and both phenyl and dimethylamino groups direct incoming phenyls gem, then the aminolysis with dimethylamine would also follow a gem pathway if its mechanism was S_N1.

More evidence in favor of the S_N2 mechanism comes from kinetic measurements. The reactions of n-propylamine with fluoro-, chloro-, and bromo-, cyclic trimers and tetramers, in acetonitrile at 25°C were followed conductimetrically.[107] The rate determining step was found to be second order in all cases. Mixed second and third order kinetics were found for the substitution of the first chlorine in $(NPCl_2)_3$ by piperidine in toluene at 0°C On the other hand the competition reaction of aniline and ethanol for $(NPCl_2)_3$ showed similar amounts of anilino and ethoxy substituted products.[108] The authors interpreted this as evidence for appreciable S_N1 character in the reaction mechanism.

The evidence concerning the reaction pathways followed by the various amines is difficult to explain. Assuming that an amino group is electron donating in comparison to a chlorine atom, substitution of one chlorine atom by NR_2 might be expected to increase the electron density on the phosphorus it is bonded to, and decrease the reactivity of that phosphorus toward nucleophilic attack. Thus this simple electronic argument would suggest that electron donating groups should lead to non-gem products if the mechanism is S_N2. A steric argument would suggest that large groups would favor non-gem substitution due to crowding in the transition state as discussed earlier. On the other hand, geminal substitution would seem to be an indication that an S_N1 mechanism is being followed, with stabilization of the P cation by the amino substituent. The experimental evidence shows that the larger amines do tend to favor nongem substitution while the smaller ones like ammonia and aziridine favor geminal pathways. The deciding factors are not entirely steric however, since the large amines aniline, and even t-butylamine, favor the geminal pathway.

Two explanations of the tendency of some amines to follow geminal substitution pathways have been offered. Both Moeller[109] and Shaw[82] have suggested that the initial monoamino derivative may lose a proton to another amine molecule, with the resulting anion aiding in the loss of chloride ion in an S_N1 type process, as shown in Figure 16. Alternately, Shaw suggested that the amino substituent might coordinate with the incoming amine through its proton, and aid in geminal attack.[82]

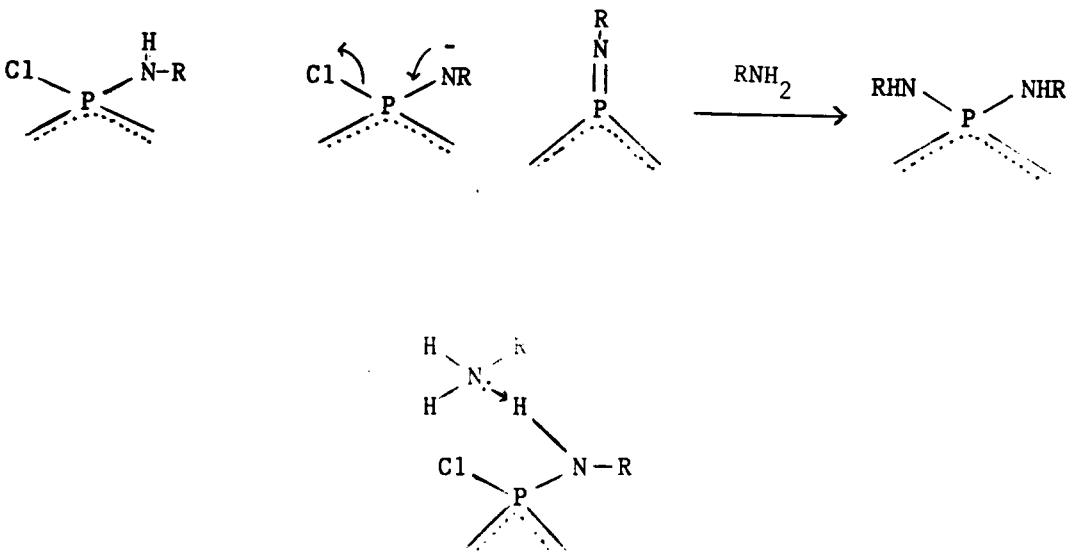


Figure 16. Explanations of geminal direction

However neither of these theories explains which amines should follow which pathway. No simple theory has been proposed which explains all of these facts. It is likely that a combination of steric and electronic effects is important.

ALKOXYPHOSPHAZENES: HISTORICAL REVIEW

A very large number of alkoxy and aryloxy substituted phosphazenes have been reported in the literature, second only to the amino derivatives. A general reaction is shown below.

$$N_3P_3Cl_6 + 6ROH \longrightarrow N_3P_3(OR)_6 + 6HCl \qquad (4)$$

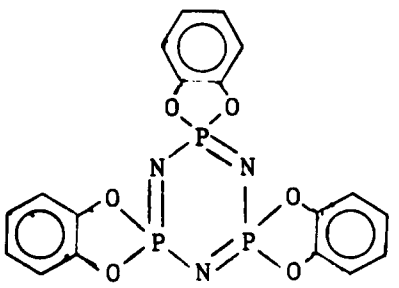
The alcohol may be almost any alcohol or phenol or their sulfur analogues. Usually the sodium salt rather than the free alcohol or phenol is employed, in which case NaCl is precipitated from the reaction mixture. This Na salt may be generated with Na metal, NaH, or sometimes NaOH in the case of phenols or strongly acidic alcohols. In cases where the free hydroxy compound is used as the nucleophile, a base such as triethylamine, pyridine, or sodium carbonate is used to react with the HCl generated in the course of the reaction. As with the amines, the gem or nongem pattern of substitution is of particular interest. Surprisingly, in spite of the large amount of research done concerning alkoxy and aryloxyphosphazenes, relatively little has been published regarding the effect of the presence of the first substituent on the site of reaction of the second nucleophile. However, the experimental results concerning the ease and degree of substitution are more consistent than those of the amines, and the mechanism is more clear cut. The following discussion will focus on those factors important in understanding the reactivity of chlorocyclotriphosphazenes toward oxygen nucleophiles.

INFLUENCE OF THE NUCLEOPHILE:

The structure of the hydroxy compounds lends itself to greater similarity in reactivities, since there is no reactive oxygen analogue of the secondary amines. Little difference can be found between the alkoxides and aryloxide ions towards the phosphazene ring. For instance both sodium isopropoxide and sodium phenoxide require refluxing terahydrofuran to force hexasubstitution.[110] The straight chain alkoxides methoxide, ethoxide and n-propoxide will fully substitute the ring at room temperature however, and mild conditions and controlled stoichiometry are necessary to synthesize partially substituted products. In substitution of the chloropolymer with alkoxides the temperature must be kept low to avoid degradation.[111]

On the subject of substitution pattern with alkoxides very little has been written. The Russian workers Sorokin and Latov reported the formation of a disubstituted product from the reaction of sodium n-butoxide with $(NPCl_2)_3$.[112] It was suggested, but not proved that this compound was nongeminally substituted. The question of substitution pattern in aryloxides is more well defined. it has been shown by several workers that $(NPCl_2)_3$ reacts with sodium phenoxide by a nongeminal manner in acetone, benzene or THF.[113,114,114] The characterizations were based upon the conversion of the phenoxychloro compounds to the phenoxyamino- or phenoxydimethylamino derivatives, followed by structural identification by ^1H nmr and melting points. The reaction using p-bromophenoxide was also shown to follow a nongeminal pathway.[113]

The reactions of chlorocyclophosphazenes with diols and diphenols sometimes leads to the formation of spiro products. For instance treatment of $(NPCl_2)_3$ with catechol (o-dihydroxybenzene) in the presence of triethylamine, sodium carbonate, or pyridine, yields the spiro product **37** in excellent yields.[116]



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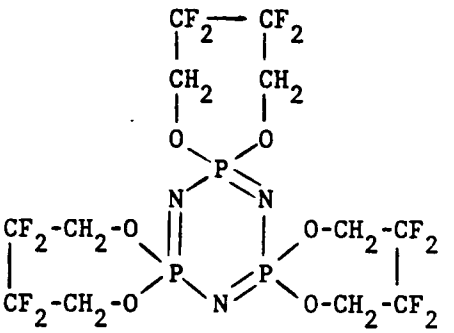
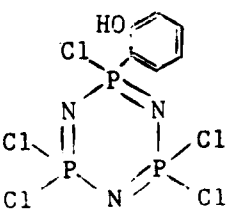


39

Figure 17. Dioxy-spiro compounds

Six and seven member spiro aryloxy systems can also be formed at phosphorus.[117] The ease of spiro ring closure is shown by the fact that no uncyclized products such as **38** could be found.[116]



38

Reaction of catechol with the higher cyclic species and with the polymer does not lead to spiro formation however. Instead the phosphazene skel-

eton is degraded to ammonium phosphorane salts.[116] Spirocyclic derivatives are also formed from the reactions of $(NPCl_2)_3$ with the sodium or triethylamine salts of flourinated propanediol and butanediol to form compounds such as **39**.[118] Less has been written concerning the simple aliphatic diols. Pornin reported that spiro compounds were formed in the reactions of 1,3-propanediol, and 1,4-butanediol with the chlorotrimer using pyridine as the base.[119] Matuszko and Chang found that at temperatures over 100°C the phosphazene acted as a dehydrating agent towards butanediol, forming the cyclic ether pyran (C_4H_8O).[120]

EFFECT OF PHOSPHORUS SUBSTITUENTS

The effect of substituents on the substitution of phospahzenes by alkoxides is the same as found in the reactions of the amines. For instance the reaction of gem-diphenyl- tetrachlorocyclotriphosphazene with phenoxide ion followed a nongeminal pathway, as did the same nucleophile with $(NPCl_2)_3$.[113] Thus the presence of gem-diphenyl groups does not change the nongeminal pathway of phenoxide or the geminal pathway of ammonia.[121]

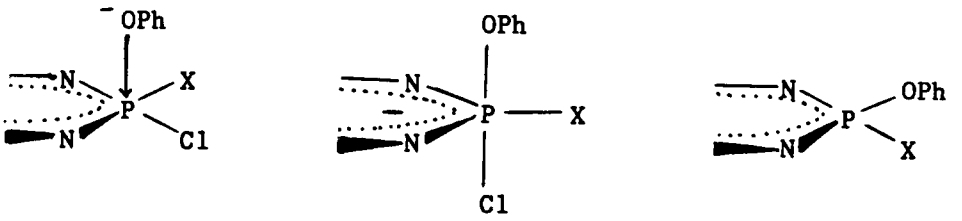
The presence of gem-diphenyl substituents also retards nucleophilic attack at adjacent PCl_2 groups by alkoxides and aryloxides. Fitzsimmons and coworkers studied the reaction of methoxide, ethoxide, n-propoxide and isopropoxide with phenylated cyclotriphosphazenes. They found that the order of ease of substitution was $(NPCl_2)_3$ > gem-$N_3P_3Ph_2Cl_4$ > gem-$N_3P_3Ph_4Cl_2$, the same order as found for substitutions by amines.[122]

REACTION MECHANISM

As in the amine reactions the mechanisms of these reactions could be either of the S_N1 or S_N2 types. The nucleophile may be either the neutral hydroxy compound or the anion. In cases where the sodium salt is used, the attacking nucleophile is undoubtedly the alkoxide or aryloxide anion rather than the free alcohol or phenol. In those cases where a chlorophosphazene is reacted with a neutral alcohol and a weak base such as triethylamine is present, the concentration of the anion is very low. However, Allcock has pointed out that the presence of triethylamine does speed the reaction, and reasons that the attacking nucleophile is still the alkoxide and not the free alcohol.[123]

A kinetic study of the reaction of $(NPCl_2)_3$ with alkoxides has been published by Sorokin and Latov.[112] Their evidence supports an S_N2 mechanism. They reported second order kinetics, first order in both phosphazene and alkoxide, and showed that when sodium ethoxide is the alkoxide, the attacking species is EtO^- and not EtONa.

Assuming that the mechanism is S_N2, explanations for the nongem substitution pathway followed by phenoxide and n-butoxide may be offered. This pattern may be most affected by either steric or electronic effects. Sterically the S_N2 intermediate or transition state is more crowded than the reactants, with 90°C between groups in the transition state and over 100° in the starting phosphazene. Assuming the phenoxy or butoxy groups to be larger than chlorine, transition state **40** is the more



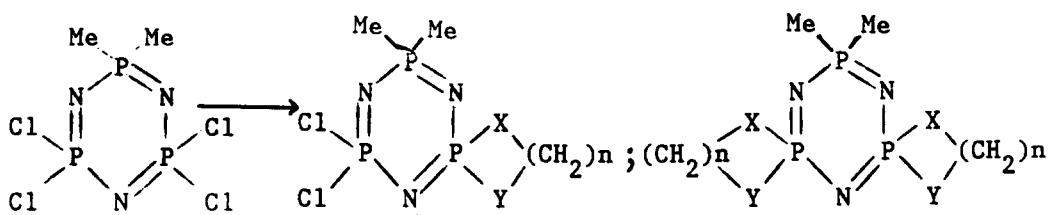
40 X = Cl
41 X = OPh

Figure 18. Transistion States in PhO^- substitution

stable of the two shown below and thus presents the lower activation energy. Electronically, nongem substitution would be the result of increased electron density at the oxygen-bearing phosphorus. It has been seen in the basicity and bond length data, that oxy substituents, especially the aryloxy groups, are not tremendously different from chlorines in their effect on the phosphazene ring. It would seem that if electronic effects were the main cause of the substitution pattern,the RO-P-CL and Cl-P-Cl centers would be similar enough that at least some gem substitution would occur. This would seem to be especially true of the poorly electron donating aryloxies, but it is in reactions with aryloxides that exclusive nongem substitution is best documented. Indeed the ease of cyclization of the spiro molecules indicates that there are no strong electronic restrictions against substitution gem to an oxy- substituent. It would appear then, that crowding in the S_N2 intermediate or transition state is the major factor in the nongem substitution pattern.

REACTIONS OF DIMETHYLCYCLOTRIPHOSPHAZENE WITH BIFUNCTIONAL NUCLEOPHILES: RESULTS

The nucleophilic substitution reactions of 1,1-dimethyl-3,3,5,5-tetraclorocyclotriphospahazene **36** with the bifunctional amines and alcohols should be comparable to those of the fully chlorinated cyclic trimer, since each requires an initial attack on a Cl-P-Cl unit. The sterics of the transition states or trigonal intermediates should be similar and the only differences should be due to the long range electronic effect of the methyl groups. Six of these reactions were found to lead to the formation of spiro products. These are shown with general characterization data in table 7. The ^{31}P nmr data are shown in Table 8, and ^{13}C nmr data are contained in Table 9.



36

42, X=Y=NH n=3
43, X=Y=NH n=4
44, X=NH Y=O n=3
46, X=Y=O n=3

45, X=NH Y=O n=3
47, X=Y=O n=3

Scheme 3

Table 7. Dimethyl Spiro Compounds

	Compound	% yield	mp ^{o}C
42,	$N_3P_3Cl_2Me_2(NHC_3H_6NH)$	75	182-183
43,	$N_3P_3Cl_2Me_2(NHC_4H_8NH)$	94	181-182
44,	$N_3P_3Cl_2Me_2(NHC_3H_6O)$	94	152-153
45,	$N_3P_3Me_2(NHC_3H_6O)_2$	37	>150(dec)
46,	$N_3P_3Cl_2(OC_3H_6O)$	92	197-198
47,	$N_3P_3Me_2(OC_3H_6O)_2$	96	209-210

1,3-Propanediamine: Typical of these reactions is that of the dimethyl phosphazene **36** with 1,3-propanediamine. With one equivalent of the diamine and two equivalents of triethylamine, or with two equivalents of the diamine, in methylene chloride at room temperature or at reflux there is the formation of a white crystalline solid, poorly soluble in hexane. The proton decoupled ^{31}P nmr spectrum of this compound is identifiable as an AMX spin system, indicative of three differently substituted P atoms. The ^{13}C nmr shows the P-CH_3 signals split into a doublet by the nearest P atom, and each of these is split into a multiplet by the remote P atoms. The ^{13}C signals of the three carbon chain of the diamine group occur as two different signals indicating a symmetrical bonding at both nitrogens. The structures which are consistent with these data are a spiro or a bino compound. An ansa linkage of the diamine would give a molecule with only two different P atoms and thus an AX_2 spin system in the ^{31}P nmr. The product can be shown to be the spiro one **42**, by its mass spectrum, which shows the molecular ion at 305 amu and a Cl_2 iosotope pattern. The lack of Cl_3 isotope patterns, or higher ones, is consistent with the other data in indicating that the bino structure is not correct.

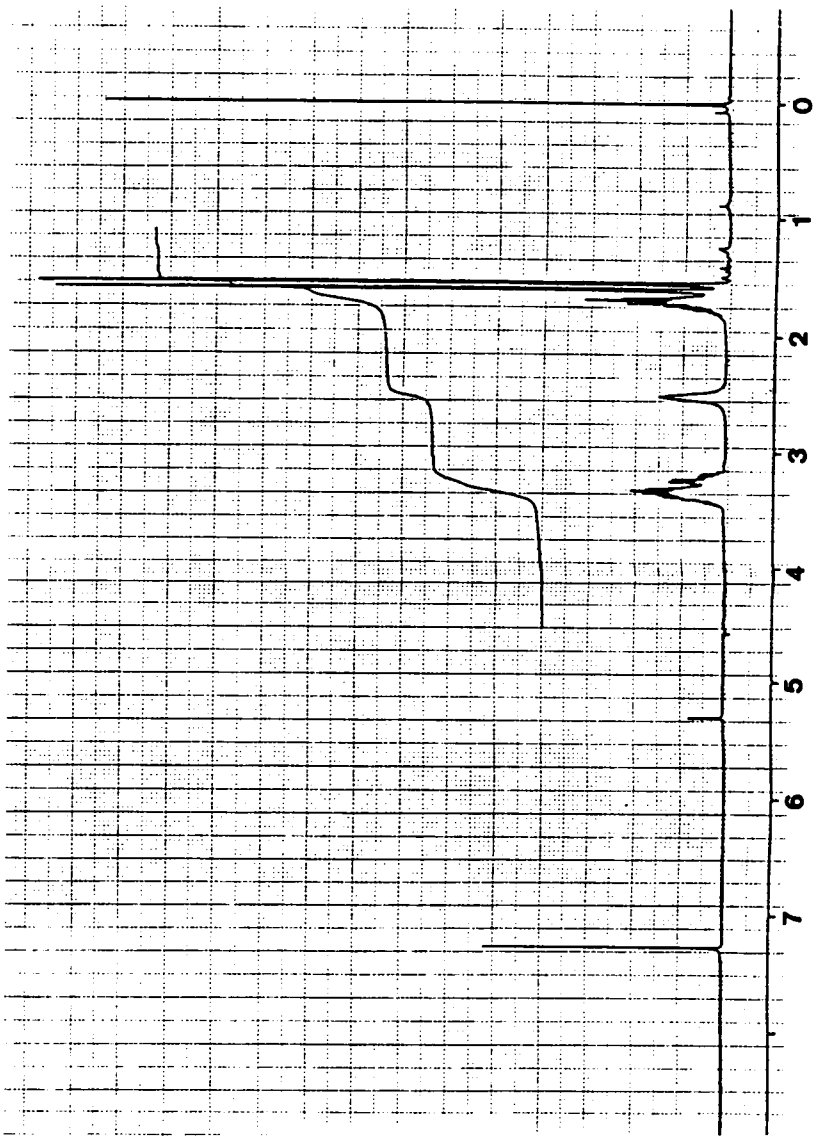
The ^{31}P nmr signals could be assigned by coupling to protons. In the coupled spectrum the upfield (10.8ppm) and downfield (33.8ppm) signals are broadened compared to the decoupled spectrum. The midfield signal (20.0ppm) is unchanged which shows it to be the PCl_2 phosphorus. The downfield signal is undoubtedly the dimethyl-phosphorus by analogy with the starting compound and other methylated cyclotriphosphazenes, all of

which show the methyl phosphorus signals below 30 ppm. The upfield signal then is assigned to the spirocyclic P atom.

In the ^1H nmr the P-NH-CH_2 region is strongly split but is quite asymmetric and appears to be two different signals. This is to be expected for the monospiro structure since the methylene protons of the diamine ligand are nonequivalent, being either on the chlorine side or the methyl side of the carbon chain. The integration of the spectrum is also consistent with the monospiro structure. Proton nmr is also useful in determining the presence of unreacted diamine, since upon bonding to phosphorus the N-CH_2 proton signal shifts from 2.7ppm to 3.1ppm and the splitting changes from a triplet to a strongly coupled multiplet. Figure 19 shows the 270 MHz ^1H nmr spectrum of this compound.

Refluxing a mixture of the dimethyl phosphazene with excess propanediamine in chloroform did not lead to any reaction at the remaining PCl_2 unit. The monospiro product was the only one isolated, even at the higher temperature. It is noteworthy that ^{31}P nmr spectra of incomplete reaction mixtures showed only the monospiro product and the unreacted dimethyl phosphazene.

1,4-Butanediamine: The reaction of the dimethyl phosophazene **36** with butanediamine proceeds in an analogous manner to the reaction with propanediamine. The sole product was identified as the monospiro compound **43**, on the basis of nmr and mass spectral data.



270 MHz ^{1}H NMR spectrum of compound 42.

Figure 19. ^{1}H NMR spectrum of compound **42**

The proton decoupled ^{31}P nmr spectrum of the product was identified as an AMX spin system, similar to that of compound **42**. Coupling to protons again identified the central resonance at, 21.7d, as belonging to the dichloro phosphorus atom. The spirocyclic P atom occured at 15.0 ppm, 4.2 ppm downfield of the corresponding atom in the propanediamine spiro molecule. The dimethyl phosphorus resonance occurred at 32.7ppm, slightly upfield of the corresponding atom in the three carbon spiro compound. The ^{31}P spectra of incomplete reaction mixtures was analogous to the propanediamine case, showing only the monospiro product and the unreacted phosphazene.

The ^{1}H nmr spectrum was also similar to that of the propanediamine spiro molecule. The doublet of multiplets corresponding to the P-CH_3 protons was easily identifiable, shifted slightly upfield of those in the starting phosphazene. These gave a readily obtained measure of the extent of reaction, or the efficiency of a recrystallization, since the signals of the product and the starting material were separated enough at 270MHz to allow an approximate integration.

The ^{13}C nmr spectrum was almost identical with that of the propanediamine product, showing the P-CH_3 doublet of multiplets and two different carbons in the diamine ligand. As would be expected, the signal corresponding to the central methylene carbons was larger than the corresponding signal in the propanediamino derivative.

The mass spectrum of the product showed the molecular ion at 321 amu and the expected Cl_2 isotope pattern, confirming the spiro structure.

Reaction of the dimethyl phosphazene **36** with excess butanediamine and higher temperatures failed to induce reaction at the remaining PCl_2 unit. Even with ten equivalents of the diamine in refluxing chloroform, only the monospiro product was formed. ^{31}P nmr spectra of incomplete reaction mixtures still showed only this product and the unreacted starting phosphazene.

3-Amino-1-propanol: The reaction of compound **36** with one equivalent of this reagent in methylene chloride at room temperature or $0^{o}C$ in the presence of triethylamine also leads to the formation of a monospiro product **44** as characterized by nmr and mass spectral data. Once again the proton decoupled ^{31}P spectrum was easily identified as an AMX spin system, indicative of three different P atoms. The midfield resonance of the three was again shown to be the dichloro phosphorus, since it did not broaden upon coupling to protons. The dimethyl phsphorus signal was at 35.3 ppm, 1.5 and 2.6ppm downfield from the dimethyl phosphorus atoms in the propanediamine and butanediamine spiro compounds respectively. The spiro P resonance was at 10.8ppm, resembling that of the propanediamine spiro more than the butanediamine, indicating the importance of ring size on ^{31}P chemical shifts. As in the case of both of the diamines, ^{31}P nmr spectra of incomplete reaction mixtures showed only the monospiro product when the reaction mixture had been kept below room temperature. At room temperature, however a small amount of the bis-spiro product **45**

can be seen to form in the ^{31}P nmr spectrum. In refluxing chloroform the bis-spiro product **45** was formed as a pair of stereoisomers in moderate yield.

The ^{1}H nmr spectrum of the monospiro product **44** is different from those of the diamino spiro compounds since the methylene group next to the nitrogen is different from the methylene group next to the oxygen. The signals for the protons on these carbons are informative. In the unreacted aminoalcohol, the protons on the methylene unit next to the nitrogen show up as a triplet at 2.7ppm. The methylene protons next to the oxygen atom also show a triplet, at 3.6ppm. Upon bonding either end of the bifunctional nucleophile to phosphorus, the signal for the methylene protons nearest that end undergoes a downfield shift and an increase in splitting. The ^{1}H nmr for the monospiro product shows the N-CH_2 proton signal at 3.1ppm, and the O-CH_2 signal at 4.1. Both signals show the coupling to phosphorus as well as the downfield shift, indicating that the attack of the second end of the bifunctional nucleophile has indeed occurred. Further evidence of this was given by the ir spectrum, which showed an N-H stretch but was lacking the O-H stretch found in the unreacted aminoalcohol. As in the diamino spiro molecules the protons on one side of the carbon chain are nonequivalent with the ones on the other side. The signals for both sets of methylene protons nearest phosphorus show increased splitting due to this.

The ^{13}C nmr data were also consistent with a monospiro structure. The signals corresponding to the N-methylene and the O-methylene carbons both showed the downfield shift and coupling to phosphorus expected.

The mass spectral data indicate that both the nitrogen and oxygen are bonded to the same P atom. The molecular ion at 304 amu is clearly visible, along with a Cl_2 isotope pattern. If the compound were a bino structure isotope patterns would reveal at least three chlorines, even if only fragments containing one phosphazene ring were seen in the spectrum.

The ^{31}P nmr spectrum of the bis-spiro product **45** consisted of a pair of overlapping AX_2 patterns as would be expected for the bis-spiro structure. The ^{1}H spectrum was very similar to that of the monospiro product **44** except for the integration of the signals. The ^{13}C nmr spectrum was also almost identical with that of **44**. The bis-spiro structure was shown by the mass spectrum, which showed a prominent signal for the molecular ion at 311 amu with no chlorine isotope pattern.

1,3-Propanediol: The reaction of the dimethyl phosphazene **36** with the sodium salt of propanediol at $0^{\circ}C$ leads to the formation of the monospiro derivative **46**. As in the monospiro compounds discussed earlier, the ^{31}P nmr spectrum was easily identified as an AMX system. Once again the midfield resonance could be assigned to the dichloro-phosphorus upon coupling to protons. The spiro phosphorus signal occurred at 5.3ppm, the furthest upfield of the compounds yet discussed. The dimethyl-phosphorus

is further downfield than any yet discussed, at 36.7ppm. Incomplete reaction mixtures once again showed only the monospiro product and the unreacted starting phosphazene in the ^{31}P nmr.

The proton nmr showed the O-methylene protons as a highly coupled signal around 4.45d. The signal appeared as two symmetric halves, each consisting of about six lines. This is shifted downfield and split from the unreacted hydroxyl compound indicating that both ends of the diol had reacted, and that both were in the same electronic environment. The splitting of the signal into two halves is similar to the behavior of the previously discussed spiro compounds. This nonequivalency is expected for the spiro structure since the protons on one side of the carbon chain are closer to a PCl_2 group, and the protons on the other side of the carbon chain are closer to a $P(CH_3)_2$ group. The protons on the central methylene unit were also seen to be nonequivalent, but less so than the protons nearer the oxygen. The signal due to the methyl groups was slightly more complex than the doublet of triplets seen in the proton nmr of the starting dimethyl phosphazene, and was different enough to allow both materials to be identified when present in the same reaction mixture.

The ^{13}C nmr indicated that there were two different types of carbons in the propanediol chain, consistent with spiro formation.

The mass spectrum showed the molecular ion at 309 with a Cl_2 isotope pattern. This is consistent along with the nmr data in indicating the monospiro structure.

When the dimethyl phosphazene **36** is reacted with two equivalents of propanediol which has been previously reacted with excess NaH, in refluxing THF, a different compound is isolated. The ^{31}P nmr spectrum for this product is identifiable as an AX_2 pattern. The dimethyl phosphorus signal, at 35.2, was the triplet, while the doublet was at 11.9 ppm . The splitting indicates that both of the original PCl_2 units have been symmetrically substituted. The ^{13}C nmr spectrum showed signals at almost identical chemical shift values to the monospiro product **46**, but with smaller coupling constants. The presence of only two types of carbons, other than the $P(CH_3)$ groups, along with the ^{31}P nmr data suggested a bis-spiro product, **47**. The ^{1}H nmr was consistent with this structure. THe region 4.40-4.50d showed a highly coupled signal, symmetric in two halves, similar to the same region in the spectrum of the mono- spiro compound. The $O-CH_2$ protons giving rise to these signals were apparently more equivalent, since the halves of the signal were closer together, than in the mono-spiro compound. Conversely, the signal corresponding to the central methylene protons was split into two halves to a greater degree than the corresponding signal in the spectrum of the monospiro compound.

Table 8. ^{31}P NMR Data for Dimethyl Spiro Compounds

Compound	$P(CH_3)_2$	PCl_2	PXY	J_{AB}	J_{AC}	J_{BC}
		(ppm)			(Hz)	
42	33.8	20.0	10.8	20	20	32
43	32.7	21.7	15.0	20	15	40
44	35.3	20.5	10.0	14.5	22.1	31.6
45	34.0	-	15.7	21.5	-	-
	34.1	-	15.8	20.5	-	-
46	36.5	21.7	5.3	10.2	30.7	45.3
47	35.2	-	11.9	30.7	-	-

Table 9. ^{13}C NMR Data for Dimethyl Spiro Compounds

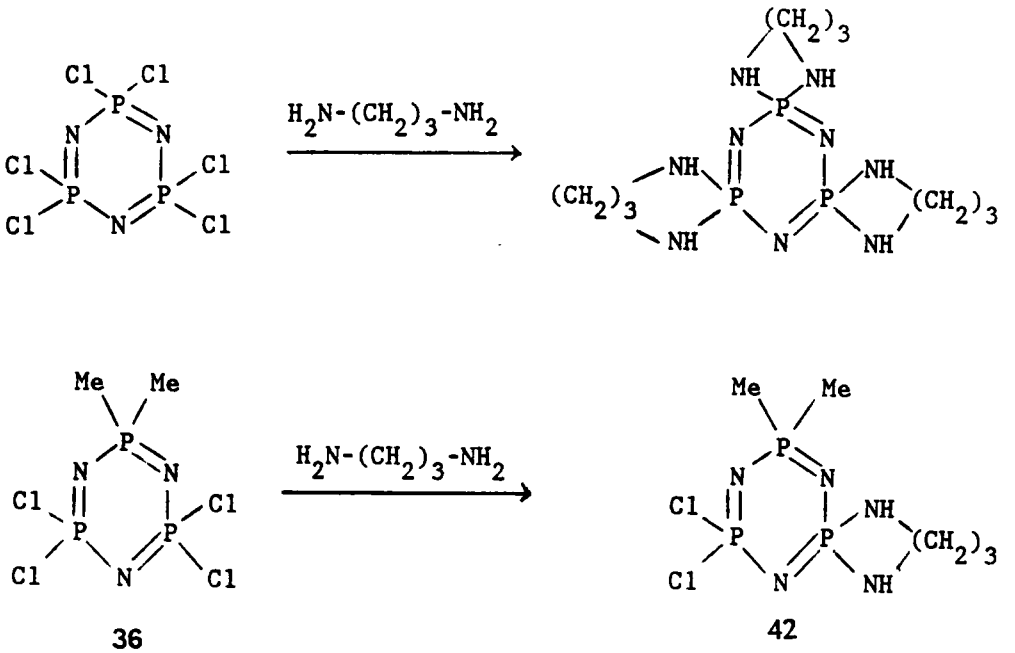
	P-X-C	P-X-C-C	P-C	J_{PXC}	J_{PXCC}	J_{PC} (J_{PNPC})
		(ppm)			(Hz)	
42	40.9d	26.1d	21.5d,t	3.5	6.1	94.6 (3.6)
43	40.3s	31.8s	21.4d	-	-	94.5
44	67.1d 41.2d	26.0d	21.4d,t	7.2 3.5	6.1	95 (4)
45						
46	67.0d	25.9d	21.3d,t	6.3	7.1	95.2 (3.7)
47	66.1d	26.0t	21.5d,t	2.3	3.5	95.6 (3.7)

DISCUSSION OF DIMETHYL REACTIONS

The effect of the geminal methyl groups on the reactivity of the remaining PCl_2 unit can most easily be seen in the reaction with neutral alcohols. The ^{31}P nmr spectra of the dimethyl phosphazene **36** after 5hr in ethanol solution showed no reaction of the phosphazene. Even after addition of triethylamine and refluxing for 2hr no reaction was observed. On the other hand hexachlorocyclotriphosphazene undergoes a variety of complex reactions in ethanol solution. The ^{31}P spectrum after 4hr shows the presence of unreacted trimer and two major products giving rise to AX_2 spin systems, one larger than the other. After 8hr the patterns are more even in size, and a variety of other signals have appeared. After 24 hr there are no identifiable coupling patterns but rather numerous small signals from -5 to about 40ppm. The two AX_2 patterns observable early in the reaction may be the mono- and di-substituted products. If so the ^{31}P spectrum shows the substitution pattern to be geminal since both AX_2 patterns show the triplet upfield and the doublet downfield. In nongem substitution the disubstituted product would show a mirror image AX_2 pattern to the mono substituted product. It is possible that the reactions of chlorophosphazenes with neutral alcohols could become synthetically useful for the preparation of partially substituted products.

The geminal methyl groups can thus be seen to decrease the reactivity of a phosphazene ring toward nucleophilic attack. This is consistent with the effect of geminal phenyl groups on reactions with amines and alkoxides

discussed earlier in the literature review. This decreased reactivity of the adjacent Cl-P-Cl unit can also be seen in the reactions of the dimethyl phosphazene **36** with the bifunctional amines. For instance the dimethyl phosphazene reacts with the three and four carbon diamines to form spirocycles at only one of the remaining two PCl_2 units. In comparison $(NPCl_2)_3$ will substitute with 3 equivalents of propanediamine to form the tris-spiro product, as illustrated below in scheme 9.



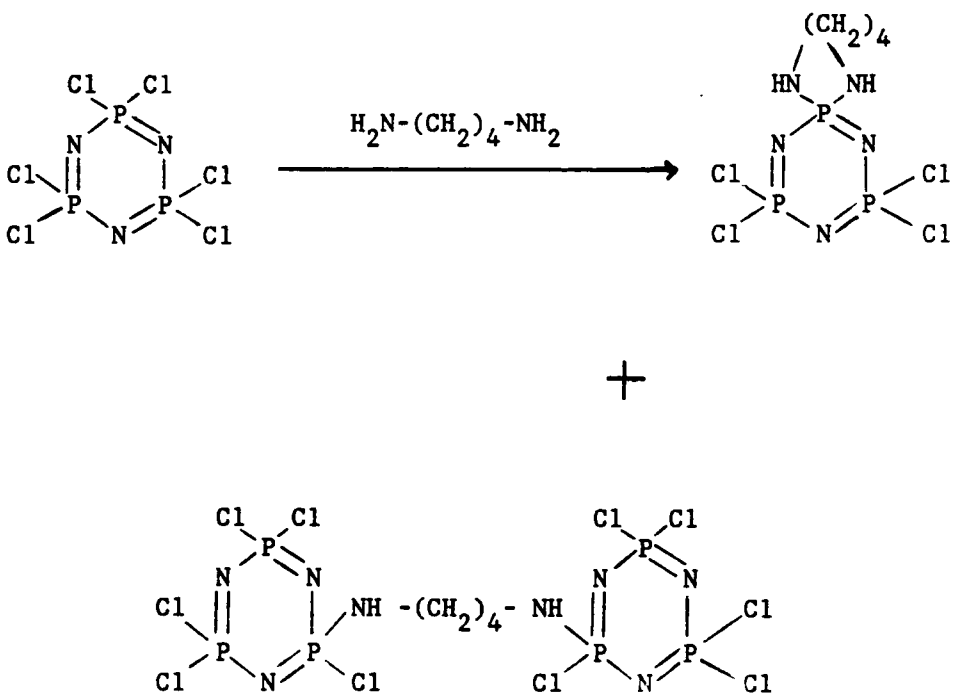
36 **42**

Scheme 9.

Thus the final PCl_2 units of compound **42** and the bis-spiro propanediamine compound are substantially different in their reactivities towards amines. That is, the reactivity of the third PCl_2 is significantly lower when the first two are substituted with two gem-methyls and two gem-aminos, than when four amino substituents are present. Since both the methyls and aminos decrease the reactivity of adjacent PCl_2 units toward

nucleophilic attack, both are acting as electron donors to that position, with the methyl group the stronger of the two.

Another difference can be seen in the reactions with butanediamine. The hexachloro phosphazene has been shown to form both the spiro compound and the bino compound in this



Scheme 10.

reaction (Scheme 10). In the reaction of the dimethylphosphazene there is no bino compound formed. The explanation can be based on electrophilicity of the two phosphazene rings. The formation of a bino compound in the reaction with a phosphazene requires nucleophilic attack on a

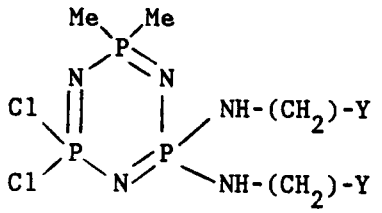
second phosphazene molecule. In the case of the hexachloro phosphazene the reactivity of a PCl on this second phosphazene must be similar to the one which leads to spiro formation. This is not the case with the dimethylphosphazene since no bino product is formed. The formation of the spiro molecule is indication that the presence of one amino substituent activates the geminal chlorine towards substitution, opposite the effect that aminos have on the adjacent chlorines. If the dimethyl tetrachloro phosphazene is so unreactive as to not permit bino formation, and aminos are assumed to decrease the reactivity of phosphazenes towards amines also, then reaction to form the spiro ring would be even less favored electronically than bino formation. The bino formation in the reaction with the hexachloro phosphazene shows that spiro formation in the dimethyl case is not simply a matter of entropically favored ring closure.

Further insight into this effect can be seen in the reaction of the dimethyl phosphazene **36** with 3-amino-1-propanol. In contrast to the diamino monospiro molecules which fail to undergo further reaction, bis-spiro compounds can be formed with propanolamine. Assuming that the amine functionality is the first to substitute, which is consistent with evidence to be discussed later, the initial nucleophilic attack on the third phosphorus must be due either to an increased nucleophilicity of the amine group of propanolamine or a decreased electrophilicity of the phosphazene, compared to the diamine case. Since the nitrogen lone pair in the aminoalcohol is likely to be engaged in intra-or intermolecular hhydrogen bonding stronger than that of the diamine, its reactivity, if anything, would be less than that of the diamine nitrogen. This suggests that the

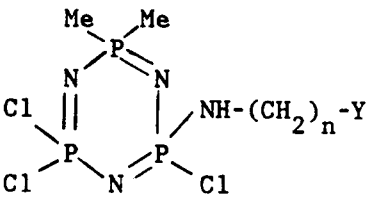
electrophilicity of the phosphazene ring is the deciding factor. Apparently there is a reactivity enhancement of a PCl_2 group adjacent to a $P(CH_3)_2$ unit and an N-P-N unit over a PCl_2 which is adjacent to a $P(CH_3)_2$ and an O-P-N unit. The added electron donation of a nitrogen atom over an oxygen atom is enough to negate the reactivity of the final PCl_2 unit towards attack by another amino molecule. The fact that the final spirocyclic ring forms with attack by the weakly nucleophilic alcohol on the pentasubstituted phosphazene is further evidence of geminal activation by nitrogen.

Another factor worthy of note comes from an examination of the diamine and the 1 to 1 propanolamine reactions prior to completion. In each of these reactions aliquots taken at various stages of reaction showed only the monospiro products and the unreacted dimethyl phosphazene in the ^{31}P nmr spectrum. No uncyclized products such as **48** were observed, nor were any disubstituted products such as **49** Apparently the second nucleophilic attack, that which closes the spiro ring, is facile, and cyclization takes place faster than attack of a second amino molecule.

The facile nature of the spiro cyclization is particularly apparent in the reaction with 3-amino-1-propanol. Here the ring closing step involves the atack of an oxygen containg species, either the free alcohol or the alkoxide ion which could be formed in low concentrations, with the amine end of the propanolamine molecule or triethylamine abstracting the proton. In view of the fact that uncyclized species such as **48** (Y=OH) are not formed, as would



48



49

be expected in an equilibrium between the free alcohol and the alkoxide, it would seem that ionization to the alkoxide is not necessary, and that cyclization occurs by attack of the free alcohol. This is surprising in view of the fact that the dimethyl phosphazene did not react when dissolved in ethanol. Once again we see a situation in which an amino substituent, which has been shown to decrease the reactivity of adjacent chlorines toward nucleophilic substitution, activates the chlorine geminal to itself, at least when entropically favorable, enough to allow substitution by the weakly nucleophilic neutral alcohol. This activation of the geminal chlorine is also seen in the absence of any ansa products.

The difference in the ease of spirocyclization to rings of six and seven members can be seen in the reaction of 4-amino-1-butanol with the dimethyl phosphazene **36**. While the reaction with the four carbon diamine proceeded smoothly to the spiro product, this was not the case with the four carbon aminoalcohol. Nmr data of a typical reaction mixture showed a variety of products. The ^{1}H nmr showed a broad triplet around 3.6 indicating one or more species bearing free OH groups. This was confirmed by the ir

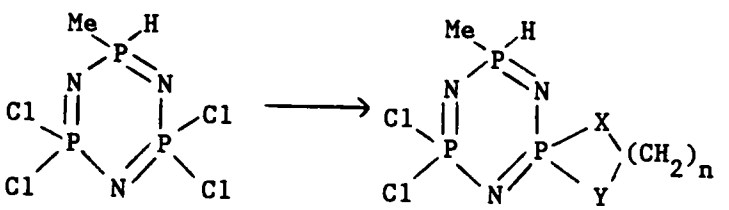
spectrum. The ^{31}P nmr showed several similar products, possibly multi-substituted products.

The reactions of the alkoxide of 1,3-propanediol with **36** are consistent with the results discussed above. Reaction of one equivalent of the diol, previosly reacted with 2.5eq of NaH, with the phosphazene at 0°C or room temperature yielded the monospiro derivative **46**. With two equivalents of the diol, treated in the same manner, in refluxing THF, the bis spiro product **47** was formed. The monospiro product **46** would be expected to be more electrophilic than the diamino or aminoalcohol spiro compounds due to the relative electron withdrawal of oxygen than nitrogen. Attack at the third PCl_2 unit by the highly nucleophilic alkoxide ion is not surprising. It is likely that the species which reacts to close the spiro rings is also the alkoxide ion, since reaction mixtures still contained live NaH after completion. It is thus difficult to gauge whether oxygen activates a geminal chlorine as the nitrogen appears to. The lack of ansa products or bino products may indicate a geminal activation by oxygen or it may just illustrate the ease of cyclization to six membered rings.

This latter possibility is supported by the reaction of the alkoxide of 1,4-butanediol with the dimethyl phosphazene **36**. In the reaction with one equivalent of the diol, previously reacted with NaH, at 0°C in THF, there was only partial cyclization to the monospiro compound. Proton nmr and ir data indicated the presence of free hydroxy compounds in the reaction mixture.

REACTIONS OF THE 1-METHYL-1-HYDRIDO COMPOUND: RESULTS

The reactions of 1 methyl 1 hydrido 3,3,5,5 tetrachlorocyclotriphosphazene **35** with the diamines and the and the aminoalcohols were followed by ^{31}P nmr and were found to parallel those of the dimethyl phosphazene **36** closely. Table 10 shows the ^{31}P nmr data for the compounds formed.



35

50, X=Y=NH n=3
51, X=Y=NH n=4
52, X=NH, Y=O, n=3

Scheme 11.

1,3-Diaminopropane: The reaction of the three carbon diamine with the methyl-hydrido compound **35** led to the formation of a monospiro derivative **50** as indicated by ^{31}P nmr and mass spectral data. The proton decoupled ^{31}P spectrum was identified as an AMX spin system. The downfield signal was a doublet of doublets at 20.90ppm (J=24Hz, 16Hz) in the usual region of a PCl_2 phosphorus. The upfield doublet of doublets (J=24Hz, 6Hz) was at 10.74ppm and was assigned to the the spiro-NH-P-NH, by analogy with the dimethyl-propanediamine spiro compound **42**, which showed the spiro

phosphorus at 10.8ppm. The remaining signal, at 12.4ppm was broad and poorly resolved but could also be recognized as a doublet of doublets (J=16Hz, 16Hz). This signal is in the range of the CH3-P-H signal from the starting phosphazene **35** at 13ppm. Removal of the proton decoupler showed this assignment to be correct. The upfield and downfield signals did not move while the CH3-P-H signal was split into two doublets of doublets. The large splitting, due to the direct P-H bond was 533Hz. Each of the two halves of this signal showed much smaller splittings (J=36Hz, 18Hz). The downfield signal was positively assigned to the PCl2 since it did not broaden upon coupling to protons. The proton decoupled and coupled ^{31}P nmr spectra are shown in Figures 21 and 22. The mass spectrum indicated that the monospiro structure of the product was correct. The molecular ion at the calculated value of 293 amu was quite apparent, with the expected Cl2 isotope pattern. A smaller signal at 292 (Cl2) corresponded to the loss of H form the molecular ion. Also visible the spectrum were the loss of the CH3 group and the loss of one and two chlorines.

Attempted chlorination: The monospiro hydrido compopund was reacted with Cl2 in 30% CH2Cl2 and 70% CCl4, in an attempt to replace the P-H with a chlorine atom. The ^{31}P and ^{1}H nmr spectra indicate the formation of a mixture of products which was not separated. The ^{31}P nmr spectrum showed that the signal at 12.38ppm which was due to the CH3-P-H was gone and three signals above 40ppm appeared. These were at 43.3, 44.3, and 45.5ppm. These signals are in the normal range of a CH3-P-Cl, indicating the formation of three different compounds containing that unit. There

were also three signals at 24.8, 25.8, and 27.3ppm, probably due to different PCl_2 groups. The final signal was at 19.0ppm, and had the appearence of a poorly resolved doublet of doublets, probably due to the spiro phosphorus. The ^1H nmr also indicated the presence of a mixture, with at least two different doublet of triplets centered at 2.12d indicating at least two different CH_3-P-Cl groups. There were two different unresolved multiplets, at 3.32d and 3.60d, probably due to P-N-CH_2 groups. A signal at 1.9d was probably due to the central methylene group of the three carbon chain of the diamine. Interestingly, there was no change in the spectrum upon treatment with D_2O.

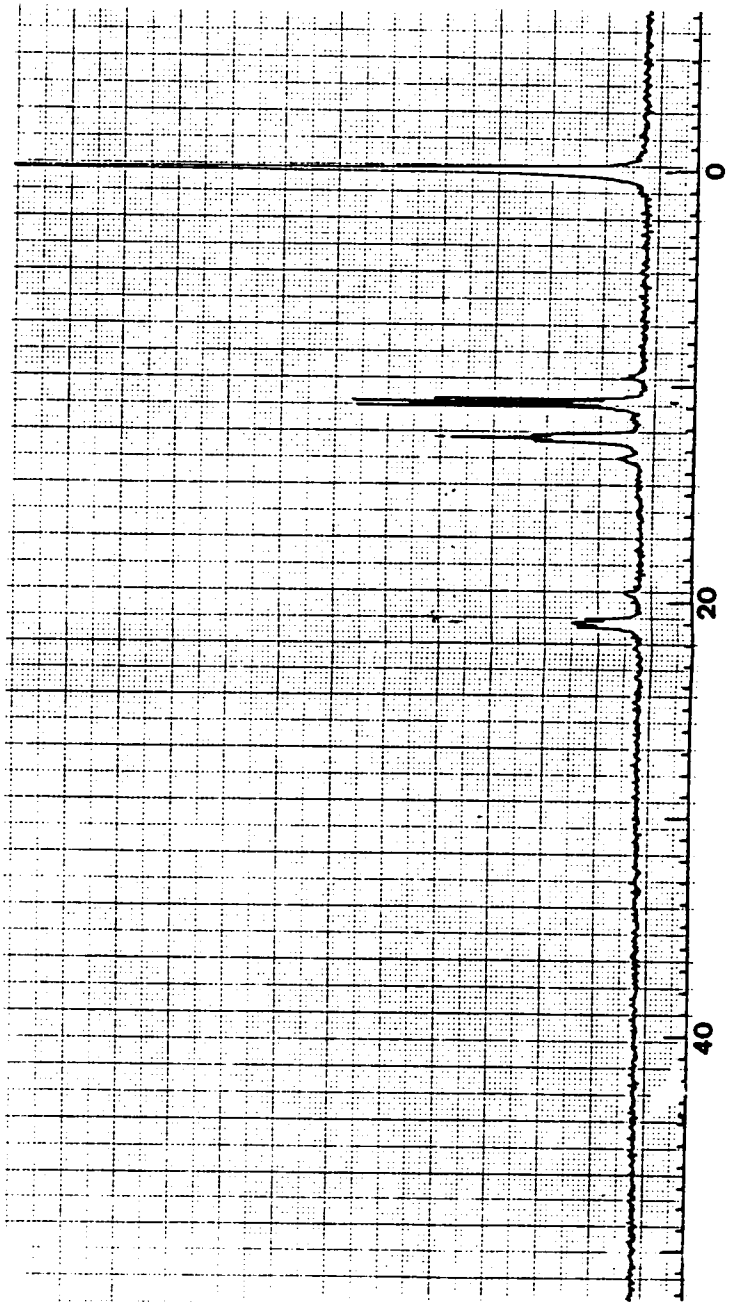
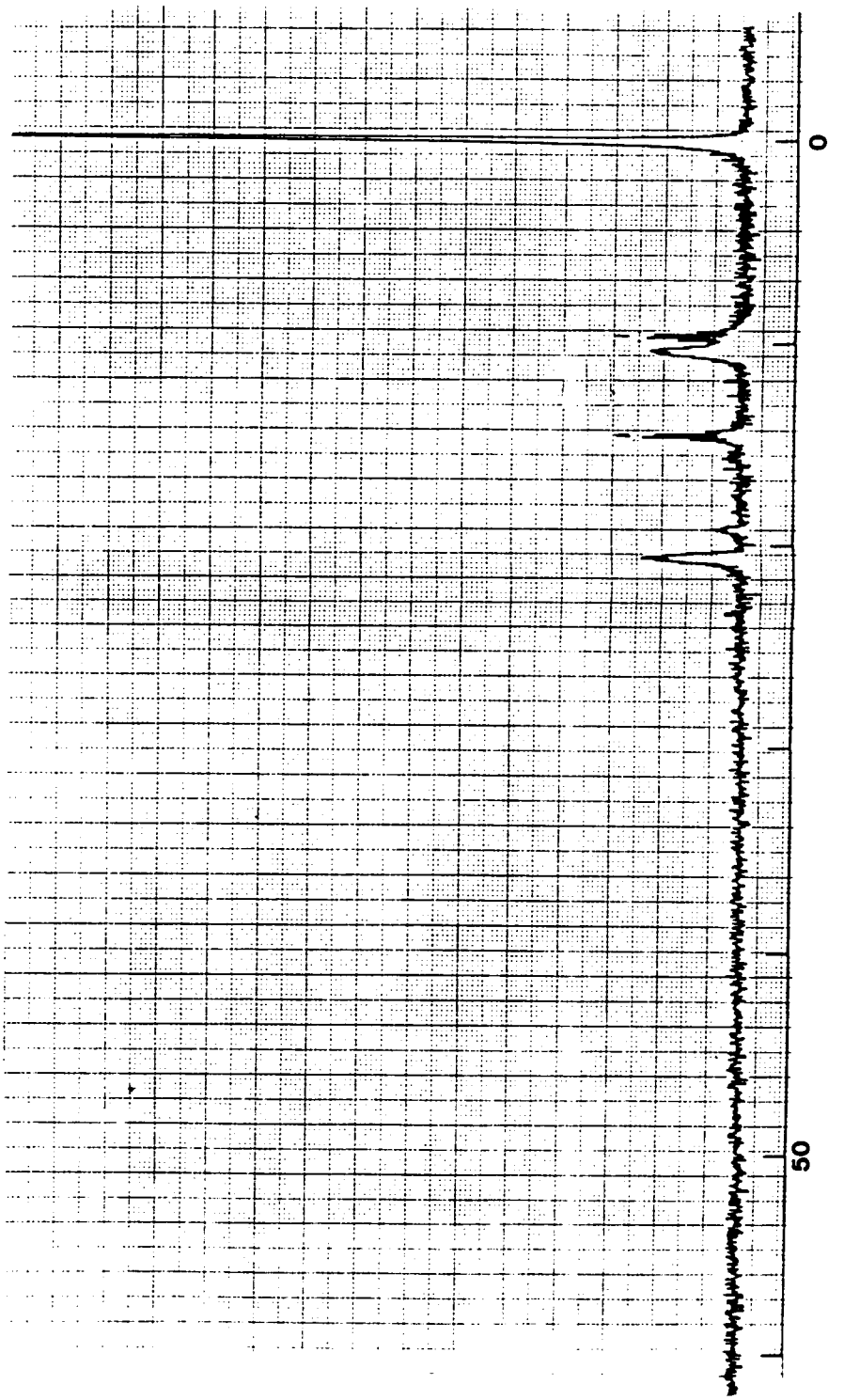


Figure 20. Proton decoupled ^{31}P NMR spectrum of compound **50**



270 MHz ^{31}P NMR spectrum (proton coupled) of compound **50**

Figure 21. Proton coupled ^{31}P NMR spectrum of compound **50**

1,4-Diaminobutane: The four carbon diamine also reacts with the methyl-hydrido phosphazene **35** to yield a product which was identified as the monospiro compound **51** from ^{31}P nmr and mass spectral data. The ^{31}P spectrum was seen to be an AMX spin system. The downfield signal was at 22.35ppm and was assigned to the PCl_2 group on the basis of normal PCl_2 chemical shifts. This signal appeared as a doublet of doublets (J=32Hz, 17Hz). The upfield signal was at 12.13ppm and broadened, suggeating it to be the CH_3-P-H phosphorus. Further evidence for this assignment comes from the chemical shift of the third signal. This is a doublet of doublets (J=32Hz,15Hz) at 15.03ppm. The spiro N-P-N phosphorus in the dimethyl butanediamine spiro compound came at 15.0ppm. In the spiro compounds of both the dimethyl and the methyl-hydrido phosphazenes the three carbon diamine gives a chemical shift of about 10ppm for the spiro phosphorus while the four carbon diamine gives a chemical shift of about 15ppm for the spiro phosphorus. This is consistent with the tendency for phosphorus chemical shifts to be very dependent on ring size, and is indication of the presence of the spiro rings in these products. The mass spectrum for compound **51** was also consistent with the spiro structure. The molecular ion was present at the calculated value of 307 amu with the expected Cl_2 isotope pattern. The loss of one and two chlorines could also be seen.

Attempted chlorination: As in the case of the three carbon diamino spiro compound, the four carbon analogue was treated with Cl_2 in CH_2Cl_2/CCl_4 in an attemt to change the P-H into a P-Cl. Again a mixture of products was seen to form, according to ^{31}P and ^{1}H nmr data. The ^{31}P spectrum was poorly resolved but indicated two different types of CH_3-P-Cl groups at

43.5ppm and 42.2ppm. The signal at 12.1ppm in the spectrum of the starting material was gone, indicating that the assignment of this signal to CH_3-P-H was correct. The chmical shift region between 20 and 30ppm showed at least four different signals, all very strongly coupled but with unrecognizable splitting patterns. A signal at 14.9ppm was visible, probably due to the spiro P atom. The ^1H nmr spectrum was also poorly resolved, showing broad humps around 2.16d, 3.12d, and 1.70d.

3-amino-1-propanol: The reaction of the methyl-hydrido phosphazene **35** with the three carbon terminal aminoalcohol led the the formation of a mono- spiro compound **52** Both stereoisomers were formed, as indicated by the proton decoupled ^{31}P nmr spectrum, shown in Figure 22. The PCl_2 phosphorus signal, for example, appeared at 21.4ppm as an overlapping pair of doublets of doublets, with seven lines visible, (J=23Hz, 20Hz). The signal at 10.1ppm also appeared as a an overlapping pair of doublets of doublets, (J=23Hz, 30Hz) with a total of five lines visible. This signal was at virtually the same shift found for the other spiro compounds containing a six membered spirocyclic ring. The midfield signals were the most separated fo the three as might be expected for the CH_3-P-H phosphorus. Since the H atom may be cis or trans to the nitrogen of the spiro ring. This phosphorus was seen as a two separated doublets of doublets, one centered at 13.95ppm (J=30Hz, 20Hz) and the other at 13.30ppm (J=30Hz, 20Hz). These chemical shifts are similar to the CH_3-P-H phosphorus in the starting phosphazene, indicating that the assignment is correct. The mass spectrum indicated the presence of the monospiro product. The molecular ion was visible at the calculated value of 294 amu, two chlorines

in the molecule. An ion formed by the loss of the CH_3 group was also seen in the spectrum, as in the other spiro compounds of the methyl-hydrido phosphazene.

Atempted chlorination: As in the case of the diamino-spiro compounds, the aminoalcohol analogue was treated with Cl_2 in $CHCl_2/CCl_4$. Again a mixture of compounds was formed as indicated by ^{31}P and ^1H nmr data. The ^{31}P spectrum was similar to the diamino cases, but the spectrum was more highly resolved. There were two signals in the CH_3-P-Cl region, at 45.1ppm (J=20Hz, 12Hz), and at 44.5ppm (J=23Hz, 16Hz). There were two signals in the PCl_2 region also, at 26.7ppm (J=37Hz, 12Hz) and at 26.0ppm (J=37Hz, 16Hz). There was also a signal at 15.7ppm, which was poorly resolved. The ^1H nmr was also poorly resolved. There were broad humps at 4.4d and 3.4d, in the range expected for P-N-CH_2 and P-O-CH_2 groups. The region expected for the CH_3-P-Cl protons, around 2.1d, was complex, as was the the area around 1.8d, corresponding to the central CH_2 protons. Treatment with D_2O made no change in the ^1H nmr spectrum, as was the case with the chlorination of compound **50**.

4-Amino-1-butanol: The reaction of the four carbon aminoalcohol with the methyl- hydrido compound **35** led to the formation of a mixture of products. The ^{31}P nmr spectrum showed broad and strongly split signals in the chemical shift ranges expected for the mono-spiro compound. There were signals at 21.5ppm, 22.0ppm, and 23.0ppm, which were not fully identifiable as doublets of doublets, but which were probably due to PCl_2 groups. A signal was seen at 12.5ppm, again with no positively identifiable

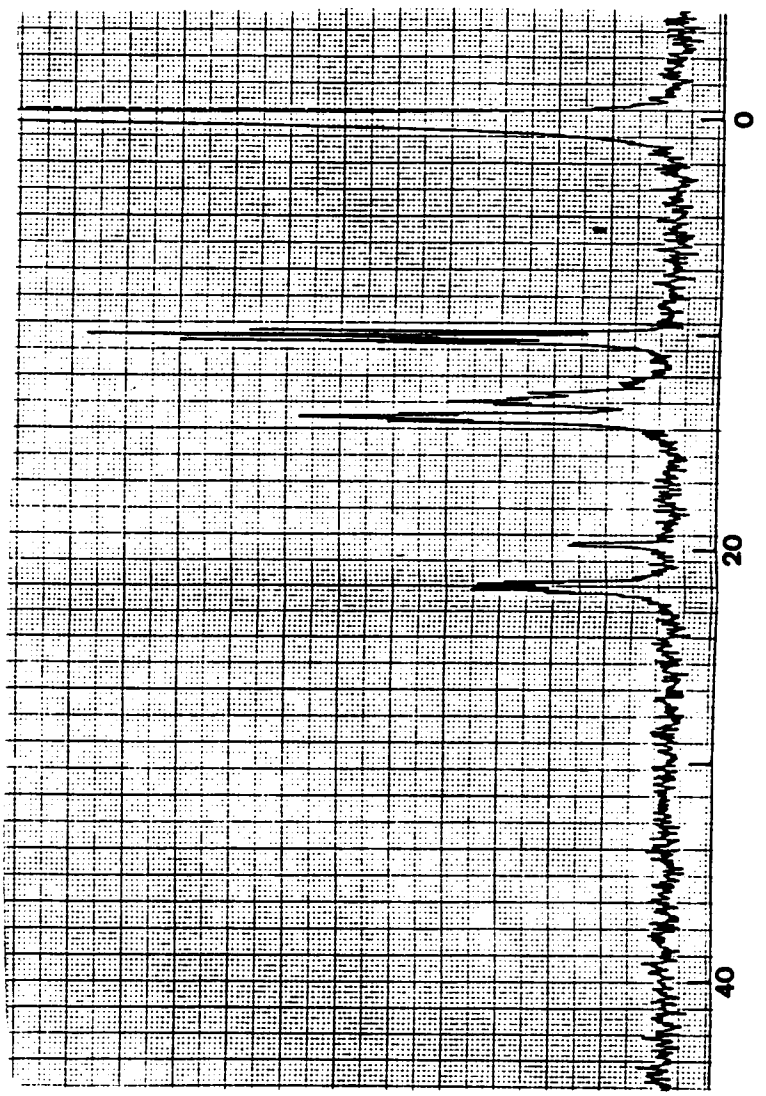


Figure 22. Proton decoupled ^{31}P NMR spectrum of compound **52**

splitting pattern. This in in the region expected for the CH_3-P-H phosphorus. A signal at 16.5ppm was sharply defined witrh five lines showing. This signal is in the range of the spiro compounds which include a seven membered spirocyclic ring. The ^1H nmr spectrum was poorly resolved, but clearly visible was a small triplet at 3.6d, indicative of a CH_2-OH group, and thus only partial cyclization to the spiro compound.

Table 10. ^{31}P NMR Data for 1-Methyl-1-Hydrido Spiro Compounds

	CH_3-P-H	PCl_2 (ppm)	PXY	J_{AB}	J_{AC} (Hz)	J_{BC}
70	12.4	20.9	10.7	16	16	24
71	12.1	22.4	15.0	17	15	32
72	14.0	21.4	10.1	20	30	23

THE 1-METHYL-1-HYDRIDO COMPOUND: DISCUSSION

The reactions of the bifunctional nucleophiles with 1-methyl-1-hydrido-3,3,5,5- tetrachloro- cyclotriphosphazene, **35**, closely parallel those of the gem-dimethyl phosphazene **36**. Thus in the reaction of **35** with 1,3-propanediamine the monospiro compound **50** was the only product. No bino, ansa, or uncyclized products were observed. Treatment with excess diamine at elevated temperatures did not lead to the formation of a bis-spiro product. Examination of the reaction mixture prior to completion of the reaction showed only the the spiro product and starting material. The results indicate that the long range electronic effects of a CH_3-P-CH_3 unit and a CH_3-P-H unit on an adjacent PCl_2 group are very similar.

The reaction of the hydrido phosphazene **35** with 1,4-butanediamine also parallels the reaction of the gem-dimethyl phosphazene with the same reagent. The monospiro compound **51** was the only product, and incomplete reaction mixtures showed only this product and unreacted starting material. There was no bino compound formed, as was the case in the gem-dimethyl reaction, and probably for the same reason.

In its reactions with the aminoalcohols the hydrido phosphazene **35** again closely parallels the gem-dimethyl phospahazene **36**. With 3-amino-1-propanol a monospiro product is formed. The cyclization step proceeds smoothly, probably by nucleophilic attack of the neutral alcohol as discussed in relation to the reaction of **36** with this same reagent. When

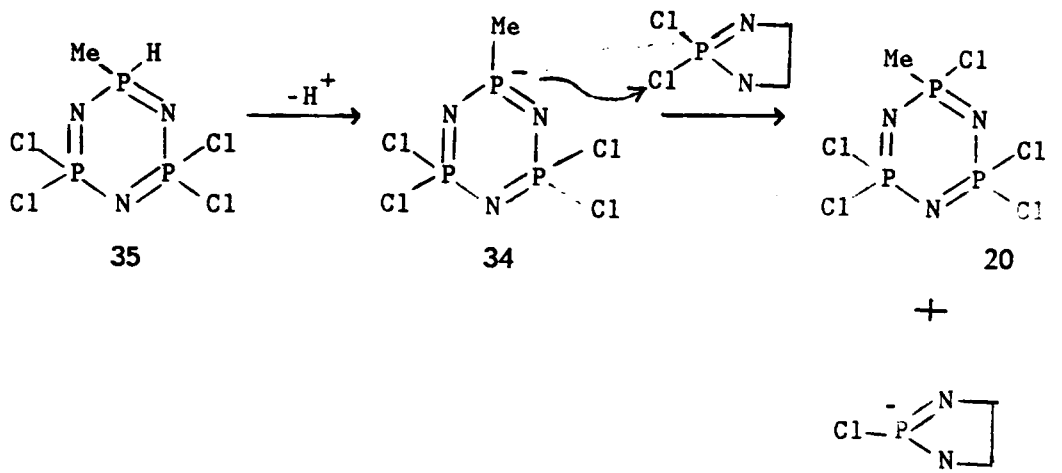
the aminoalcohol is increased in length by one methylene unit however, spirocyclization remains incomplete. These results illustrate the preferred spiro cyclization to rings of six members. The fact that the four carbon diamine does smoothly cyclize shows the greater nucleophilicity of the amine than the alcohol.

The attempted chlorination of the P-H group in these spiro compounds was not entirely successful. While the nmr spectra were roughly as expected, and indicated that the P-H was indeed converted into a P-Cl in each case, the lack of exchangeable protons indicated by treatment with D_2O suggests that the Cl_2 interacted with the amine functionality. These reactions were not pursued further.

One major difference in the reactivity of the methyl-hydrido phosphazene compared to the dimethyl phosphazene could be seen in the reactions with the strongly nucleophilic alkoxide ions formed from propanediol and butanediol. These reactions did not yield dioxy spiro compounds, but instead led to extensive degradation of the phosphazene species. When filtered and stripped the crude reaction mixtures were strongly lachrymating, and turned brown or black in air in a period of hours. The ^{31}P nmr spectra of these reaction mixtures were very complex, showing a variety of highly coupled signals and broad multiplets from 5ppm to over 40ppm. Proton nmr spectra were poorly resolved and complex, but showed a doublet of triplets in the 1.8d region, typical of an CH_3-P-OR group. The most likely origin of this P-O bond is via an intermediate compound

in which the P-H has been converted to a P-Cl. Normal nucleophilic substitution by RO^- on this P-Cl would lead to the observed CH_3-P-OR unit.

The methyl-hydrido compound **35** is formed by protonation of the corresponding anion **34** which could be regenerated in the presence of an alkoxide ion. Attack of this anion on a chlorine of another phosphazene molecule (metal-halogen exchange) would lead to the CH_3-P-Cl group which is the assumed precursor of the observed CH_3-P-OR unit. The phosphazene which has been displaced from chlorine will leave as an anion, different from the first one. This formation of different, highly reactive species could explain the multitude of products and perhaps the lachrymating nature of the reaction mixtures (Scheme 12).



Scheme 12.

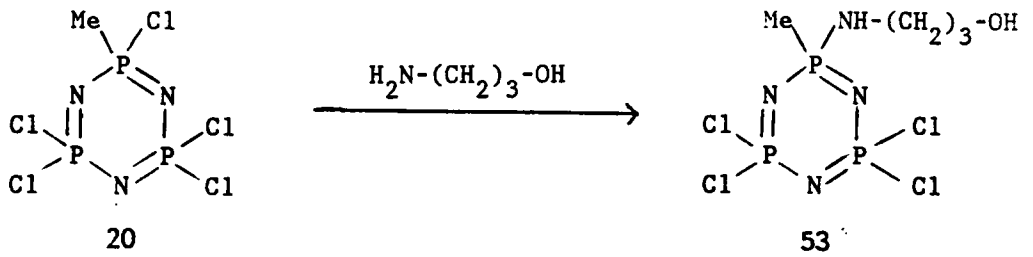
To test the possibility that the anion **34** chlorinates by metal-halogen exchange, to form the CH_3-P-Cl group, the reactions were run in the

presence of added CCl_4, known to be a substrate facile towards metal-halogen exchange. In the reactions of both diols, with CCl_4 present, the reaction mixtures were less lachrymating and more air-stable, and the nmr spectra were more resolved. The ^1H nmr spectra showed a major doublet of triplets around 1.8d, corresponding to CH_3-P-OR, and in some reactions a smaller doublet of triplets at 2.1d corresponding to unreacted CH_3-P-Cl residues. This improved behavior in the presence of CCl_4 is indication that metal-halogen exchange is occurring in the reactions of alkoxide ions with the methyl-hydrido phosphazene.

REACTIONS OF MONOMETHYL: RESULTS

According to arguments by Allcock and others, the electron donating ability of the methyl group, which is demonstrated in its effect on the reactivity of the adjacent PCl_2 units in the dimethyl phosphazene **36**, should increase the electron density on the adjacent P atom, thereby decreasing its reactivity towards nucleophiles. Preliminary studies however, indicated increased reactivity of the chlorine gem to the methyl group, and almost exclusive formation of geminally substituted products. This feature lends itself to several synthetic possibilities, since the methyl group not only increases reactivity at the phosphorus it is bonded to, but also acts as a blocking group, preventing spiro formation. In the reaction of monomethylpentachlorocyclotriphosphazene **20** with bifunctional nucleophiles, the possibility exists for intramolecular ring closure via substitution of the second functionality of the nucleophile on an adjacent PCl_2 unit. Tables 11, 12, and 13 contain nmr and characterization data for the compounds formed in these reactions.

3-Amino-1-propanol: Important information concerning the reactivity of the monomethyl phosphazene **20** can be obtained by an examination of the reaction of with 3-amino-1-propanol. In ether, methylene chloride, toluene, or THF, at $0^{\circ}C$, room temperature or reflux, the major compound formed is compound **53**, in which the amino group has substituted geminally to the methyl group. The proton acceptor may be either triethylamine or an added equivalent of the aminoalcohol. This compound



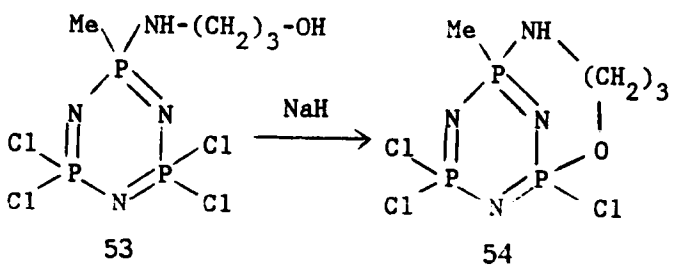
Scheme 13.

was formed in yields as high as 98%. It was a colorless oil, poorly soluble in hexane. The ^1H nmr (Figure 23) spectrum showed a triplet at 3.8d, almost unchanged form the starting aminoalcohol. This is indication that the hydroxy group has not undergone reaction. This is supported by the ir spectrum, which shows a broad absorption in the region of 3400-3200cm^{-1}. The proton nmr also clearly shows that the amino group has undergone substitution at phosphorus. The original triplet corresponding to the methylene group adjacent to the NH2 has shifted from 2.7d to 3.1d and has become split into a broad multiplet. Removal of the NH and OH from the spectrum with D_2O improves the symmetry of this signal but it remains quite broad and unresolved. The doublet of triplets shown in the monomethyl starting phosphazene at 2.1d has shifted upfield to 1.67d. This corresponds to a change from a CH_3-P-Cl unit to a CH_3-P-NHR unit, and is indicative of the geminal substution of the amine. The remaining proton signal was a multiplet corresponding to the protons of the central methylene group of the three carbon chain.

The proton decoupled ^{31}P nmr of this compound was identifiable as an AX_2 splitting pattern. The downfield triplet at 25.0ppm (J_{PNP}=19.5Hz) broadened upon coupling to protons and was assigned to the CH_3-P-NHR phosphorus. The doublet at 19.8ppm remained unchanged upon coupling to protons and was assigned to the PCl_2 phosphorus atoms. The change of the CH_3-P-Cl group to a CH_3-P-NHR group is also clearly shown in the ^{31}P spectrum by the shift of the downfield triplet from 40ppm in the starting phosphazene to 25ppm in the product.

The mass spectrum supports the structure suggested by the nmr and ir data. The molecular ion at 364 amu was visible as well as the expected Cl_4 isotope pattern. The major loss was of 74 amu corresponding to the loss of the amino ligand. Losses of the methyl group and chlorines were also seen. Correct microanalytical data were also obtained.

Treatment of **53** with NaH: Stirring at room in THF with suspended NaH led to the formation of the ansa compound **54** (Scheme 14). This was indicated by the nmr,ir, and mass spectral data.



53 54

Scheme 14.

Comparison of the ^{1}H nmr spectrum of this compound (Figure 24) with that of compound **53** shows that the major change has occurred in the $O-CH_2$ group. The triplet seen in the spectrum of **53** has shifted downfield and undergone extensive splitting, indicating that the oxygen atom has become bonded to phosphorus. This splitting is due not only to the phosphorus but also due to the fact that in the ansa structure each proton of the bridging group is magnetically different. The doublet of triplets corresponding to the $P-CH_3$ group occurs at 1.71d, indicating that the $CH_3-P-NHR$ group is still intact. The broad multiplet at 3.1 corresponding to the $P-NH-CH_2$ protons supports the fact that nitrogen is still bonded to phosphorus. These facts alone suggest an ansa structure, although a bino structure would still be a possibility.

The proton decoupled ^{31}P nmr spectrum was interpreted as an AMX spin system. Assignment of the signals to the three phosphorus atoms of the ansa structure was possible by examination of the proton coupled spectrum. This spectrum also gave added evidence of the ansa structure. The furthest downfield signal, at 29.3ppm, was assigned to the $CH_3-P-NHR$ phosphorus. This was based on its chemical shift, which is in the general region for an alkyl-phosphorus, and also the fact that it became the most severely broadened signal of the three upon proton coupling. The furthest upfield signal, at 24.5ppm was assigned to the PCl_2 phosphorus since it was unchanged upon coupling to protons. The central resonance then, at 29.3ppm was assigned to the $Cl-P-OCH_2$ phosphorus. Upon coupling to protons this signal becomes split into a triplet, indicating the presence of the two methylene protons nearby and suggesting the ansa structure.

Also notable are the differences in the chemical shifts of the phosphorus atoms in the ansa compound compared to similar substituted one in molecules not containing the bicyclic structure. For instance the CH_3-P-NH group in the uncyclized starting material **53** occurs at 25.0ppm. The CH_3-P-NH group in the ansa molecule **54** occurs at 31.2ppm. Likewise the PCl_2 phosphorus of the starting compound is at 19.8 ppm, and most other PCl_2 groups occur very close to 20ppm. In the ansa compound however, the PCl_2 resonance is at 24.5ppm.

The mass spectrum of this compound was also consistent with the ansa structure. The molecular ion appeared at the calculated value of 328 amu, confirming the structure as the ansa rather than a bino-linkage. The Cl_3 isotope pattern was also consistent with the proposed ansa structure.

As final proof of the structure of compound **54**, a single crystal x-ray diffraction study was performed. This clearly indicated the ansa bridge between two phosphorus atoms of the same phosphazene ring. This was the first time that an ansa compound containing a simple organic bridging unit had been synthesized. Previously reported ansa structures had recently been proven to be erroneous by x-ray diffraction studies of the compounds. In addition to the ansa bridge, the x-ray structure also revealed a substantial pucker to the phosphazene ring. Simple calculations showed that the through-space P-P distance was no shorter than in other non-ansa cyclo- triphosphazenes. This indicates that the pucker of the phospazene ring is not due to the two bridged phosphorus atoms moving closer together, but possibly due to a rotation of these atoms about the P-N bonds.

The structure of this molecule as determined by x-ray crystallography is shown in Appendix A.

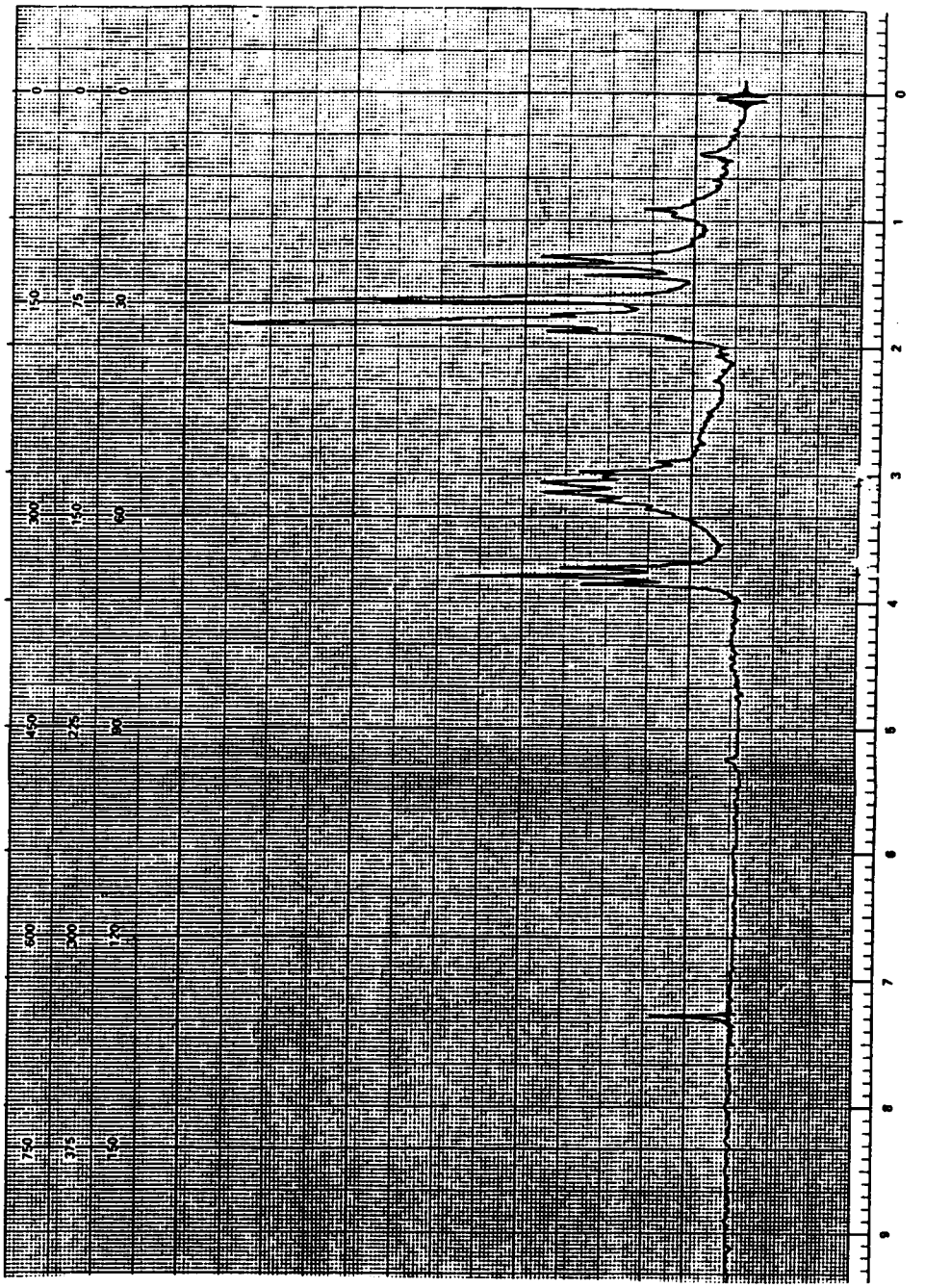


Figure 23. ^{1}H NMR spectrum of compound **53**

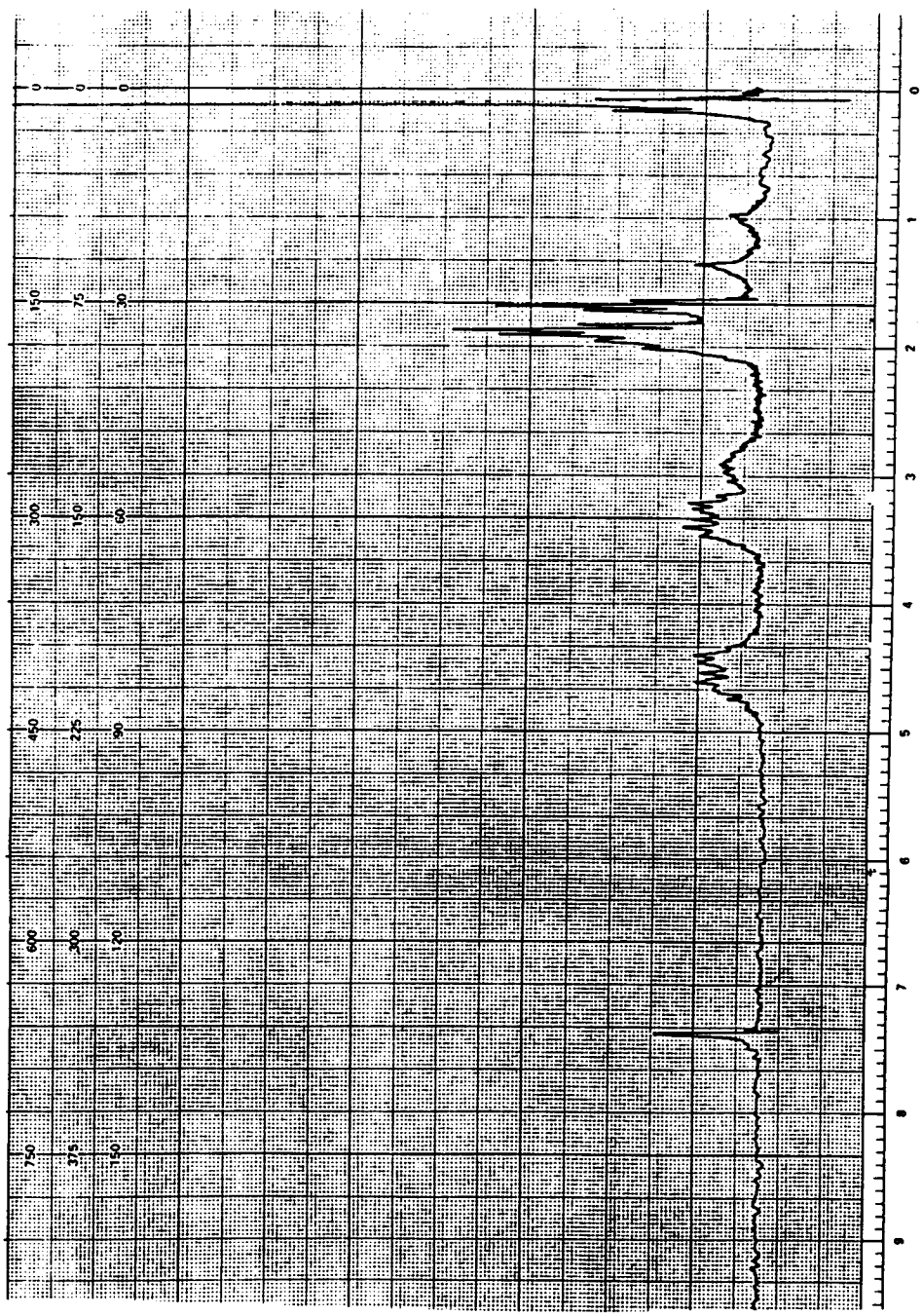
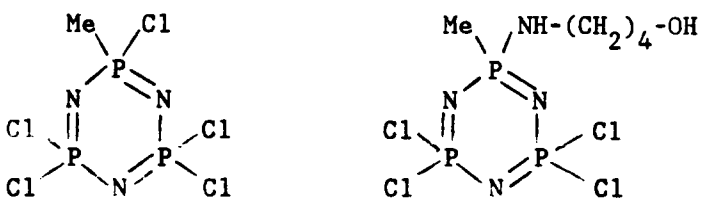


Figure 24. ^{1}H NMR spectrum of compound **54**

4-Amino-1-Butanol: The puckered phosphazene ring revealed by the x-ray diffraction studies of the ansa compound **54** suggested that an increase in the carbon chain of the bridging group might alleviate this strain and lead to increased yields and/or shorter reaction times.

The reaction of 4-amino-1-butanol with the monomethyl phosphazene **20** proceeded in an analaogous manner to the reaction with propanolamine discussed above. The product, **55**, was exclusively amino-substituted, exclusively geminal to the methyl group,



20 **55**

Scheme 15.

with the hydroxyl group intact (Scheme 15). This was indicated by the ^{1}H nmr spectrum. The P-CH_3 protons appeared as a doublet of triplets at 1.61d, in the range typical of a CH_3-P-NH group. The doublet of triplets at 2.1d corresponding to the CH_3-P-Cl group of the starting material was gone. Amino-substitution was indicated by the broad multiplet at 3.1d. Compared to the triplet at 2.7d for the corresponding protons in the unreacted aminoalcohol, the downfield shift and additional splitting indicates bonding to phosophorus. On the other hand the O-CH_2 protons signal shows that the hydroxyl group has not substituted at phosphorus. The signal appears as a triplet, split on by its neighboring methylene pro-

tons. The chemical shift of 3.7d is very nearly the same as the corresponding signal in the unreacted aminoalcohol. A D_2O wash of the product to remove the NH and OH protons improved the symmetry of the N-CH_2 region of the spectrum, but it remained broad and unresolved.

The ^{31}P nmr spectrum was identified as an AX_2 spin system. This is indicative that substitution has occured exclusively geminal to the methyl group and the the PCl_2 groups remain unchanged. The downfield triplet at 25.1d (J=26.5Hz) was assigned to the CH_3-P-NHR phosphorus and the doublet at 20.6 (J=26.5Hz) was assigned to the by analogy to the propanolamine product which shows an almost identical spectrum.

The ir spectrum was very similar to that of product **53** also. The NH and OH stretches were visible in the region 3600-3100 cm^{-1}. Also visible were aliphatic CH stretches at 298 and 2940cm^{-1} and the PN vibration at 1230 and 1180 cm^{-1}.

The mass spectrum was also comparable to that of compound **53**. The molecular ion at 378 amu with a Cl_4 isotope pattern was small but visible. An ion at 360 amu due to loss of water was also small. THe majority of the ion current was carried by an ion at 290 amu, corresponding to the loss of the ligand by cleavage of the exocyclic P-N bond, but with the methyl group and the four chlorines still on the intact phosphazene skeleton. The propanolamine substitution product **53** also shows this ion at as the base peak of its mass spectrum.

Treatment of **55** with NaH: It was hoped that upon treatment with NaH, intramolecular substitution would occur smoothly to yield the ansa molecule with the bridging chain increased in length by one methylene unit. However, stirring a THF suspension of **55** at room temperature for 24hr yields almost none of the expected ansa compound. Instead a white crystalline solid, **56**, was isolated in about 40% yield with the following spectral properties.

The ^{31}P nmr spectrum was an AX_2 spin system, different from the AB2 of the compound **55**. The upfield doublet came at 21.6ppm, typical of PCl_2 groups. The downfield triplet came at 33.4ppm, downfield from the starting material but still in the range of a CH_3-P-N unit. This spectrum suggested a reaction taking place near the CH_3-P-N phosphorus atom, and not at the dichloro- substituted phosphorus atoms.

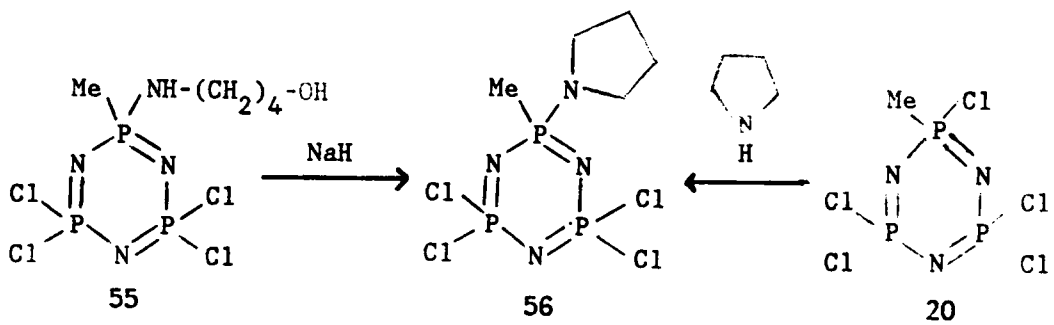
The ^{1}H spectrum showed a doublet of triplets for the P-CH_3 protons at 1.61d, essentially unchanged from compound **55**. There was an unresolved multiplet around 1.81 due to the central methylene protons and a more highly coupled, and very symmetric, signal at 3.08 corresponding to P-N-CH_2 protons. There were no other signals in the spectrum. The triplet which had been at 3.7d in the starting material, corresponding to the O-CH_2 protons was missing entirely. There were no exchangeable protons with D_2O. The lack of exchangeable protons suggests the formation of a secondary amino substitutent on the phosphazene. The change of the amino ligand from primary to secondary would also be consistent with the ^{31}P nmr data. The loss of the signal at 3.7d, without any replacement

further downfield can only be explained by the loss of the oxygen atom. This suggests a loss of water, consisting of the NH proton and the hydroxyl group.The infrared spectrum confirmed the absence this loss of water by the absence of OH and NH stretching frequencies.

The ^{13}C nmr spectrum also confirmed the loss of the oxygen atom. Besides the doublet of triplets for the P-CH_3 carbon, there were only two other types of carbons. The downfield signal doublet at 35.1ppm is in the region expected for a P-N-C carbon and shows coupling to phosphorus. (J=3.4Hz). The other signal at 26.1ppm is in the region expected for a P-N-C-C carbon. Interestingly this signal also shows coupling to phosphorus (J=9.5Hz).

The mass spectrum of the compound showed an ion at 360 amu with a Cl_4 isotope pattern. The chlorine pattern is consistent with the two PCl_2 groups suggested by the ^{31}P nmr. The weight of 360 amu suggested a ligand of molecular weight 70 on the methylpentachloro cyclophospazene skeleton. This latter fragment weighing 290 amu was the largest signal in the spectrum, typical of the 1 methyl 1 aminotetrachloro 1-methyl-1-amino tetrachloro- derivatives discussed previously.

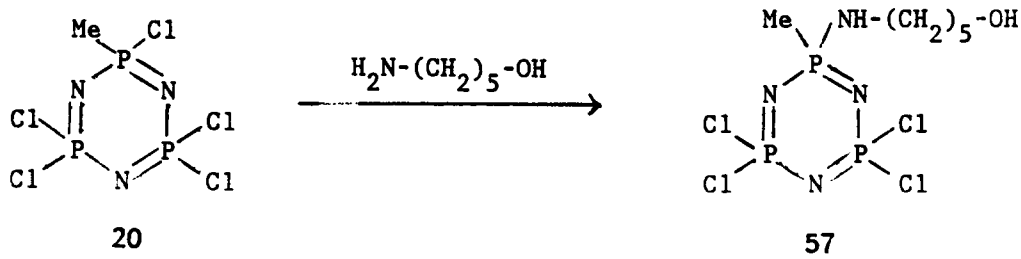
The nmr, ir, and ms data suggested that the compound was 1-methyl-1-pyrrolidino-tetrachloro cyclotriphosphazene. Final substantiation that this structure was correct came from the synthesis of the pyrrolidino derivative by a separate route. This molecule was prepared by the treatment of the monomethyl pentachloro phosphazene **20** with pyrrolidine.



Scheme 16.

All spectra and physical properties were found to be identical with product **56**.

5-amino-1-pentanol: The reaction of the monomethyl phosphazene **20** with the five carbon aminoalcohol also yields an exclusivley amino- substituted, exclusively geminal product, **57**, with the hydroxyl group



Scheme 17.

intact. The ^1H nmr of the product showed a doublet of triplets for the P-CH_3 protons at 1.67d, indicating that substitution geminal to the methyl group had occurred. That the amino group of the aminoalcohol was the substituted site of the nucleophile was shown by the downfield shifted and broadened signal corresponding to P-N-CH_2. at 2.95d. Removal of the

NH and OH protons with D_2O showed that they were under this signal. The ir spectrum was also consistent with this structure, showing a broad absorption about 3260 cm^{-1} corresponding to the OH and NH stretches. The mass spectrum showed the molecular ion at 392 with the expected Cl_4 isotope pattern. As in the analogous compounds with three and four carbon chains in the amino- alcohol ligand, the major signal in the mass spectrum corresponded to the loss of the ligand, with the methyl group and four chlorine still on the intact phosphazene skeleton. Interestingly, in contrast to its three and four carbon analogues, this compound was a solid, recrystallizable from hexane.

Treatment of **57** with NaH: Compound **77** was refluxed in THF with suspended NaH. Although no pure compound was isolated, the results of this reaction resemble the ansa formation shown by compound **53**, much more than they do the side chain cyclization reaction undergone by compound **55**.

The ^1H nmr spectrum of the crude reaction product showed that the triplet at 3.65d was almost gone, and had been replaced with a highly complex signal in the region of 4.1 to 4.6d. This indicated that the OH group of the aminoalcohol ligand had substituted at phosphorus. The N-methylene multiplet at 2.95 was still present and exchange with D_2O showed the NH proton signal to be under the P-N-CH_2 signal. The multiplet above 4.0d and the one at 2.95d showed equal integrations after the D_2O exchange. The signal due to the P-CH_3 protons showed the large splitting into doublets as usual, but each of the two signals was more complex than the triplets of the starting compound. These results suggest that ansa for-

mation, and not a side chain cyclization reaction had occurred. Also present in the ^{1}H nmr spectrum were a pair of large broad signals at 0.9 and 1.3d. These signals are in the normal range for aliphatic protons, and suggest some kind of product derived from the organic side group.

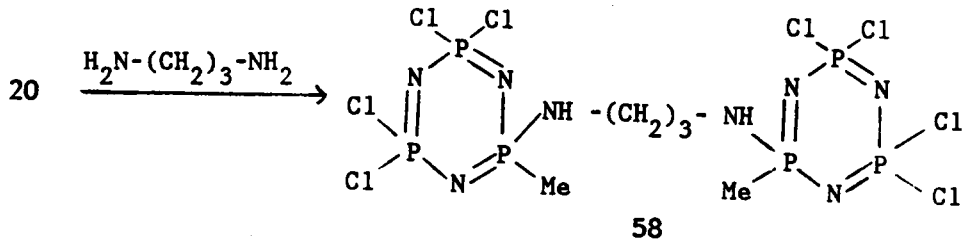
The ^{31}P spectrum was complex and showed a variety of small signals, including unreacted starting compound **57**. The largest signals were identifiable as as AMX spin pattern, with poorly resolved doublets of doublets centered at 18.7ppm, 22.8ppm, and 26.2ppm. These shifts are quite different from those of the ansa compound **54**, but they may be due to the different geometry of the three carbon and five-carbon ansa molecules. Also present in the ^{31}P nmr spectrum was a large unresolved multiplet centered at 24.9ppm, which could not be identified.

The ir spectrum of the product showed a broad absorption around 3300cm^{-1} indicating an N-H group, and probably also the O-H stretch of the unreacted starting material. The P-N region was very broad, probably due to the presence of different phosphazenes.

The mass spectrum also indicated the presence of the ansa compound, showing the molecular ion at 356 with a Cl_3 isotope pattern. This ion was the largest signal in the spectrum. The molecular ion of the ansa molecule **54** also carried a large percentage of the total ion current.

1,3-Diaminopropane: It was hoped that reaction of the monomethyl phosphazene **20** with the three carbon diamine would lead to ansa formation in

analogus fashion to the three carbon aminoalcohol. This was not the case however. While reaction of the first amine functionality proceeded as expected, the second amino group was resistant to intramolecular cyclization. The only hexane soluble product of this reaction is the bino compound **58**.



58

Scheme 18.

This product was seen in greatest yields in reactions with rapid additions of the reagents and could be eliminated entirely with a slow addition of **20** to the diamine at 0°C.

The bino compound **58** was identified on the basis of nmr, ir, and ms data. The ^{31}P nmr spectrum of the compound was identified as an AX_2 splitting pattern. The upfiled signal was a doublet at 20.7ppm (J=22Hz), assigned to the PCl_2 phosphorus atoms. The downfield signal was a triplet at 24.8ppm (J=22Hz) in the range expected for a CH_3-P-N group. This indicates that the geminal chlorine has been exclusively substituted with an amino group.

The ^1H nmr spectrum of compound **58**, after treatment with D_2O, shows a broad five line multiplet centered at 3.10d. This signal was perfectly

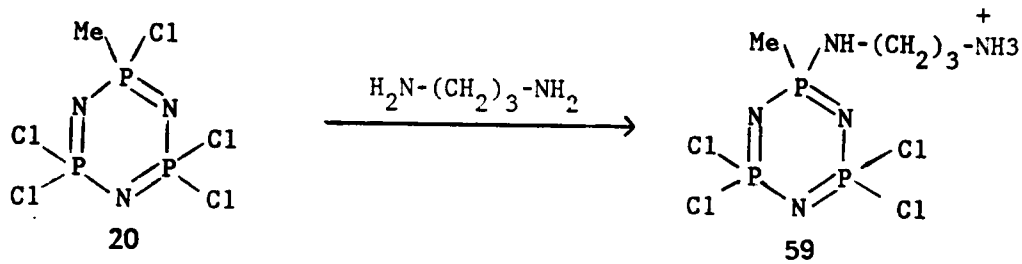
symmetrical, indicating that both ends of the three carbon chain are in identical environments. The P-CH_3 protons give a doublet of triplets centered at 1.69d, overlapping with central methylene protons of the diamino ligand. The integration of the downfiled multiplet to the total signal of the P-CH_3 and the central methylene group was 2 to 1, in accordance with the bino structure.

The infrared spectrum of the compound showed a sharp single band at 3310cm^{-1}. This indicates that the amino substituent retains one proton, and is consistent with both amino groups of the starting diamine being in identical bonding situations. The aliphatic C-H stretches come at 2940 and 2890cm^{-1}. The P-N skeletal vibrations are at 1230 and 1175cm^{-1} similar to the other 1,1-disubstituted phosphazenes discussed thus far.

The mass spectrum of the compound did not show the molecular ion at 652 amu. However a variety of high molecular weight ions up to 630 amu were seen, giving credence to the bino structure. The base peak was at 364 amu with a Cl_4 isotope pattern. This corresponds to the loss of one of the phosphazene rings of the bino compound by fragmentation at a P-N bond. The other major signal in the spectrum was at 290 amu, also with a Cl_4 isotope pattern, corresponding to the $N_3P_3Cl_4CH_3$ unit.

The controlled addition of the monomethyl compound **20** to one equivalent of 1,3-diaminopropane led to the formation of a white pasty precipitate that was thought to be the hydrochloride salt **59**. This compound was insoluble in all solvents tried except for DMSO, with which it undergoes

an uncharacterized reaction. It was also slightly soluble in water and aqueous base.



Scheme 19.

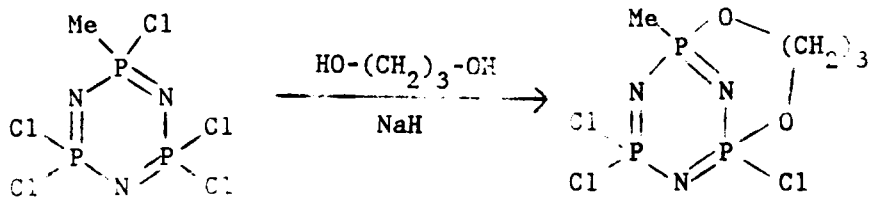
The ^{31}P nmr spectrum of this compound in D_2O shows two poorly resolved signals which may be an AX_2 pattern. The signal at 22.5ppm resembles a broadened doublet, while the signal at 27.5 has the rough symmetry of a triplet. This spectrum is consistent with amino substitution gem to the methyl group.

The ^1H nmr spectrum was also poorly resolved. The doublet of triplets due to the P-CH_3 protons was visible at 1.70d. This indicates that substitution of the gem-chlorine was complete. There was a large unresolved hump extending from 2.55-3.10d in the region expected for the N-CH_2 protons. The two different nitrogens suggested by structure **59** cannot be seen. Washing the sample with D_2O removed a smaller unresolved hump at 2.5d but did not aid in resolution of the spectrum.

The infrared spectrum of the compound was quite different from that of the bino compound **58**. It showed a broad absorption from 3200-3500cm^{-1}.

due to N-H steretches, quite different from the sharp signal at 3310 in the spectrum of the bino compound. Another noticeable diffrence in the two spectra is in the region of the P-N skeletal vibrations. These are seen at 1180 and 1100cm^{-1} in compound **59** at lower freqencies than the same absorptions in the bino compound. This suggests that the phosphazene skeleton may be the site of protonation. Experimentally it can be seen that compound **59**, while having little tendency toward intramolecular substitution to form the ansa compound, will readily substitute the geminal chlorine of an additional equivalent of **20** to yield the bino compound **58**. Treatment of the salt **59** in methylene chloride with one equivalent of the monomethyl phosphazene **20** and one equivalent of triethylamine at room temperature leads to almost quantitative formation of the bino compound. On the other hand the salt **59** can be refluxed in methylene chloride, chloroform, or toluene in the presence of triethylamine without change. Addition of an extra equivalent of **20** to these mixtures leads to formation of the bino compound **58**.

The sodium salt of 1,3-propanediol: The diol was refluxed in THF with 2.5eq of NaH to form the alkoxide. Treatment of the monomethyl phosphazene **20** with this salt led to the isolation of the ansa derivative **60** in moderate yields.



20 **60**

Scheme 20.

The ^1H nmr (Figure 25) showed the signal for the P-CH_3 protons as a doublet of multiplets centered at 1.70d. The chemical shift indicates the formation of a CH_3-P-O unit from the CH_3-P-Cl unit of **20**. The additional splitting compared to the doublet of triplets found in the spectrum of **20** indicates that reaction has occurred at one of the two PCl_2 groups. The central methylene protons showed a slightly irregular pentet at 2.2d. The O-CH_2 protons showed up as a complex multiplet from 4.0d to 4.6d. The upfield region of this signal consisted of two well defined triplets (J=15Hz) rising above the continuation of the remainder of the signal. These are probably due to the O-CH_2 protons closer to the P-methyl group, based upon the typical shielding tendencies of methyl versus chlorine. The Cl-P-OCH_2 protons are probably those giving rise to the broader, more highly coupled signal in the 4.0-4.6 region. It is not clear why the signal from one set of O-CH_2 protons is much more highly coupled than the signal from the other set of O-CH_2 protons.

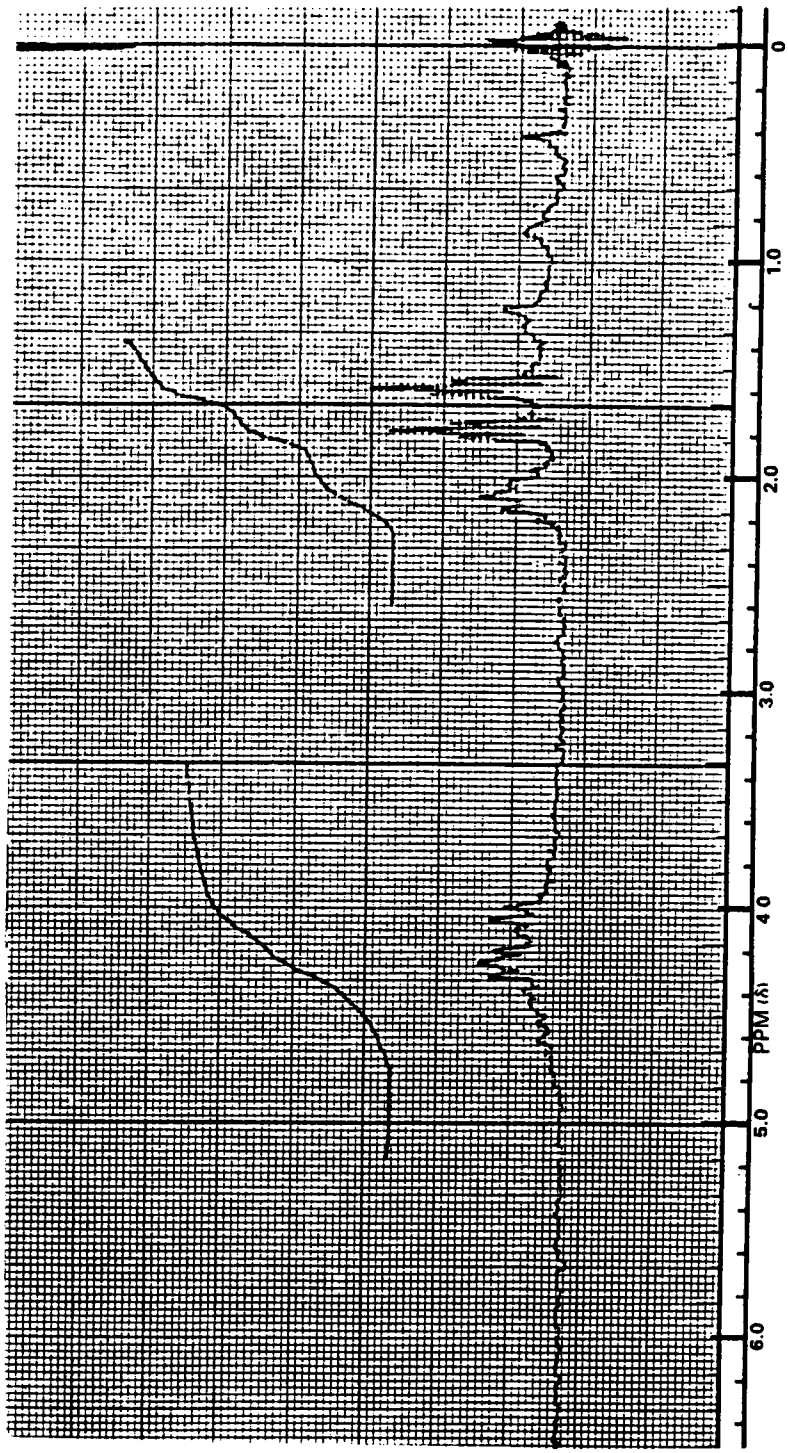
The infrared spectrum was consistent with the ansa structure, showing no OH stretch in the 3300cm^{-1} region. The aliphatic C-H stretches were at 2950cm^{-1} and the P-N vibrations of the phosphazene skeleton showed up at 1210 and 1190cm^{-1}.

The proton decoupled ^{31}P nmr spectrum was identifiable as an AMX spin system, similar to that of the ansa compound **54**. The furthest upfield signal was a doublet of doublets (J=50Hz, 12Hz) at 24.9ppm. This is

probably due to the PCl_2 group by analogy to **54**, but spectra were not run coupled to protons. The midfield signal was a broad doublet (J=50Hz). The individual signals of this doublet did not show any resolved couplings. The downfield signal appeared as a unresolved multiplet at 36.3ppm, and could be assigned to the methyl-phosphorus on the basis of chemical shift.

The ^{13}C nmr spectrum showed the two different $O-CH_2$ carbons, both split by phosphorus into doublets. The further downfield (67.1ppm, J=6.2Hz) was assigned to the methylene carbon nearest the chlorine, while the further upfield (62.4, J=7.3Hz) was assigned to the methylene closer to the methyl group. The central methylene carbon appeared at 30.7ppm as as singlet. The other signals were due to the P-methyl carbon and appeared as a slightly irregular doublet of triplets centered at 15.5ppm (J=147.2Hz, 9.5Hz).

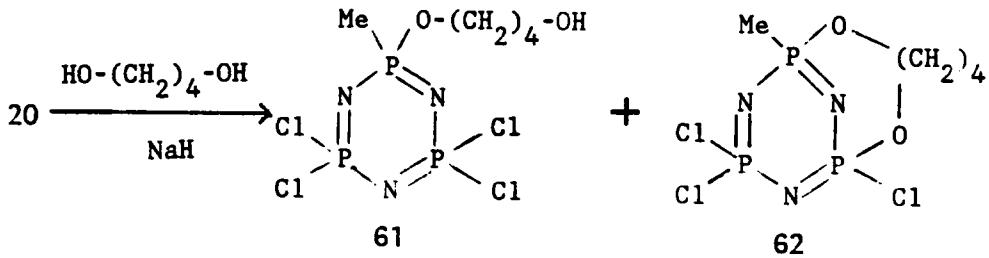
The mass spectrum confirmed the ansa structure, showing the molecular ion at 329 amu with a Cl_3 isotope pattern as predicted. The molecular ion was large, as in the case of the ansa compound **54**. The loss of the methyl group could be seen with a signal at 314 with a Cl_3 isotope pattern. A signal at 294 with a Cl_2 isotope pattern was also present, corresponding to the loss of chlorine from the molecular ion.



90 MHz ^{1}H NMR spectrum of compound **60**

Figure 25. ^{1}H NMR spectrum of compound **60**

The Sodium Salt of 1,4-Butanediol: The diol was refluxed in THF with 2.5eq of NaH to form the alkoxide. Treatment of the monomethyl phosphazene **20** with this salt yielded mixtures of the noncyclized geminally substituted compound **61** and the ansa compound **62**, which could separated by recrystallization of the ansa compound from methylene chloride-pentane. The compounds were characterized by nmr, ir and ms data.



Scheme 21.

The ^{31}P nmr spectrum of compound **61** showed an AX_2 splitting pattern, indicative that only the geminal chlorine had been replaced by the organic group. The upfield doublet was at 21.4ppm (J=22Hz), in the typical range of a PCl_2 phosphorus. The downfield triplet at 30.2ppm (J=22Hz) was in the range expected for a CH_3-P-O phosphorus.

The ^{1}H nmr spectrum of compound **61** indicated that one hydroxyl group of the diol had substituted at phosphorus and the other had not. This was indicated by the triplet at 3.70d from the methylene protons closer to the hydroxyl group, split only by the two central methylene protons, and the multiplet at 3.95d for the P-O-CH_2 protons, shifted downfield and split by the proximity of the phosphorus. This signal was very symmetric, like a broadened quartet in appearence. The central methylene protons

appeared as a broad multiplet showing five lines centered at 1.80d. The $P\text{-}CH_3$ protons appeared as a doublet of triplets centered at 1.66d.

The ^{13}C nmr spectrum gave additional information to the ^{1}H nmr. As in the proton nmr, the two different $O\text{-}CH_2$ groups, one of which showed coupling to phosphorus were apparent. The downfield signal at 64.8ppm was a doublet (J=4Hz), and was assigned to the $P\text{-}O\text{-}CH_2$ carbon, based on the downfield chemical shift and the coupling to phosphorus. The $CH_2\text{-}OH$ carbon appeared at 62.0ppm as a singlet, essentially unchanged from the starting diol. Unlike the proton nmr however, the ^{13}C spectrum shows the two central carbons of the four carbon chain as separate signals, further indication that the two ends of the four carbon chain are in different electronic environments. A singlet at 29.5ppm is the further downfield of the two and is probably due to the carbon closer to the phosphorus, while the further upfield of the two was a singlet at 28.6ppm and was assigned to the central carbon closer to OH group.The $P\text{-}CH_3$ carbon appeared as a doublet of triplets centered at 17.0ppm (J=145.5Hz, 7Hz).

The infrared spectrum confirmed the presence of the free hydroxyl group, showing the OH stretch as a broad absorption around $3575cm^{-1}$. The other major bands in the ir were the CH stretches at 3000, and $2950cm^{-1}$, the P-N skeletal vibrations at 1260 and 1210, and another broad absorption around 1050, probably due to a C-O stretching frequency.

The mass spectrum was also consistent with structure **61**. THe molecular ion at 379 amu with a Cl_4 isotope pattern was visible, as was another

signal at 361 (Cl_4) probably due to loss of water from the molecular ion. The base peak was at 290 amu (Cl_4), corresponding to the loss of the organic ligand. This is the same base peak as seen in the mass spectra of compound **53** and **55**, indicating that cleavage of both P-N and P-O bonds occurs in the mass spectrometer.

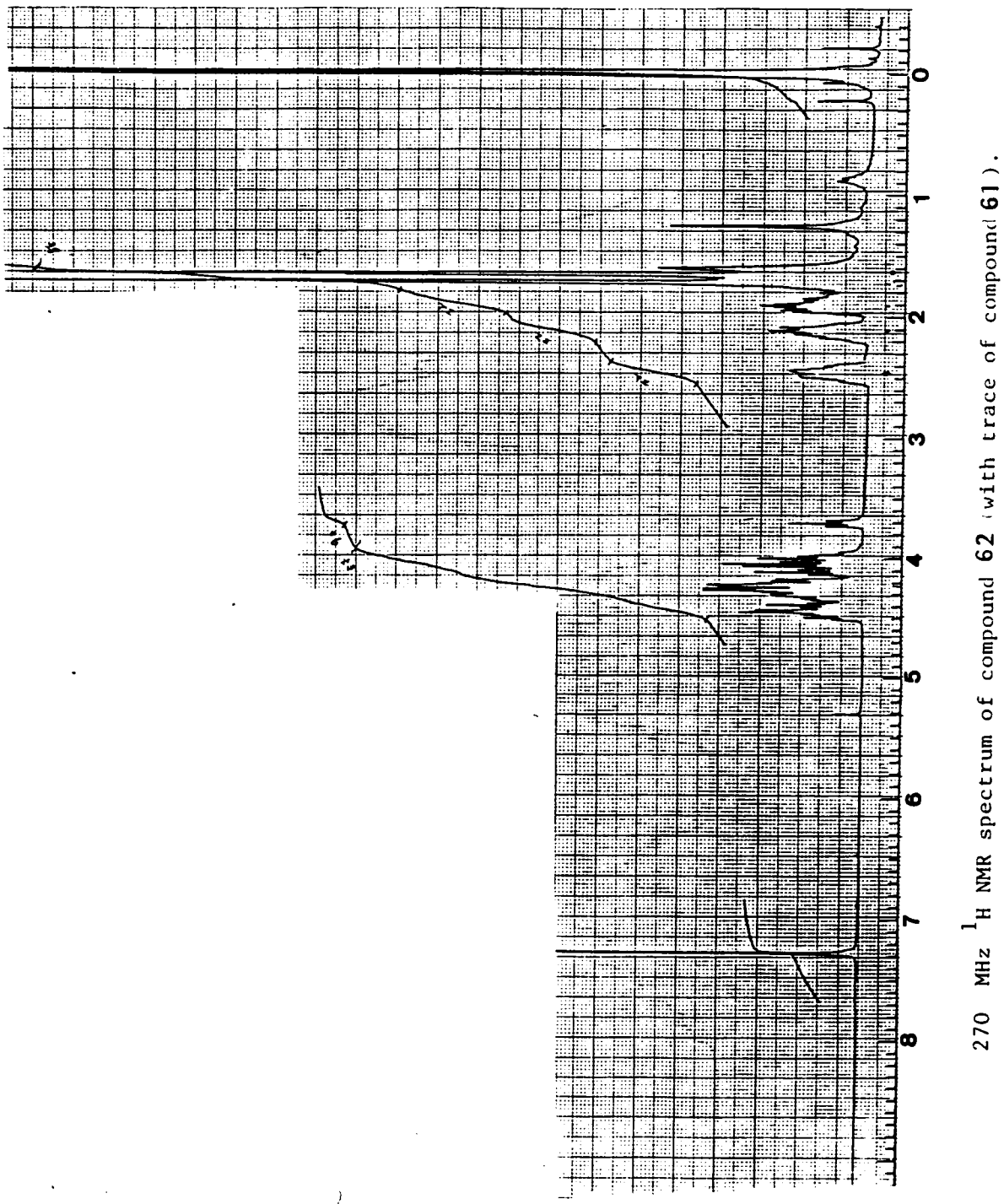
The proton decoupled ^{31}P nmr spectrum of the ansa compound **62** was interpreted as an AMX spin system. The upfield signal was a clearly resolved doublet of doublets at 24.3ppm (J=50Hz, 12Hz) which was probably due to the PCl_2 group by analogy to the ansa compound **54**. The midfield resonance was also a clearly resolved doublet of doublets at 25.6ppm (J=50Hz, 16HZ). The downfield doublet of doublets was the least resolved of the three, at 34.2ppm (J=16Hz, 12Hz). This was also the case with the corresponding signals in the ^{31}P nmr spectra of the ansa compounds **54** and **60**.

The ^{13}C nmr spectrum was consistent with the ansa structure **62**. Two different doublets in the region expected for P-O-C carbons were seen. The downfield signal was at 68.4ppm (J=5.7Hz), further downfield than any of the signals in the uncyclized molecule **61**. This signal is probably due to the methylene carbon closest to the chlorine. The other signal showing coupling to phosphorus was a doublet at 63.2 ppm (J=7.4Hz), assigned to the methylene closest to the CH_3 group. The two central methylene carbons also gave separate signals, singlets at 27.3ppm and 24.8ppm. The CH_3 carbon appears as a doublet of triplets centered at 15.9ppm (J=148.0Hz, 7.0Hz). It is interesting to compare the ^{13}C spectrum of the uncyclized molecule with that of the ansa molecule. In going from

61 to **62** all of the resonances are shifted upfield except for the CH_2OH/CH_2OP carbon.

The ^1H nmr spectrum of compound **62**, shown in Figure 26 also indicates the ansa structure. There is no triplet in the region expected for CH_2OH protons. Instead there is an extremely complex multiplet from 3.95d to 4.55d. This signal has roughly the symmetry of a triplet with nine lines visible in each of the outer peaks and eleven lines visible in the central one in the 270MHz spectrum. This complex splitting is due not only to coupling of the two different methylene groups to the two different P atoms, but also due to the fact that each proton of the four carbon chain is in a unique magnetic environment. This is further illustrated in the ^1H nmr spectrum since each of the four protons on the two central carbons exhibits it own resonance. Unresolved multiplets with integrations of one proton are seen at 2.45d, 2.10d, and 1.90d. The fourth signal can be seen beneath the doublet of triplets corresponding to the CH_3 protons, both centered at 1.70d.

The ir spectrum showed no OH absorption in the region above $3000cm^{-1}$. The only major absorptions were the aliphatic C-H stretches at $2990cm^{-1}$ and the P-N vibrations at $1180cm^{-1}$. The mass spectrum showed the molecular ion at the calculated value of 344 amu with the expected Cl_3 isotope pattern.



270 MHz ^{1}H NMR spectrum of compound **62** (with trace of compound **61**).

Figure 26. ^{1}H NMR spectrum of compound **62**

The experimental facts relating to the reaction of the sodium salt of 1,4-butanediol with the monomethylpentachloro phosphazene **20** indicate that the uncyclized molecule **61** is not a precursor to the ansa molecule **62**. Reaction at -78°C leads to the formation of the uncyclized molecule only, with no ansa present. The maximum formation of ansa was in reactions in which addition of the reagents took place at reflux temperatures. The order of addition was not found to be important. Treatment of the uncyclized product **61** with NaH in refluxing THF did not lead to ansa formation as shown by ^{31}P nmr spectra of crude reaction mixtures, but instead only unreacted starting material and organic degradation products were observed. Proton nmr showed signals in the alkyl region, at 0.9 and 1.3, indicating some reaction of the diol side chain. The stubborn reactivity of the terminal OH group was investigated further. The uncyclized compound **61** was treated with NaH in refluxing toluene, but ^{31}P nmr still showed the presence of starting material and no ansa formation. Refluxing with NaH in 1,4-dioxane and in ethoxy ethyl ether also failed to convert **61** into **62**. Different cations were also tried unsuccessfully. Refluxing **61** with CaH2, and potassium metal in the above solvents did not lead to ansa formation, nor did treatment with $AlCl_3$. Apparently, the ansa compound which is formed in the additions at reflux derives from non-geminal substitution of the alkoxide to a PCl_2 unit follwed by closure to the ansa molecule by substitution of the chlorine which is activated by the methyl group (Scheme 15). It is interesting that there is no evidence of the formation of a spiro compound in this reaction. If ansa formation is indicative of the occurrence of non-geminal substitution this could take place to put the diol ligand either cis

or trans to the methyl group. Only when this ligand is trans to the methyl group and cis to the geminal chlorine can ansa formation proceed. The cis isomer apparently does not lead to spiro compounds but rather to other, unidentified products.

Table 11. ^{31}P NMR Data for Gem-Substituted Monomethyl Compounds

Compound	CH_3-P-Ar, t	Cl-P-Cl, d	J_{PNP}	% yield
53	25.0	19.5	19.5	98
55	25.1	20.6	26.5	67
56	33.4	21.6	34.0	43(94)
57	25.0	20.5	27.4	81
58	24.8	20.7	22.0	86
61	30.2	21.4	22.0	95

Table 12. ^{13}C NMR Data for Gem-Substituted Monomethyl Compounds

Compound	P-X-**C**	P-X-C-**C**	P-X-C-C-**C**	P-X-$(C)_3$-**C**	P-X-$(C)_4$-**C**	(J_{PNPC})
53	37.6	32.8	60.6	-	-	18.6 (124.) (6.)
55	39.8	29.5	27.9	62.2	-	18.3 (120.) (6.)
56	46.1 (3.4)	26.1 (9.5)	-	-	-	17.9 (125.) (6.)
57	39.9	30.8	22.7	32.0	62.4	18.5 (126.)

Compound	P-X-C	P-X-C-C	P-X-C-C-C	P-X-$(C)_3$-C	P-X-$(C)_4$-C	(J_{PNPC})
58	37.2	31.5	-	-	-	18.7 (124.8)
61	64.8	29.5	28.6	62.6	-	17.0 (145.5) (7.0)

Table 13. ^{31}P NMR Data for Ansa Compounds

	CH_3-P-X	O-P-Cl	PCl_2	J_{AB}	J_{AC}	J_{BC}
		(ppm)			(Hz)	
54	31.2	29.3	24.5	9.8	4.0	48.8
60	36.3	27.9	24.9	small	12	50
62	34.2	25.6	24.3	12	16	50

Table 14. ^{13}C NMR Data for Ansa Compounds

Compound	P-O-C (JPOC)	P-N-C	P-O-C-C	P-C (J_{PC}) (J_{PNPC})	(ppm) (Hz) (Hz)
54	67.2 (6.6)	38.5	32.1	18.1 (130.0)	(10.0)
60	67.1, 62.4 (6.2),(7.3)	-	30.77	15.5 (147.2)	(9.5)
62	68.4, 63.8 (6.2),(7.4)	-	27.3, 24.8	16.0 (148) (10)	

REACTIONS OF MONOMETHYL: DISCUSSION

The factors which determine the reactivity of monomethyl pentachloro cyclotriphosphazene **20** with the bifunctional nucleophiles are the same as those seen in the reactions of the dimethyl phosphazene **36**, although they operate to different degrees in their effects on the nature of the products. The site of the first nucleophilic attack is determined by the activation of the geminal-chlorine by the CH_3 group, although the strongly nucleophilic alkoxides may substitute non-gem to a degree. The reactivity of the second functionality is largely a factor of the chain length and the nature of the nucleophile.

Let us first examine the reactivity of the second functionality of the nucleophile towards the PCl_2 groups. Ring formation to ansa compounds is found to be less favored than cyclizations to spiro products. This is due to a combination of factors. First of all, spiro formation is undoubtedly aided by geometric factors which are less favorable in the formation of ansa molecules. The puckered phosphazene ring indicated by the x-ray crystallographic study of the ansa molec **54** is indication that the transition state is also strained. X-ray structures of spiro molecules, particularly those with six membered spirocyclic rings show phosphazene rings with normal angles and bond distances, probably indicating a geometrically unstrained transition state. The second factor which favors spiro formation but does not favor ansa formation is activation of geminal chlorines by nitrogen and oxygen. Ansa formation requires

nucleophilic attack at Cl-P-Cl unit while spiro formation is completed by attack at a N-P-Cl or O-P-Cl unit. The powerful geminal directing ability of the CH_3 group in the first nucleophilic substitution on **20** shows that electron donation to a phosphorus atom labilizes the remaining chlorine towards substitution. While it is difficult to estimate the relative extent that the geometry of the transition state and the activation of the chlorine control the cyclization to spiro products, neither of these factors work in favor of ansa cyclizations.

The intramolecular cyclizations to form ansa compounds are more complicated. The most important factors in determining whether a potential ansa compound will undergo cyclization are the chain length of the potential bridging group, and the nature of the nucleophile which substitutes to form the ansa ring.

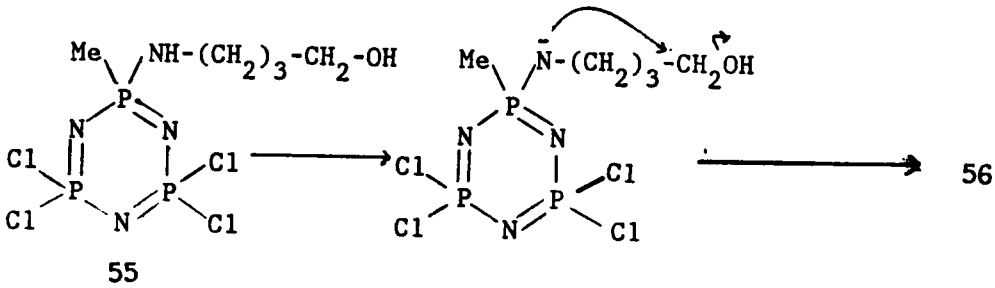
The Attacking Nucleophile: The evidence concerning the nature of the nucleophile necessary to effect intramolecular substitution is clear cut. The failure of the hydrochloride salt **59** to cyclize to the ansa compound while still forming bino compounds with additional **20** indicates that an amine functionality is not a powerful enough nucleophile to intramolecularly attack a PCl_2 unit. It has been shown that the gem-dimethyl phosphazene **36** will undergo intermolecular substitution with amines. Since elctron donation at one phosphorus has been shown to retard nucleophilic substitution at adjacent phosphorus atoms, the dimethyl phosphazene **36** should be even slower to attack by amines than the potential diamino ansa precursor **59**, all other effects being equal. The fact that **59** may be

protonated at ring nitrogen might be expected to increase the reactivity of the phosphorus toward nucleophilic attack, if anything. Thus it is clear that the failure of the diamino ansa molecule to form is not due to electronic factors disfavoring substitution by amines, but must be due to a combination of steric constraints imposed by the carbon chain, and the relatively weak nucleophilicity of the amine. The synthesis of the propanolamine ansa compound **59** suggests that of amines, alcohols, or alkoxides, only alkoxides are strong enough nucleophiles to effect intramolecular substitution and ansa formation.

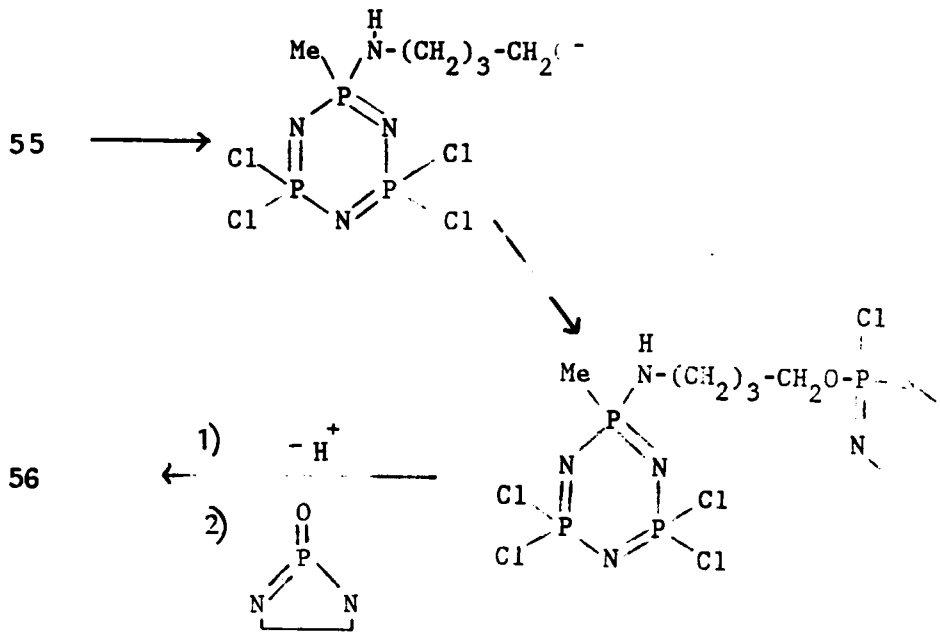
Chain Length: The importance of the chain length in bridging two phosphorus atoms of a cyclotriphosphazene is apparent from the results of these reactions. These results are surprising and are probably the result of particular favored conformations leading to the observed products.

The reactions of the aminoalcohols are illustrative. Reaction of the three, four, or five carbon, terminal aminoalcohols leads to the formation of the ansa precursors **53**, **55**, and **57**. Treatment of the three carbon derivative with NaH leads to ansa formation, presumably by the formation of the sodium akloxide, followed by intramolecular nucleophilic substitution to cyclize to the ansa molecule. The rather severely puckered phosphazene ring revealed by the x-ray diffraction structure suggested that an additional methylene unit in the bridging ligand would relieve this strain and aid in ansa formation. However, treatment of the four carbon potential ansa precursor gave rise not to intramolecular cyclization but to a different reaction. As discussed earlier, the aminoalcohol

side chain cyclization occurs via the formal loss of a molecule of water. Two likely mechanisms can be envisioned for this side chain cyclization. The simpler of these two mechanisms (Scheme 22) begins with the abstraction of the proton from the amino nitrogen to leave an anion. This anion may be delocalized into the phosphazene ring or stabilized by inductive withdrawal. It is also likely to be in equilibrium with the alkoxide ion. Intramolecular Sn2 at CH_2-OH with OH- as the leaving group would yield the observed product. The other reasonable mechanism (Scheme 23) involes formation of the alkoxide ion, followed by intermolecular substitution on another phosphazene to yield a bino-type structure. Formation of the anion at N, followed by Sn2 at CH_2-O-P would kick out a species containing the stable P=O bond as the leaving group, and yield the observed product. Evidence supporting the first of these two mechanisms will be discussed with regard to the reactions of **20** with butanediol.



Scheme 22.



Scheme 23.

The side chain cyclization reaction just discussed leads to the formation of a five membered ring. It was expected that a further increase in the length of the carbon chain by one methylene unit would favor the side chain cyclization even more than in compound **55**, since the potential ring would be six instead of five members. However, treatment of the five carbon analogue **57** with NaH led to a reaction which resembled the three carbon case more than the four carbon case. No side chain cyclization to the six membered ring occurred. Instead, a moderate amount of ansa formation was observed. Apparently in the four carbon case ansa formation is somehow disfavored and as a result the ligand cyclization side reaction is allowed to proceed. In the three and five carbon cases, ansa formation is allowed, and no side chain cyclization is observed.

The syntheses of dioxy ansa molecules provides supporting evidence. Treatment of the monomethyl phosphazene **20** with the sodium salt of 1,3-propanediol leads in one step to the ansa compound. Even in the reaction of **20** with neutral propanediol and triethylamine some ansa product can be seen to form. This fact suggests that the uncyclized propanediol-substituted phosphazene is indeed a precursor to the ansa molecule.

On the other hand, the uncyclized four carbon diol analogue was stubborn towards ansa formation, just as the four carbon aminoalcohol analogue had been. This compound was treated with NaH, CaH_2, Na, and K, at various

temperatures with no ansa formation observed. Treatment with $AlCl_3$ in an attempt to close the ansa ring via attack on a P^+ ion also failed to yield the ansa product. The difference between the aminoalcohol case and the diol case is the inability of the diol compound to undergo side chain cyclization. Instead no reaction is observed in the ^{31}P nmr, only starting material. The lack of bino or polymer formation in the treatment of the four carbon diol compound **61** suggests that bino formation is not involved in the side chain cyclization reaction of the four carbon aminoalcohol analogue, and that the mechanism involving the loss of OH^- is closer to correct. Even with the addition of an extra equivalent of **20** in the presence of NaH the terminal OH group did not react, surprising since the first OH of the diol will substitute the gem chlorine of **20** in the presence of triethylamine. This extreme stubbornness to undergo nucleophilic substitution probably explains the occurrence of side chain cyclization rather than ansa formation in the four carbon aminoalcohol case.

Simple molecular models do not indicate why the four carbon aminoalcohol and diol analogues are reluctant to engage in ansa formation. The isolation of the four carbon diol ansa compound **62** which is presumed to arise via attack of the alkoxide at a PCl_2 unit first, followed by substitution of the activated CH_3-P-Cl, shows that the product is stable, it is just not formed via substitution of the CH_3-P-Cl first and the Cl-P-Cl second. A strong intramolecular hydrogen bond between the terminal OH and a ring nitrogen was suspected but the OH stretches in the ir spectra of the three and four carbon analogues are similar. For whatever reason, the terminal

OH groups of the four carbon ligands are very reluctant to act as nucleophiles.

Geminal Activation: Let us now examine the substitution of the chlorine geminal to the methyl group in **20** . This chlorine can be smoothly and exclusively substituted with amines and even with neutral alcohols. The enhanced reactivity of the geminal chlorine compared to the PCl_2 chlorines is particularly noticeable in the reaction with propanediamine, in which the formation of bino compounds is favored. Only in the case of the alkoxide of 1,4-butanediol is there any evidence of substitution at a site other than geminal to the methyl group. This activation can also be seen to a lesser extent in the spiro cyclizations of diamines and diols. The most important thing to explain in these reactions is the means by which the electron donating methyl group activates a phosphorus towards nucleophilic attack.

Allcock and others have suggested that electron donating substituents on a given phosphorus ought to increase electron density on that phosphorus, and thus disfavor attack at that position by nucleophiles. They use this line of reasoning to explain the tendency toward non-geminal substitution pathway by electron donating nucleophiles like dimethyl amine. However the methyl group is undoubtedly an electron donating substituent and it is seen to activate, not deactivate the phosphorus it is bonded to towards nucleophilic substitution. That the methyl group is in fact an electron donor in this sytem is indicated by the spectral data of the 1-aryl-1-alkyl-tetrachlorocyclotriphosphazenes. This data showed that

the phosphazene was an electron withdrawer from the phenyl and the other aryl groups, that is, the aryl groups were donors to the phosphazene, with the majority of the donation taking place by an inductive mechanism. The methyl group is commonly accepted to be a better inductive donor than the phenyl group and this could be seen in the basicity data for the ethyl group versus the phenyl group discussed earlier. Thus the methyl group is undoubtedly acting as an electron donor in the monomethyl phosphazene **20**.

In order to explain the activation of the chlorine geminal to a methyl group, and to nitrogen and oxygen as well, we must explain how an electron donating substituent bonded to a phosphorus atom actually decreases the electron density at that phosphorus rather than increasing it, thus rendering it more attractive to nucleophiles, not less. At the same time we must explain the decrease in reactivity at the adjacent PCl_2 groups, separated by a nitrogen atom, which is also caused by the presence of the same electron donating substituent.

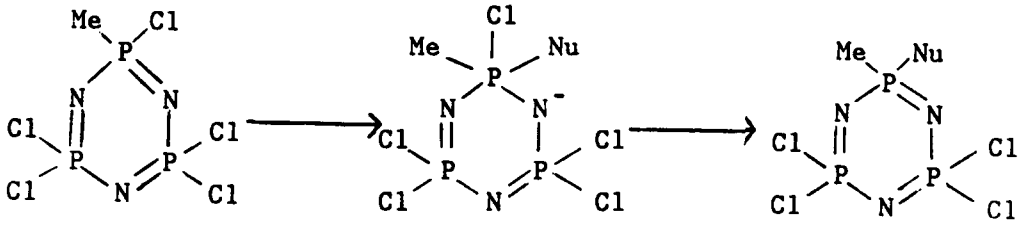
It is clear that the effect is not a simply a case of inductive electron donation being localized on the immediate phosphorus bearing the donor. This would explain neither the geminal activation nor the remote deactivation of the PCl_2 groups. Indeed it is not likely that the effect is felt by the phosphazene is inductive at all, since the substituent is three bonds away from the PCl_2 phosphorus, too far for inductive effects to make a major difference in reactivity.

To explain the different effects felt by the immediate and the adjacent phosphorus atoms, separated by a nitrogen atom, it would seem necessary to consider the effect of an electron donating substituent on the d-p pi system of the phosphazene ring. It has been discussed in the historical sections that the presence of electron donating substituents has the effect of lengthening endocyclic P-N bonds, and decreasing their infrared vibrational frequencies. This has been explained in terms of the decreasing extent of d-p pi bonding with donating substituents, related to expansion of the phosphorus d orbitals which are though to overlap with the nitrogen 2p orbital. Conversely, contraction of the d orbitals by electron withdrawing substituents, effecting an increased pi bonding between P and N, has been cited as the reason that flourophosphazenes are more resistent to skeletal degradation than the chlorophosphazenes in reactions with Grignard and organolithium reagents. In addition, basicity measurements indicate that donating substituents increase the electron density on the nitrogen which separates the two phosphorus atoms. Thus the elctron donation caused by a methyl group for example, is felt as withdrawal at the immediate phosphorus, and donation at the adjacent nitrogen.

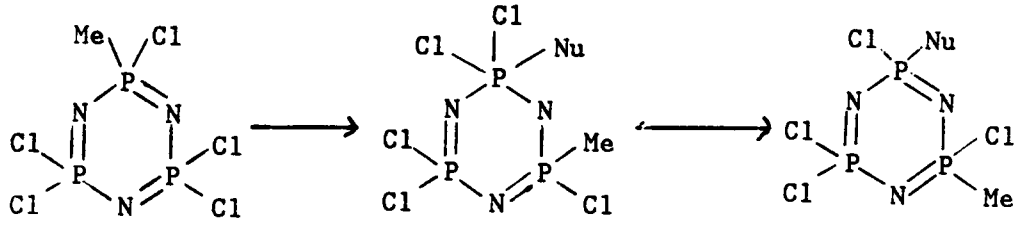
This combination of effects can be explained by an expansion of the d orbitals on the phosphorus bearing the donating substituent. The d-p pi bond can be viewed as a back-bonding situation between N^- and P^+, as seen in structure **12** and **13** on page 10. Expansion of the d orbitals of phosphorus by an electron donating substituent would yield a bonding hybrid in which structure **12** is a greater contributor than when a more with-

drawing substitutent is present. The result is a more pronounced P^{+}-N^{-} dipole than before the presence of the donating substituent. This dipole would explain both the activation of the immediate P atom towards nucleophilic substitution, since it bears a partial positive charge, and the increase in basicity of N, since it bears a partial negative charge. Thus electron donation from a substituent to a phosphorus is transformed into electron withdrawal from that phosphorus to the adjacent nitrogen, due to the loss of back-bonding from N caused by d orbital expansion.

The preference for substitution geminal to the electron donor can be explained in terms of the energy diagrams (Figure 27) for geminal and non-geminal substitution (Schemes 24 and 25) using the assumption that the donor decreases pi bonding from N to P.



Scheme 24.



Scheme 25.

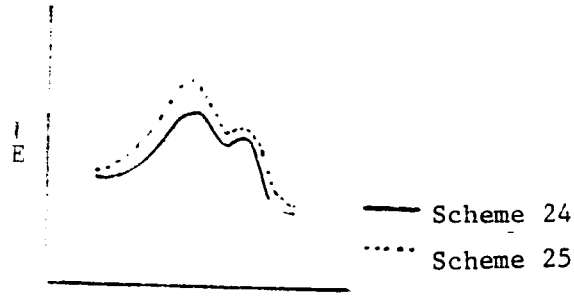


Figure 27. Energy diagrams for gem vs. nongem substitution

Attack of the nucleophile M^+Nu^- to the P bearing the donating substituent leads to a structure **83**, in which Nu^- neutralizes the P^+ and M^+ balances the N^- charge. In the case of neutral nucleophiles like amines and alcohols, H^+ would take the place of M^+ in this mechanism. Loss of chloride ion from this intermediate would yield the geminally substituted product. Species **63** is treated as an actual intermediate, at an energy minimum, and not a transition state. The forward reaction from this intermediate, loss of chloride, is pictured as having a lower activation energy than the reverse reaction, loss of the nucleophile and return to starting materials. This is consistent with experimental fact since the reactons of amines alcohols and alkoxides have never been found to be reversible. For example, while some reports of removal of amine groups from phosphazenes have been reported, conditions are extreme and yields are low. Thus the addition of the nucleophile to the phosphazene is the rate determining step, and not the loss of chloride.

Scheme 25 shows the analogous mechanism which would lead to non-geminal substitution, with an energy diagram for this process also shown in Figure 27. The intermediate **64** leading to nongeminal substitution can be seen to be less stable or higher in energy than the intermediate **63** wich leads to geminal substitution, and presumably the activation energy needed to reach **64** is also greater than the one needed to reach **63**.

This greater activation energy leading to intermediate **64** than **63** can be thought of as deriving from at least two sources. First of all, the structure as drawn carries two negative charges, one induced by the attack

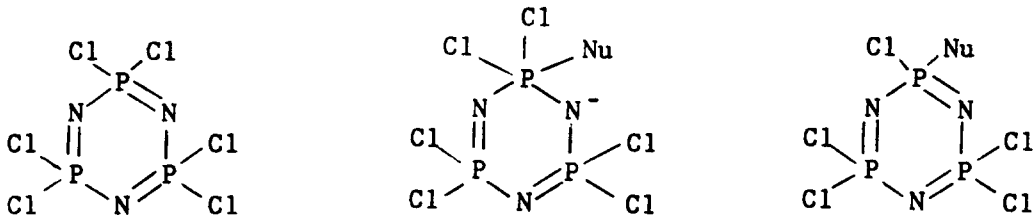
of Nu-, and the other, a partial charge, is induced by the electron donating substituent. In comparison, intermediate **63** has only the charge induced by the attack of the nucleophile. This has the effect of raising the energy of intermediate **64**. Secondly, attack by a nucleophile at a PCl_2 phosphorus must disrupt a new P-N pi bond, while attack by the nucleophile at R-P-Cl, leads to reaction at a pi bond which has already been largely disrupted by the substituent. This further increases the energy gap between the starting compound and the intermediate. The net result is that geminal substitution is the lower energy pathway.

The decreased reactivity towards nucleophiles of a PCl_2 group separated by a nitrogen from the phosphorus bearing the donating substituent can also be related to the increased polarity of of the P-N bond induced by d orbital expansion. The electron-rich nitrogen next to the PCl_2 group could retard nucleophilic substitution there in at least two ways.

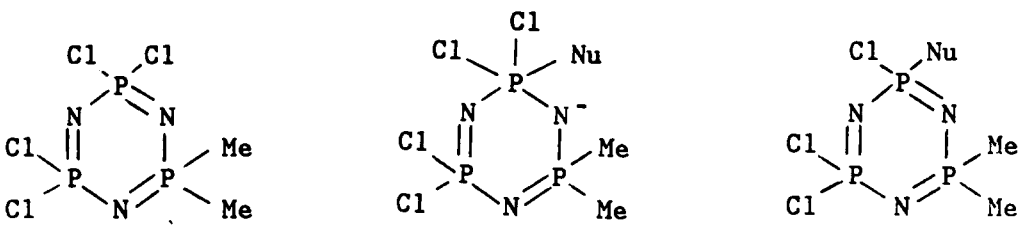
One possible mechanism for this inhibition of substitution would use the increased electron density on N to create a stronger pi bond with the PCl_2 phosphorus. If the donating substituent is thought to expand the d orbitals on the phosphorus bearing it, then the d orbitals on the PCl_2 phosphorus would be the more energetically favorable for overlap with the nitrogen. The orbitals of nitrogen would also be expected to be expanded by the partial negative charge, leading to better overlap with the d orbitals of the PCl_2 phosphorus. This increased pi bonding would correspond to a drift in pi density away from the P-N unit closest to the donating substituent, and towards the P-N units closest to the electron withdrawing

chlorines. This drift of pi density would then increase the electron density around the PCl_2, resulting in decreased attraction toward nucleophiles, and decreased tendency toward substitution.

In the other conceivable mechanism for the deactivation of the remote PCl_2 groups it is not necessary to invoke increased pi bonding at the PCl_2 phosphorus. If we reason that the electron density remains on the nitrogen, rather than delocalizing to phosphorus, the result would still be to retard nucleophilic substitution at the phosphorus. The argument is similar to that used to explain the preference for substitution geminal to the donating group. Consider the reactions of a PCl_2 group of the 1, 1-dimethyl phosphazene **36**, versus the hexachloro analogue with M^+ Nu^- as shown in Schemes 26 and 27. While the attack by Nu^- disrupts a P=N pi bond in each case, indicating roughly equal starting energies, the trigonal intermediate formed in the reaction of the dimethyl compound is destabilized in comparison with the trigonal intermediate formed in the reaction of the hexachloro phosphazene (Figure 28). This destabilzation would be due to the presence of two negative charges, the one formed by nucleophilic attack, and the partial one induced by the electron donation of the methyl groups. If we assume, as before, that only the forward reaction is energetically feasible, and that the transition state leading to the the less stable intermediate reflects this instability and is thus higher in energy than the transition state leading to the more stable intermediate, then the dipole induced by the methyl groups would slow reaction at the remote PCl_2 group, without increasing electron density at that phosphorus.



Scheme 26.



Scheme 27.

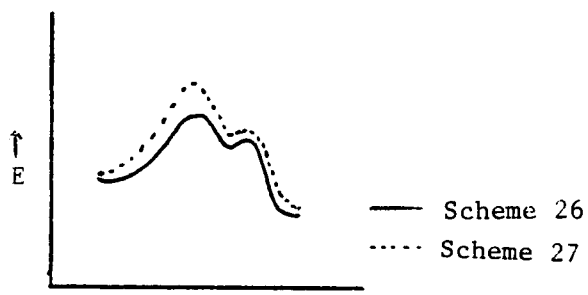


Figure 28. Energy diagram showing deactivation of remote PCl_2 group

It is not easy to differentiate between these two mechanisms. If the increased pi-bonding model is correct, the starting phosphazenes might be expected to show higher frequency infra-red absorptions for the P-N skeletal vibrations, since this is basically a ground state argument. Unfortunately, the P-N absorptions are very broad, and minor variations in the frequency are not always noticeable. The other mechanism is based upon the higher energy intermediate. Intermediates of this type are labile, and while suspected to occur in various reactions of phosphazenes, they have avoided detection thus far. Even the general mechanism for nucleophilic substitution is still in doubt, and drawing subtle distinctions between two similar mechanisms for this deactivating effect is impossible at this time. Nevertheless, the deactivation by electron donating groups is the expected effect, and it is likely that other reasonable mechanisms can be envisioned.

CONCLUSIONS

The reactions investigated in this study shed light on the nature of the patterns of nucleophilic substitutions of cyclotriphosphazenes.

Much has been written concerning the substitution patterns of various nucleophiles in the multisubstitution of cyclotriphosphazenes. Table 15 lists the nucleophiles for which these patterns have been deduced, and the geminal or nongeminal nature of the patterns.

The reasons for the preference of one of these patterns over the other are not immediately obvious and various explanations have appeared in the literature. For example, Allcock has presented a model for amine substitutions in which electronic factors are dominant. He argued that the replacement of the first chlorine on a phosphorus by an amino group should increase electron density on the same phosphorus, by both inductive and resonance electron donation from N to P. Thus the normal pathway for amine substitution would be nongem. Steric effects, in this argument, would also favor a nongem pathway since a trigonal intermediate with two large amino groups on the same P would be more crowded than one which has two chlorines and one amino group. Thus Allcock considers the nongem substitution pathway of large amines normal by both electronic and steric effects, and the gem pathway followed by smaller, or less electron donating amines anomolous. In this latter category he puts ammonia, aziridine, and the anilines. The gem substitution pathway of t-butylamine,

which is both large and strongly electron donating does not fit well into Allcocks explanation.

Other explanations for geminal substitution have been discussed earlier. Both Moeller and Shaw have suggested that a proton may be removed from the first amino-substituent. Loss of the geminal chloride ion leads to an iminium type intermediate (Figure 16, page 71) which rapidly reacts with another amine molecule. This mechanism resembles an S_N1 mechanism, with the P^+ formed by loss of Cl^- stabilized by donation from N. By suggesting an S_N1 rather than an S_N2 type mechanism, it is simple to explain geminal direction by electron donors. Shaw has suggested a similar mechanism for the substitution of t-butylamine. Another explanation offered by Shaw is that the incoming nucleophile coordinates to the amino group already present (Figure 16, page 71) forcing the second amine to substitute geminally. However, neither of these mechanisms explains the gem substitution pathway followed by aziridine, which has no proton on the amino substituent to stabilize an iminium intermediate or coordinate with an incoming molecule.

The powerful geminal directing ability of the CH_3 group shows that electron donating substituents electronically favor geminal rather than nongeminal nucleophilic substitution. Sterically, the methyl group is generally considered similar in size to chlorine. This is convenient, since the trigonal intermediates for gem and nongem substitution should be sterically similar, thus allowing a direct comparison of the electronic effects of CH_3 versus chlorine. Since amino groups, like the methyl

group, are electron donors in comparison to chlorine, geminal substitution pathways should be favored electronically in amine substitutions. Thus the nongem pathway followed by large amines such as diethylamine can be attributed to steric effects, with a less crowded intermediate leading to nongem substitution than to gem. The tendency towards gem substitution by N nucleophiles when unaffected by steric crowding can be seen in the substitutions by NH_3.

Another factor which may be important but which has rarely been alluded to in the literature is the selectivity of the nucleophile. A relatively weak attacking nucleophile may be expected to be more selective, assuming similar mechanisms, than a stronger one, and thus favor reaction at the electronically activated geminal position. A stronger nucleophile on the other hand, would be energetic enough to substitute at either the gem or nongem positions. Since with amines the larger ones tend to be the more nucleophilic, these effects would both work towards a preponderence of nongem substitution products. Also favoring nongem substitution for those amines nucleophilic to attack a PCl_2 group is the statistical advantage that there are four nongem chlorines and only one gem chlorine.

The increased selectivity of a weaker nucleophile can be seen by comparing the substitutions of isopropylamine and aniline. These are both similar in size, being branched primary amines, but the aromatic amine is a much weaker nucleophile due to delocalization of the nitrogen lone pair throughout the benzene ring. Consequently aniline shows an exclusively geminal substitution pattern while the isopropylamine is less selective,

substituting both geminally and nongeminally. The gem substitution pattern of aziridine can also be explained in terms of selectivity. The small ring angles require the use of substantial p character in the endocyclic bonds. This puts the lone pair in an orbital of substantial s character, reducing its nucleophilicity by the proximity to the nucleus.

The amine which would still seem anomolous is the very large t-butylamine, which substitutes by a geminal pathway. This could be due to a different mechanism being followed in substitutions by t-butylamine, for example via coordination through N-H or via the stabilized iminium ion formed by loss of the N-H. However, the large size of the t-butyl group would seem to preclude the close approach of the incoming amino group to the amino substituent that both of these mechanisms imply. Perhaps a better explanation is that the t-butylamino group is a strong enough electron donor that the electronic effects favoring gem substitution are enough to overcome the large steric bulk of the amine, and lead to gem substitution.

Concerning oxygen nucleophiles, Allcock has used a similar argument to amino substitution to explain the observed nongem pathways of phenoxides and alkoxides. That is, the nongem pathway derives from electronic effects, donation from O to P, and steric effects. It is unfortunate that the substitution pathways have not been elucidated for more oxygen nucleophiles. However the argument presented above is adequate to explain the nongem pathways which have been observed.

Electronically, the oxy substituents are apparently not very different from chlorines, but can be seen to be weak donors by basicity measurements and bond lengths. This electron donation favors geminal substitution, not nongem as described by Allcock. Aryloxy substituents are weaker donors than alkoxies for the same reason that aniline is a weaker nucleophile than aliphatic amines. Thus the nongem pathways followed by aryloxides and alkoxides can be seen to be controlled by a combination of poor gem activation due to poor electron donation from O to P, and the strong nucleophilicity of the attacking oxyanions. While phenoxide might be expected to show more selectivity than an alkoxide, the geminal activation by a phenoxy substitiuent is less than that caused by an alkoxy substituent. The steric argument cannot fully explain the nongem pathway followed by alkoxides, and certainly by phenoxide, since phenoxide ion and aniline are very similar in size and aniline follows a geminal pathway. It might be expected that a small alkoxide such as methoxide would show both gem and nongem substitution products.

Additional information into the effect of oxy-substituents on further substitution can be gained from the reaction of $(NPCl_2)_3$ with neutral alcohols. While these reactions are synthetically limited, and thus poorly investigated, a simple experiment can be performed by dissolving the phosphazene in the alcohol and observing the ^{31}P nmr spectrum over a period of time. For example, in methanol, a single AX_2 pattern becomes visible within about thirty minutes. With time this signal gets larger with respect to the $(NPCl_2)_3$ signal. After several hours a second, smaller AX_2 pattern can be seen to appear. It is likely that the first

of these two AX_2 patterns belongs to the monosubstituted product and that the second belongs to the disubstituted product. If this is so, the substitution pattern can clearly be seen to be geminal. This is because both AX_2 systems show doublets in the PCl_2 chemical shift range, and triplets in the P-OR region. If the smaller AX_2 pattern belonged to a nongeminally substituted product, the PCl_2 phosphorus would show as a triplet, split by two Cl-P-OCH_3 groups, and the Cl-P-OCH_3 would show up as a doublet. Similar behavior was observed with $(NPCl_2)_3$ dissolved in ethanol and n-propanol. It would appear from this evidence that neutral alcohols substitute geminally, in contrast to alkoxide ions. Thus the OCH_3 group can be seen as a geminal director in substitutions with the weakly nucleophilic and highly selective methanol molecule, but not with the highly nucleophilic and poorly selective methoxide ion.

Table 15. Substitution Pattern of Selected Nucleophiles In Reaction with $(NPCl_2)_3$

Compound	Substitution Pattern	Reference
NH3	gem	81, 82
MeNH2	gem and nongem	85
EtNH2	nongem	87
iPrNH2	gem and nongem	90
tBuNH2	gem	88
PhNH2	gem	89
mClPHNH2	gem	89
Me2NH	mainly nongem	92
Et2NH	nongem	123
nPr2NH	nongem	123
nBu2NH	nongem	123
C2H4NH	gem	56, 57
C4H8NH	nongem	98
C5H10NH	nongem	100
NaOPh	nongem	113, 114
NaOBu	nongem	112
MeOH, EtOH, nPrOH	gem?	this work

EXPERIMENTAL

General:Hexachlorocyclotriphosphazene $(NPCl_2)_3$, was supplied by Ethyl Corp. or by Shinisso Kako Ltd. and was purified by sublimation followed by recrystallization from n-hexane until a melting point of 112°C was attained. Methyl Grignard reagents were supplied by Aldrich Chem. Co. as 2.5-3.0M solutions in THF. Other Grignard reagents were prepared from the appropriate aryl bromide by standard methods and were titrated under nitrogen against 1.0M sec-butyl alcohol in toluene, with 1,10-phenthroline hydrate as the indicator.[125] m Bromo N,N dimethylaniline was prepared from m-bromoaniline by the method of Billman.[126] The bifunctional amines, aminoalcohols, and diols, were supplied by Aldrich and were vacuum distilled before use. THF was distilled from a sodium benzophenone ketyl drying agent, and dichloromethane was distilled from P_4O_{10}.

Nuclear magnetic resonanc spectra were obtained with the use of either a Perkin-Elmer EM 390, a PS 100, an NR 80, a Bruker JEOL 200, or a Bruker JEOL 270MHz spectrometer. An internal standard of tetramethylsilane was used as a reference for all ^1H and ^{13}C spectra. The ^{19}F spectra were referenced to internal CCl_3F, and the ^{31}P spectra were referenced to a capillary of 85% H_3PO_4 inserted into the sample. Infrared spectra were obtained with the use of a Perkin Elmer 710B spectrometer. the samples were prepared as KBr pellets. Ultraviolet spectra were obtained on a Hitachi Perkin Elmer 100-60 spectrometer. Mass spectral data were ob-

tained by the use of a Varian MAT 112 magnetic instrument operating at 70 eV.

1-methyl-1-(3-hydroxypropylamino)-3,3,5,5-tetrachlorocyclotriphosphazene, **53**:

Monomethylpentachlorocyclotriphosphazene **20** (1.00g, 3.07mmol) and triethylamine (0.34g, 3.40mmol) were dissolved in dichloromethane (75ml) and cooled to 0°C. A solution of 3-amino-1-propanol (0.21g, 2.79mmol) in dichloromethane (25ml) was dropped in with stirring over a period of 15min. The reaction mixture was allowed to warm to room temperature and stirred for 8hr. The mixture was water washed (2x100ml) to remove amine hydrochloride and any unreacted amine. The organic layer was dried with $MgSO_4$ and the solvent removed under vacuum. The residue washed several times with hexane to remove excess **20** and leave the product as a colorless oil, 1.10g, 98%.

^{31}P NMR (200 MHz, in ppm, proton decoupled, $CDCl_3$ solution):

25.0 t (J=19.5Hz) CH_3-**P**-N

19.5 d (J=19.5Hz) Cl-**P**-Cl

^{1}H NMR (90MHz, in ppm, after treatment with D_2O, $CDCl_3$ solution):

1.67 d of t (J=15.9Hz, J=2.^{1}Hz, 3H) P-C**H**$_3$

1.80 unres. m (2H) P-N-C-C**H**$_2$

3.10 unres. m (2H) P-N-C**H**$_2$

3.75 t (J=7.0Hz, 2H) P-N-C-C-C**H**$_2$

^{13}C NMR (80MHz, $CDCl_3$ solution):

18.6 d,t (J=124.0Hz, J=6.7Hz) P-**C**

37.6 s P-N-**C**

32.8 s P-N-C-**C**.

60.6 d (J=6.6Hz) P-N-C-C-**C**

IR (CCl_4, cm^{-1})

3320 (N-H, O-H), 2940, 2890 (C-H), 1390 (C-H bend), 1230, 1180 (P-N)

MS (EI, 70 eV):

364 Cl_4 (M^+), 290 Cl_4 (loss of ligand)

Anal. Calcd: C 13.11 H 3.00 N 15.30

Anal. Found: C 13.20 H 2.94 N 15.18

1-methyl-ansa-(1-aza-3-oxapentyl)-3,5,5-trichlorocyclotriphosphazene **54**:

A suspension of NaH (0.12g of 60% NaH in oil, washed with hexane, 2.85mmol) in dry THF was prepared under a nitrogen atmosphere and cooled to 0°C. A solution of 1-methyl-1-(3-hydroxypropylamino)-3,3,5,5 tetrachlorocyclotriphosphazene **53** (0.70g, 1.92mmol) in THF (25ml) was dropped in over a period of 15min. The mixture was allowed to warm to room temperature and stirred for 36hr. The THF was removed under vacuum and dichloromethane was added to the residue. This solution was water washed (2x75ml) to remove NaCl and any NaOH which was present. The organic layer was dried with $MgSO_4$ and the solvent removed under vacuum to leave a mixture of the product and a white resinous material. The mixture was extracted repeatedly with boiling hexane. The extracts were filtered and combined and the solvent removed under vacuum to leave the crude product as a white solid (0.38g, 60%). Final purification was effected by recrystallization from dichloromethane-hexane solution. Mp 144-145°C.

^{31}P NMR (200 MHz, in ppm, proton decoupled, $CDCl_3$ solution):

24.5 d,d (J=48.8Hz, J=9.3Hz) Cl-**P**-Cl

29.3 d,d (J=48.8Hz, J=4.0Hz) Cl-**P**-O

31.2 d,d (J=9.8Hz,J=4.0Hz) CH_3-**P**-N

^{1}H NMR (90MHz, in ppm, after treatment with D_2O, $CDCl_3$ solution):

1.71 d of t (J=16.9Hz, J=3.3Hz, 3H) P-CH_3

1.85 unres. m (2H) P-N-C-CH_2

3.04 unres. m (1H) P-N**H**

3.30 unres. m (2H) P-N-CH_2

4.45 unres m (2H) P-O-CH_2

^{13}C NMR (80MHz, $CDCl_3$ solution):

18.1 d,t (J=130.0Hz, J=10.0Hz) P-**C**

32.1 s P-N-C-**C** (P-O-C-**C**)

38.5 s P-N-**C**.

67.2 d (J=6.6Hz) P-O-**C**

IR (CCl_4, cm^{-1})

3310 (N-H), 2970, 2940, 2890 (C-H), 1390 (C-H bend), 1190 (P-N)

MS (EI, 70 eV):

328 Cl_3 (M^+), 293 Cl_3 (loss of CH_3)

Anal. Calcd: C 14.57 H 3.03 N 17.00

Anal. Found: C 14.76 H 3.06 N 16.87

1-methyl-1-(4-hydroxybutylamino)-3,3,5,5-tetrachlorocyclotriphosphazene, **55**:

Monomethylpentachlorocyclotriphosphazene (2.00g, 6.15mmol) and triethylamine (0.66g, 6.52mmol) were dissolved in dichloromethane (125ml) and

cooled to 0°C. A solution of 4-amino-1-butanol (0.50g, 5.61mmol) dissolved in dichloromethane (25ml) was dropped in with stirring over a period of 15min. The reaction mixture was allowed to warm to room temperature and stirred for 8hr. The mixture was water washed (2x100ml) to remove amine hydrochloride and any unreacted amine. The organic layer was dried with $MgSO_4$ and the solvent removed under vacuum. The residue washed several times with hexane to remove excess starting phosphazene **20** and leave the product as a colorless oil, 1.55g, 67%.

^{31}P NMR (200 MHz, in ppm, proton decoupled, $CDCl_3$ solution):

25.1 t (J=26.5Hz) CH_3-**P**-N

20.6 d (J=26.5Hz) Cl-**P**-Cl

^{1}H NMR (90MHz, in ppm, after treatment with D_2O, $CDCl_3$ solution):

1.61 d of t (J=16.0Hz, J=3.0Hz, 3H) P-CH_3

1.80 unres. m (4H) P-N-C-CH_2-CH_2

3.10 unres. m (2H) P-N-CH_2

3.70 t (J=7.0Hz, 2H) P-N-C-C-CH_2

^{13}C NMR (80MHz, $CDCl_3$ solution):

18.3 d,t (J=120.0Hz, J=6.0Hz) P-**C**

39.8 s P-N-**C**

29.5 s P-N-C-**C**.

27.9 P-N-C-C-**C**

62.2 d (J=6.6Hz) P-N-C-C-C-**C**

IR (CCl_4, cm^{-1})

3450, 3325 (N-H, O-H), 2975, 2910 (C-H), 1430, 1300 (C-H bend), 1260 (P-N

MS (EI, 70 eV):

378 Cl_4 (M^+), 290 Cl_4 (loss of ligand) 275 Cl_4 (loss of CH_3 and ligand)

Attempted Synthesis of 1-methyl-ansa-(1-aza-3-oxahexyl)-3,5,5-trichloro cyclotriphosphazene:

A suspension of NaH (0.20g of 60% NaH in oil, washed with hexane, 5.00mmol) in dry THF was prepared under a nitrogen atmosphere and cooled to 0°C. A solution of 1-methyl-1-(4-hydroxybutylamino)-3,3,5,5 tetrachlorocyclotriphosphazene **55** (1.25g, 3.31mmol) in THF (25ml) was dropped in over a period of 15min. The mixture was allowed to warm to room temperature and stirred for 16hr. The THF was removed under vacuum and dichloromethane was added to the residue. This solution was water washed (2x75ml) to remove NaCl and any NaOH which was present. The organic layer was dried with $MgSO_4$, the solvent removed under vacuum, and the mixture extracted repeatedly with boiling hexane. The extracts were filtered and combined and the solvent removed under vacuum to leave the crude product **56** as a white solid (0.51g, 43%). Final purification was effected by recrystallization from hexane solution. Mp 93-94°C.

^{31}P NMR (270 MHz, in ppm, proton decoupled, $CDCl_3$ solution):

33.4 t (J=34.0Hz) CH_3-**P**-N

21.6 d (J=34.0Hz) Cl-**P**-Cl

^{1}H NMR (100MHz, in ppm, after treatment with D_2O, $CDCl_3$ solution):

1.70 d,t (J=16.5Hz, J=2.0Hz, 3H) P-C**H**$_3$

1.92 res. m (4H) P-N-C-C**H**$_2$

3.15 res. m (4H) P-N-C**H**$_2$

3.75 t (J=7.0Hz, 2H) P-N-C-C-C**H**$_2$

^{13}C NMR ($80MHz$, $CDCl_3$ solution):

17.9 d,t (J=125.0Hz, J=6.2Hz) P-**C**

26.1 d (J=9.5Hz) P-N-C-**C**

35.1 d (J=3.4Hz) P-N-**C**

IR (KBr, cm^{-1})

2980, 2940, 2900, 2860 (C-H), 1440 (C-H bend), 1230, 1170 (P-N)

MS (EI, 70 eV):

360 Cl_4 (M^+), 290 Cl_4 (loss of ligand) 275 Cl_4 (loss of CH_3 and ligand)

1-methyl-1-pyrrolidino-3,3,5,5-3,3,5,5-tetrachlorocyclotriphosphazene, **56**:

Monomethylpentachlorocyclotriphosphazene **20** (0.50g, 1.54mmol) and triethylamine (0.16g, 1.58mmol) were dissolved in dichloromethane (50ml) and cooled to 0^oC. A solution of pyrrolidine in dichloromethane (0.11g, 1.55mmol in 10ml) was dropped in over a period of 10min. The reaction mixture was allowed to warm to room temperature and stirred for 4hr. The solvent was removed under vacuum and the residue extracted with boiling hexane. The hexane solutions were filtered and combined and the solvent removed under vacuum to leave the crude product as a white solid (0.52g, 94%). Final purification was effected by recrystallization from hexane. Mp 93-94^oC. All spectral data identical with product **56** as described above..

1-methyl-1-(5-hydroxypentylamino)-3,3,5,5-tetrachlorocyclotriphosphazene **57**:

Monomethylpentachlorocyclotriphosphazene **20** (1.0g, 3.10mmol) and triethylamine (0.39g, 3.90mmol) were dissolved in dichloromethane (75ml) and cooled to 0°C. A solution of 5-amino-1-pentanol (0.32g, 3.10mmol) dissolved in dichloromethane (25ml) was dropped in with stirring over a period of 15min. The reaction mixture was allowed to warm to room temperature and stirred for 16hr. The mixture was water washed (2x100ml) to remove amine hydrochloride and any unreacted amine. The organic layer was dried with $MgSO_4$ and the solvent removed under vacuum to leave the crude product as a white solid (0.98g, 81%). Final purification was effected by recrystallization from hexane. Mp 72-73°C.

^{31}P NMR (270MHz, proton decoupled, in ppm, $CDCl_3$ solution):

25.0 t (J=27.4Hz) CH_3-**P**-N

20.5 d (J=27.4Hz) Cl-**P**-Cl

^{1}H NMR (270MHz, in ppm, after treatment with D_2O, $CDCl_3$ solution):

1.67 d (J=18Hz, 3H) P-C**H**$_3$

1.50 unres. m (6H) P-N-C-C**H**$_2$-C**H**$_2$-C**H**$_2$

2.95 unres. m (2H) P-N-C**H**$_2$

3.65 t (J=7.0Hz, 2H) P-N-C-C-C-C-C**H**$_2$

^{13}C NMR (80MHz, $CDCl_3$ solution):

18.5 d (J=126.4Hz) P-**C**

22.7 s P-N-C-C-**C**

30.8 s P-N-C-**C**

32.0 s P-N-C-C-C-**C**

39.9 s P-N-**C**

62.4 s P-N-C-C-C-C-**C**

IR (KBr, cm^{-1})

3260 (N-H, O-H), 2950, 2870 (C-H), 1315 (C-H bend), 1220, 1180 (P-N)

MS (EI, 70 eV):

392 Cl_4 (M^+), 374 Cl_4 (loss of H2O), 290 Cl_4 (loss of ligand),

275 Cl_4 (loss of CH_3 and ligand)

Attempted Synthesis of 1-methyl-ansa-(1-aza-3-oxaheptyl)-3,3,5-trichlorocyclotriphosphazene:

A suspension of NaH (0.12g of 60% NaH in oil, washed with hexane, 3.00mmol) in dry THF was prepared under a nitrogen atmosphere and cooled to 0^oC. A solution of 1-methyl-1-(5-hydroxypentylamino)-3,3,5,5 tetrachlorocyclotriphosphazene **57** (0.80g, 2.04mmol) in THF (25ml) was dropped in over a period of 15min. The mixture was boiled at reflux and stirred for 16hr. The THF was removed under vacuum and dichloromethane was added to the residue. This solution was water washed (2x75ml) to remove NaCl and any NaOH which was present. The organic layer was dried with $MgSO_4$, the solvent removed under vacuum, and the residue extracted repeatedly with boiling hexane. The hexane solvents were filtered and combined and the solvent removed under vacuum.

^{31}**P NMR** (270MHz, proton decoupled, in ppm, $CDCl_3$ solution):

26.2 unres. m CH_3-**P**-N

22.4 d,d (J=58Hz, J=20Hz) Cl-**P**-O

18.8 unres. m Cl-**P**-Cl

^{1}**H NMR** (90MHz, in ppm, after treatment with D_2O, $CDCl_3$ solution):

1.68 d (J=26Hz) P-CH_3

1.70 unres. m P-N-C-CH_2-CH_2-CH_2

3.00 unres. m P-N-CH_2 suggests ansa

4.25 unres. m P-O-CH_2 suggests ansa

IR (CCl_4, cm^{-1})

3330 (N-H), 2980, 2890 (C-H), 1370 (C-H), 1220, 1170 (P-N)

MS (EI, 70 eV):

356 Cl_3 (M^+ for ansa compound)

Bino-1,1'-dimethyl-1,1'-(1,3-propanediamino)-3,3,3',3',5,5,5',5'-octachlorocyclotriphosphazene, **58**:

A solution of 1,3-propanediamine (0.06g, 0.81mmol) and triethylamine (0.17g, 1.70mmol) in dichloromethane (50ml) was prepared. A solution of monomethylpentachlorocyclotriphosphazene in dichloromethane (0.52g, 1.60mmol, in 25ml) was dropped in at room temperature over a period of 30min and the reaction mixture stirred for 2hr. The mixture was water washed (2x75ml) to remove amine hydrochloride and any unreacted amine, the organic layer dried with $MgSO_4$, and the solvent removed under vacuum. The residue was extracted repeatedly with boiling hexane. The hexane solutions were filtered and combined and the solvent removed under vacuum to leave the crude product as a white solid (0.55g, 86%). Final purification was effected by recrystallization from hexane. Mp 154-155°C.

^{31}P NMR (270MHz, proton decoupled, in ppm, $CDCl_3$ solution):

24.8 t (J=22.0Hz) CH_3-**P**-N

20.7 d (J=22.0Hz) Cl-**P**-Cl

^{1}H NMR (90MHz, in ppm, after treatment with D_2O, $CDCl_3$ solution):

1.69 d (J=9.8Hz) P-CH_3

1.70 unres. m (together with P-CH_3, 8H) P-N-C-CH_2

3.10 d,t (J=12Hz, J=6Hz) P-N-CH_2

^{13}C NMR (80MHz, $CDCl_3$ solution):

18.7 d (J=124.8Hz) P-**C**

31.5 s P-N-C-**C**

37.2 s P-N-**C**

IR (KBr, cm^{-1})

3310 (N-H), 2940. 2890 (C-H), 1230, 1175 (P-N)

MS (EI, 70 eV):

364 Cl_4 (M^+-$N_3P_3Cl_4CH_3$), 290 Cl_4 ($N_3P_3Cl_4CH_3$)

1-methyl-ansa-1,3-(1,3-propanedioxy)-3,5,5-trichlorocyclotriphosphazene, **60**:

To a solution of 1,3-propanediol in dry THF under a nitrogen atmosphere (0.18g, 2.36mmol in 125ml) was added NaH (0.30g of 60% NaH in oil, washed with hexane, 7.50mmol). This suspension was boiled at reflux for 30min and cooled to 0°C. A solution of monomethylpentachlorocyclotriphosphazene **20** in THF (0.77g, 2.37mmol in 25ml) was dropped in over a period of 30min. The mixture was allowed to warm to room temperature and stirred for 16hr. The solvent was removed under vacuum and the reaction mixture extracted with warm hexane. The hexane extracts were filtered and combined and the solvent removed under vacuum to yield a mixture of two colorless oils of different viscosity. The thinner oil was removed by washing with 0°C hexane (2x10ml) and discarded. The residue solidified under vacuum. This solid was recrystallized from hexane to yield the product as a white crystalline solid. Mp 59-60°C.

^{31}P NMR (270MHz, proton decoupled, in ppm, $CDCl_3$ solution):

36.3 m O-**P**-CH_3

27.9 d,m (J=50Hz) Cl-**P**-O

24.9 d,d (J=50Hz, 12Hz) Cl-**P**-Cl

^{1}H NMR (100MHz, in ppm, after treatment with D_2O, $CDCl_3$ solution):

1.70 d,t (J=18Hz, J=3Hz, 3H) P-CH_3

2.10 br. p (J=5Hz, 2H) P-O-C-CH_2

4.20 d,t (J=18Hz, J=5Hz, 2H) P-O-CH_2

4.40 unres. m (2H) P-O-CH_2

^{13}C NMR (80MHz, $CDCl_3$ solution):

15.5 d,t (J=147.2Hz, J=9.5Hz) P-**C**

30.7 s P-O-C-**C**

62.4 d (J= 7.3Hz) CH_3-P-O-**C**

67.1 d (J= 6.2Hz) Cl-P-O-**C**

IR (KBr, cm^{-1})

3000, 2950 (C-H), 1480, 1420, 1380, 1320 (C-H bend), 1220, 1180 (P-N)

MS (EI, 70 eV):

329 Cl_3 (M^+), 314 Cl_3 (loss of CH_3), 294 Cl_2 (loss of Cl)

1-methyl-1,3-ansa-(1,4-butanedioxy)-3,5,5-trichlorocyclotriphosphazene, **62**:

To a solution of 1,4-butanediol in dry THF under a nitrogen atmosphere (0.20g, 2.22mmol in 125ml) was added NaH (0.27g of 60% NaH in oil, washed with hexane, 6.75mmol). This suspension was boiled at reflux for 30min. A solution of monomethylpentachlorocyclotriphosphazene **20** in THF (0.72g, 2.21mmol in 25ml) was dropped in rapidly at reflux. The mixture was al-

lowed to cool to room temperature and stirred for 16hr. The solvent was removed under vacuum and replaced with dichloromethane (100ml). This solution was water washed (2x100ml), the organic layer dried with $MgSO_4$, and the solvent removed under vacuum. The residue was extracted repeatedly with cold hexane. The hexane solutions were filtered and combined and the solvent removed under vacuum to leave the crude product as a low melting white solid (0.20g, 25%). Final purification was effected by dissolving the crude solid in dichloromethane (1ml) in a sample vial. This vial was placed open in a covered jar containing 1/2 inch of pentane. Upon cooling the jar to $0^{o}C$ the product recrystallized from the dichloromethane. The product was filtered and washed with cold pentane. Mp53-55^{o}C.

^{31}P NMR (270MHz, proton decoupled, in ppm, $CDCl_3$ solution):

34.2 d,d (J=16Hz, J=12Hz) CH_3-**P**-O

25.6 d,d (J=50Hz, J=16Hz) Cl-**P**-O

24.3 d,d (J=50Hz, J=12Hz) Cl-**P**-Cl

^{1}H NMR (90MHz, in ppm, after treatment with D_2O, $CDCl_3$ solution):

1.70 d,d (J=18Hz, J=3Hz) P-C**H**$_3$

1.70 m (together with P-C**H**$_3$, 4H) P-O-C-C**H**

1,90 m (1H) P-O-C-C**H**

2.10 m (1H) P-O-C-C**H**

2.45 m (1H) P-O-C-C**H**

4.23 m (4H) P-O-C**H**$_2$

^{13}C NMR (80MHz, $CDCl_3$ solution):

16.0 d,t (J=148hz, J=10Hz) P-**C**

24.8 s CH_3-P-O-C-**C**

27.3 s Cl-P-O-C--C

63.8 d (J=7.4Hz) CH_3-P-O-**C**

68.4 d (J=5.7Hz) Cl-P-O-**C**

IR (KBr, cm^{-1})

3000 (C-H), 1470, 1430, 1335 (C-H bend), 1250, 1200 (P-N)

MS (EI, 70 eV):

343 Cl_3 (M^+)

1-methyl-1-(4-hydroxybutoxy)-3,3,5,5-tetrachlorocyclotriphosphazene, **61**: To a solution of 1,4-butanediol (0.14g, 1.55mmol, in 100ml) in dry THF under a nitrogen atmosphere was added NaH (0.18g of 60% NaH in oil, washed with hexane, 4.50mmol). This suspension was boiled at reflux for 30min and cooled to -78°C. A solution of monomethylpentachlorocyclotriphosphazene **20** in THF (0.55g, 1.71 mmol, in 25ml) was dropped in with stirring over a period of 30min. The mixture was allowed to warm to room temperature and stirred for 16hr. The solvent was removed under vacuum and replaced with dichloromethane (100ml). This solution was water washed (2x100ml), the organic layer dried with $MgSO_4$, and the solvent removed under vacuum to leave a colorless oil. This oil was washed with cold hexane to remove unreacted starting phosphazene and any ansa complound which may have formed, leaving the product as a colorless oil (0.61g, 95%).

^{31}P NMR (270MHz, proton decoupled, in ppm, $CDCl_3$ solution):

30.2 t (J=22Hz) CH_3-**P**-O

21.4 d (J=22Hz) Cl-**P**-Cl

^{1}H NMR (90MHz, in ppm, after treatment with D_2O, $CDCl_3$ solution):

1.66 d (J=18Hz, 3H) P-CH_3

1.80 unres. m (4H) P-O-C-CH_2

3.70 t (J=8Hz, 2H) P-O-C-C-C-CH_2

3.95 d,t (J=7Hz, J=7Hz, 2H) P-O-CH_2

^{13}C NMR (80MHz, $CDCl_3$ solution):

17.0 d,t (J=145.5Hz, J=7.0Hz) P-**C**

28.6 s P-O-C-C-**C**

29.5 s P-O-C-**C**

62.6 s P-O-C-C-C-**C**

64.8 d (J=4Hz) P-O-**C**

IR (CCl_4, cm^{-1})

3475 (O-H), 2950 (C-H), 1490, 1470, 1420, 1380 (C-H bend), 1260, 1200 (P-N)

MS (EI, 70 eV):

361 Cl_4 (M^+-H2O), 290 Cl_4 (loss of ligand)

1,1-dimethyl-spiro-3,3-(propanediamino)-5,5-dichlorocyclotriphosphazene, **42**:

A solution of 1,1-dimethyl-3,3,5,5- tetrachlorocyclotriphosphazene **36** (1.0g, 3.28mmol) and triethylamine (0.75g, 7.41mmol) in dichloromethane (75ml) was prepared. A solution of 1,3-propanediamine in dichloromethane (0.25g, 3.37mmol, in 25ml) was added dropwise with stirring over a period of 15min and the reaction mixture allowed to stir for 36hr. The reaction mixture was water washed (2x100ml) to remove amine hydrochloride and unreacted amine, the organic layer dried with $MgSO_4$, and the solvent removed under vacuum to leave the crude product as a white solid (0.75g, 75%).

Final purification was effected by recrystallization from dichloromethane-hexane solution. Mp 182-183°C.

^{31}P NMR (270MHz, proton decoupled, in ppm, $CDCl_3$ solution):

33.8 d,d (J=32Hz, J=20Hz) C-**P**-C

20.0 d,d (J=32Hz, J=20Hz) Cl-**P**-Cl

10.8 d,d (J=20Hz, J=20Hz) N-**P**-N

^{1}H NMR (270MHz, in ppm, $CDCl_3$ solution)

1.58 d,t (J=14.2Hz, J=1.5Hz, 3H) P-CH_3

1.70 unres. m (2H) P-N-C-C**H**

2.50 br s (exchanges with D20, 1H) P-N**H**

3.23 unres m and

3.30 unres m (2H) P-N-CH_2

^{13}C NMR (80MHz, $CDCl_3$ solution):

21.5 d,t (J=94.0Hz, 3.6Hz) P-**C**

26.1 d (J=6.^{1}Hz) P-N-C-**C**

40.9 d (J=3.5Hz) P-N-**C**

IR (KBr, cm^{-1})

3350 (N-H), 2975, 2960, 2885 (C-H), 1420, 1385, 1335 (C-H bend)

1230, 1150 (P-N)

MS (EI, 70 eV):

307 Cl_2 (M^+), 292 Cl_2 (loss of CH_3) 235 C12 (loss of ligand)

Anal. Calcd: C 19.50 H 4.58 N 27.74

Anal. Found: C 19.12 H 4.42 N 21.13

1,1-dimethyl-spiro-3,3-(butanediamino)-5,5-dichlorocyclotriphosphazene, **43**:

A solution of 1,1-dimethyl-3,3,5,5- tetrachlorocyclotriphosphazene **36** (1.0g, 3.28mmol) and triethylamine (0.75g, 7.41mmol) in dichloromethane (75ml) was prepared. A solution of 1,4-butanediamine in dichloromethane (0.29g, 3.29mmol, in 25ml) was added dropwise with stirring over a period of 15min and the reaction mixture allowed to stir for 36hr. The reaction mixture was water washed (2x100ml) to remove amine hydrochloride and unreacted amine, the organic layer dried with $MgSO_4$, and the solvent removed under vacuum to leave the crude product as a white solid (0.96g, 94%). Final purification was effected by recrystallization from dichloromethane-hexane solution. Mp 181-182°.

^{31}P NMR (270MHz, proton decoupled, in ppm, $CDCl_3$ solution):

32.7 d,d (J=20Hz, J=15Hz) C-**P**-C

21.7 d,d (J=40Hz, J=20Hz) Cl-**P**-Cl

15.0 d,d (J=40Hz, J=15Hz) N-**P**-N

^{1}H NMR (270MHz, in ppm, $CDCl_3$ solution):

1.55 d (J=15Hz) P-CH_3

1.59 unres m (together with P-CH_3, 10H) P-N-C-CH_2

2.82 br s (exchanges with D_2O, 1H) P-N**H**

3.05 unres m, and

3.10 unres m (4H) P-N-CH_2

^{13}C NMR (80MHz, $CDCl_3$ solution):

21.4 d (J=94.5Hz) P-**C**

31.8 s P-N-C-**C**

40.3 s P-N-**C**

IR (KBr, cm^{-1})

3320 (N-H), 2950. 2925 (C-H), 1425, 1395 (C-H bend), 1270, 1170 (P-N)

MS (EI, 70 eV):

321 Cl_2 (M^+)

1,1-dimethyl-spiro-3,3-(propanolamino)-5,5-dichlorocyclotriphosphazene, **44**:

A solution of 1,1-dimethyl-3,3,5,5- tetrachlorocyclotriphosphazene **36** (0.8g, 2.62mmol) and triethylamine (0.50g, 4.95mmol) in dichloromethane (75ml) was prepared. A solution of 3-amino-1-propanol in dichloromethane (0.18g, 2.40mmol, in 25ml) was added dropwise with stirring over a period of 15min and the reaction mixture allowed to stir for 36hr. The reaction mixture was water washed (2x100ml) to remove amine hydrochloride and unreacted amine, the organic layer dried with $MgSO_4$, and the solvent removed under vacuum to leave the crude product as a white solid (0.76g, 76%). Final purification was effected by recrystallization from dichloromethane-hexane solution. Mp 152-153°.

^{31}P NMR (270MHz, proton decoupled, in ppm, $CDCl_3$ solution):

35.3 d,d (J=22.^{1}Hz, J=14.5Hz) C-**P**-C

20.5 d,d (J=31.6Hz, J=14.5Hz) Cl-**P**-Cl

10.0 d,d (J=31.6Hz, J=22.^{1}Hz) N-**P**-O

^{1}H NMR (270MHz, in ppm, $CDCl_3$ solution):

1.55 d (J=7Hz) CH_3-P-N-P-N

1.60 d (J=7Hz, together with 1.55 d, 6H) CH_3-P-N-P-O

2.00 unres m (2H) P-N-C-C**H** and P-O-C-C**H**

2.60 br s (exchanges with D_2O, 1H) P-N**H**

2.28 m and 2.43 m (2H) P-N-CH_2

3.32 d,m and 3.45 m (2H) P-O-CH_2

^{13}C NMR ($80MHz$, $CDCl_3$ solution):

21.4 d,t (J=95Hz, J=4Hz) P-**C**

26.0 d (J=6.^{1}Hz) P-N-C-**C** (P-O-C-**C**)

41.2 d (J=3.5Hz) P-N-**C**

67.1 d (J=7.2Hz) P-O-**C**

IR (KBr, cm^{-1})

3290 (N-H), 2980, 2940, 2890 (C-H), 1420, 1335, 1310 (C-H bend)

1225, 1175 (P-N)

MS (EI, 70 eV):

308 Cl_2 (M^+), 293 Cl_2 (loss of CH_3), 273 Cl1 (loss of Cl)

Anal. Calcd: C 19.44 H 4.24 N 18.13

Anal. Found: C 19.89 H 4.56 N 18.12

1,1-dimethyl-spiro-3,3-(propanolamino)-spiro-5,5-(propanolamino)cyclotriphosphazene, **45**:

A solution of 1,1-dimethyl-3,3,5,5- tetrachlorocyclotriphosphazene **36** (0.40, 1.31mmol) and triethylamine (0.58g, 5.74mmol) in chloroform (50ml) was prepared. A solution of 3-amino-1-propanol in chloroform (0.20g, 2.66mmol, in 10ml) was added dropwise with stirring over a period of 15min and the reaction mixture boiled at reflux for 36hr. The reaction mixture was water washed (2x100ml) to remove amine hydrochloride and unreacted amine, the organic layer dried with $MgSO_4$, and the solvent removed under vacuum to leave the crude product as a white solid (0.16g, 37%). Final purification was effected by recrystallization from dichloromethane-hexane solution. Mp >150 dec

^{31}P NMR (270MHz, proton decoupled, in ppm, $CDCl_3$ solution):

33.95 t (J=21.5Hz) and

34.13 t (J=20.5Hz) C-**P**-C

15.68 d (J=21.5Hz) and

15.77 d (J=20.5Hz) N-**P**-O

^{1}H NMR (90MHz, in ppm, $CDCl_3$ solution):

1.50 d,t (J=12Hz, J=2Hz, 6H) P-C**H**$_3$

1.70 unres. m (2H) P-N-C-C**H**$_2$

2.50 br s (exchanges with D_2O, 2H) P-N**H**

3.35 unres m (4H) P-N-C**H**$_2$

4.35 unres m (4H) P-O-C**H**$_2$

^{13}C NMR (80MHz, $CDCl_3$ solution):

22.1 d (J=94.8Hz) P-**C**

26.3 s P-N-C-**C**

41.0 s P-N-**C**

66.6 s P-O-**C**

IR (KBr, cm^{-1})

3300 (N-H), 2990, 2940, 2880, (C-H), 1220, 1180 (P-N)

MS (EI, 70 eV):

311 C10

1,1-dimethy-spiro-3,3-(1,3-propanedioxy)-5,5-dichlorocyclotriphoshazene, **46**:

To a solution of 1,3-propanediol in dry THF (0.25g, 3.28mmol) under a nitrogen atmosphere was added NaH (0.40g of 60% NaH in oil, washed with hexane, 10.ommol). This suspension was refluxed for 30min and cooled to

$0^{o}C$. A solution of 1,1-dimethyl-3,3,5,5- tetrachlorocyclotriphosphazene **36** in THF (1.00g, 3.28mmol, in 25ml) was dropped in over a period of 30min. The mixture was allowed to warm ot room temperature and stirred for 24hr. The THF was removed under vacuum and dichloromethane (150ml) was added. This solution was water washed (2x150ml) to remove sodium salts and any unreacted diol. Separation of layers was aided by neutralization of the aqueous layer with 10% HCl. The organic layer was dried with $MgSO_4$ and the solvent removed under vacuum to leave the crude product as a white solid (0.93g, 92%). Final purification was effected by recrystallization from dichloromethane-hexane solution. Mp 197-198^{o}C.

^{31}P NMR (270MHz, proton decoupled, in ppm, $CDCl_3$ solution):

36.5 d,d (J=30.7Hz, J=10.2Hz) C-**P**-C

21.7 d,d (J=45.3Hz, J=10.2Hz) Cl-**P**-Cl

5.3 d,d (J=45.3Hz, J=30.7Hz) O-**P**-O

^{1}H NMR (270MHz, in ppm, $CDCl_3$ solution):

1.60 d,t (J=13Hz, J=^{1}Hz, 6H) P-CH_3

2.20 unres. m (2H) P-O-C-CH_2

4.32 m and 4.55 m (4H) P-O-CH_2

^{13}C NMR (80MHz, $CDCl_3$ solution):

21.3 d,t (J=95.2Hz, J=3.7Hz) P-**C**

25.9 d (J=7.^{1}Hz) P-O-C-**C**

67.0 d (J=6.3Hz) P-O-**C**

IR (KBr, cm^{-1})

3000, 2980, 2920 (C-H), 1420, 1310 (C-H bend), 1180, 1240 (P-N)

MS (EI, 70 eV):

309 Cl_2 (M^+), 294 Cl_2 (loss of CH_3)

1,1-dimethy-spiro-3,3-(1,3-propanedioxy)-spiro-5,5-(1,3-propanedioxy)-cyclotriphosphazene, **47**:

To a solution of 1,3-propanediol in dry THF (0.50g, 6.57mmol, in 100ml) under a nitrogen atmosphere was added NaH (0.80g of 60% NaH in oil, washed with hexane, 20.1mmol). This suspension was refluxed for 30min and cooled to $0^{o}C$. A solution of 1,1-dimethyl-3,3,5,5-tetrachloro- cyclotriphosphazene in THF (1.00g, 3.28mmol, in 25ml) was dropped in over a period of 30min. The mixture was allowed to warm ot room temperature and then brought to refluxd for 16hr. The THF was removed under vacuum and dichloromethane (150ml) was added. This solution washed with 1M NaOH (1x150ml) and the aqueous layer saturated with NaCl. to reduce the water solubility of the product. The organic layer was dried with $MgSO_4$ and the solvent removed under vacuum to leave the crude product as a white solid (0.98g, 96%). Final purification was effected by recrystallization from dichloromethane-hexane solution. Mp 209-210^{o}C.

^{31}P NMR (270MHz, proton decoupled, in ppm, $CDCl_3$ solution):

35.2 t (J=30.7Hz) C-**P**-C

11.9 d (J=30.7Hz) O-**P**-O

^{1}H NMR (90MHz, in ppm, after treatment with D_2O, $CDCl_3$ solution):

1.55 d (J=14Hz, 6H) P-C**H**$_3$

1.95 unres. m (4H) P-O-C-C**H**$_2$

4.40 m (8H) P-O-C**H**$_2$

^{13}C NMR (80MHz, $CDCl_3$ solution):

21.8 d,t (J=95.6Hz, J=3.7Hz) P-**C**

26.0 t (J=3.5Hz) P-O-C-**C**

66.1 d (J=2.3Hz) P-O-**C**

IR (KBr, cm^{-1})

3000, 2950, 2910 (C-H), 1490, 1425, 1310 (C-H bend), 1230, 1155 (P-N)

MS (EI, 70 eV):

313 C10 (M^+), 298 C10 (loss of CH_3)

Anal. Calcd: C 30.68 H 5.79 N 13.42

Anal. Found: C 30.98 H 5.65 N 13.31

1-methyl-1-hydrido-spiro-3,3-(1,3-propanediamino)-5,5-dichlorocyclotriphosphazene, **50**:

A solution of 1-methyl-1- hydridotetrachlorocyclotriphosphazene **35**, prepared by standard methods[124] immediately prior to use (1.65g, 5.67mmol) and triethylamine (1.2g, 11.9mmol) in dichloromethane (125ml was prepared under a dry nitrogen atmosphere. A solution of 1,3-propanediamine in dichloromethane (0.42g, 5.67mmol in 25ml) was added dropwise at room temperature over a period of 30min and the mixture stirred for 36hr. The solvent was removed under vacuum and the residue extracted repeatedly with boiling hexane. The hexane solutions were filtered and combined and the solvent removed under vacuum to leave the crude product as a white solid (1.10g, 66%).

^{31}P NMR (270MHz, proton decoupled, in ppm, $CDCl_3$ solution):

20.90 d,d (J=24Hz, J=16Hz) Cl-P-Cl

12.38 d,d (J=16Hz, J=16Hz) CH_3-P-H

10.74 d,d (J=24Hz, J=16Hz) N-P-N

MS (EI, 70eV)

293 Cl_2 (M^+), 292 Cl_2 (loss of H), 278 Cl2 (loss of CH_3)

1-methyl-1-hydrido-spiro-3,3-(1,3-butanediamino)-5,5-dichlorocyclotriphosphazene, **51**:

A solution of 1-methyl-1- hydridotetrachlorocyclotriphosphazene **35**, prepared by standard methods[124] immediately prior to use (1.65g, 5.67mmol) and triethylamine (1.2g, 11.9mmol) in dichloromethane (125ml) was prepared under a dry nitrogen atmosphere. A solution of 1,3-propanediamine in dichloromethane (0.42g, 5.67mmol in 25ml) was added dropwise at room temperature over a period of 30min and the mixture stirred for 36hr. The solvent was removed under vacuum and the residue extracted repeatedly with boiling hexane. The hexane solutions were filtered and combined and the solvent removed under vacuum to leave the crude product as a white solid (1.10g, 66%).

^{31}P NMR (270MHz, proton decoupled, in ppm, $CDCl_3$ solution):

22.35 d,d (J=32Hz, J=17Hz) Cl-**P**-Cl

15.03 d,d (J=32Hz, J=15Hz) N-**P**-N

12.13 d,d (J=17Hz, J=15Hz) N-**P**-N

MS (EI, 70eV)

307 Cl_2 (M^+), 272 Cl1 (loss of Cl)

1-methyl-1-hydrido-spiro-3,3-(1,3-propanolamino)-5,5-dichlorocyclotriphosphazene, **52**:

A solution of 1-methyl-1- hydridotetrachlorocyclotriphosphazene **35**, prepared by standard methods[124] immediately prior to use (1.65g, 5.67mmol) and triethylamine (1.2g, 11.9mmol) in dichloromethane (125ml) was prepared under a dry nitrogen atmosphere. A solution of 1,3-propanediamine in dichloromethane (0.42g, 5.67mmol in 25ml) was added dropwise at room

temperature over a period of 30min and the mixture stirred for 36hr. The solvent was removed under vacuum and the residue extracted repeatedly with boiling hexane. The hexane solutions were filtered and combined and the solvent removed under vacuum to leave the crude product as a white solid (1.10g, 66%).

^{31}P NMR (270MHz, proton decoupled, in ppm, $CDCl_3$ solution):

21.40 overlapping d,d (J=23Hz, J=20Hz)

13.95 d,d (J=30Hz, J=20Hz), and

13.30 d,d (J=30Hz, J=20Hz) CH_3-**P**-H

10.10 overlapping d,d (J=30Hz, J=23Hz) N-**P**-O

MS (EI, 70eV)

294 Cl_2 (M^+), 279 Cl_2 (loss of CH_3)

1-methyl-1-aryl-3,3,5,5-tetrachlorocyclotriphosphazenes: All of these compounds were prepared by an identical procedure. The following is a typical example: Monomethylpentachlorocyclotriphosphazene **20** (2.0g, 6.10mmol) was dissolved in dry THF under a nitrogen atmosphere and cooled to 0°C. Phenylmagnesium bromide 18mmol, solution in THF) was added dropwise over a period of 30min and the reaction mixture allowed to warm to room temperature and stirred for 24hr. The solvent was removed under vacuum and the residue was dissolved in dichloromethane (100ml). This solution was filtered through neutral alumina to remove magnesium salts and the solvent again removed under vacuum. The crude product was dissolved in toluene (50ml) and the solution washed with 10% HCl (1x100ml). For the amine compounds the distilled water was used in place of the HCl. The organic layer was dried with $MgSO_4$, and the solvent removed under

vacuum to leave the crude product. Final purification was effected by recrystallization from hexane.

1-methyl-1-phenyl-3,3,5,5-tetrachlorocyclotriphosphazene, **21**:

^{31}P NMR (200MHz, proton decoupled, in ppm, $CDCl_3$ solution):

29.0 t (J=1^{1}Hz) C-P-**C**

18.6 d (J=1^{1}Hz) Cl-**P**-Cl

^{1}H NMR (200MHz, in ppm, $CDCl_3$ solution):

1.83 d,t (J=14.6Hz, J=2.6Hz, 3H) P-C**H**

7.49 br m (J=8.0Hz, 2H) P-C-C-C**H**

7.51 m (J=8.0Hz, J=1.5hz, ^{1}H) P-C-C-C-C**H**

7.85 m (J= 13.6Hz, J=8.0Hz, J=1.5Hz, 2H) P-C-C**H**

IR (KBr, cm^{-1}):

3010, 2950 (C-H), 1610, 1500, 1480, 1450 (aromatic) 1160, 1240 (P-N)

MS (EI, 70eV, in amu):

367 Cl_4 (M^+), 352 Cl_4 (loss of CH_3)

Anal. Calcd: C 22.76, H 2.17, N 11.38, P 25.20, Cl 38.48

Anal. Found: C 22.71, H 2.30, N 11.03, P 24.73, Cl 38.31

1-methyl-1-(p-dimethylaminophenyl)-3,3,5,5-tetrachlorocyclotriphosphazene, **22**:

^{31}P NMR (200MHz, proton decoupled, in ppm, $CDCl_3$ solution):

30.0 t (J=8.8Hz) C-**P**-C

18.3 d (J=8.8Hz) Cl-**P**-Cl

^{1}H NMR (200MHz, in ppm, $CDCl_3$ solution):

1.77 d,t (J=14.7Hz, J=2.4Hz, 3H) P-C**H**

3.02 s (6H) N-CH_3

6.68 d,d (J=9.0Hz, J=3.0Hz, 2H) P-C-C-CH

7.60 d,d (J=13.2Hz, J=9.0Hz, 2H) P-C-CH

IR (KBr, cm^{-1}):

3000, 2960 (C-H), 1590, 1490, 1460 (aromatic), 1160, 1240 (P-N)

MS (EI, 70eV, in amu):

410 Cl_4 (M^+), 395 Cl_4 (loss of CH_3)

Anal. Calcd: C 26.21, H 3.16, N 13.58, P 22.57, Cl 34.47

Anal. Found: C 26.41, H 3.41, N 13.35, P 22.19, Cl 34.51

1-methyl-1-(m-dimethylaminophenyl)-3,3,5,5-cyclotriphosphazene, **23**:

^{31}P NMR (200MHz, proton decoupled, in ppm, $CDCl_3$ solution):

30.6 t (J=7.3Hz) C-P-C

18.1 d (J=7.3Hz) Cl-P-Cl

^{1}H NMR (200MHz, in ppm, $CDCl_3$ solution):

1.82 d,t (J=15.0Hz, J=2.5Hz, 3H) P-CH

3.03 s (6H) N-CH_3

7.1 br m (4H) aromatic H

IR (KBr, cm^{-1}):

3010, 2960 (C-H), 1620, 1500, 1450 (aromatic), 1150, 1250 (P-N)

MS (EI, 70eV, in amu):

410 Cl_4 (M^+), 395 Cl_4 (loss of CH_3)

1-methyl-1-(p-diethylaminophenyl)-3,3,5,5-tetrachlorocyclotriphosphazene, **24**:

^{31}P NMR (200MHz, proton decoupled, in ppm, $CDCl_3$ solution):

30.0 t (J=9.7Hz) C-**P**-C

18.2 d (J=9.7Hz) Cl-**P**-Cl

^{1}H NMR (200MHz, in ppm, $CDCl_3$ solution):

1.20 t (J=7.2Hz, 6H) N-C-C**H**

1.80 d,t (J=14.7Hz, J=2.4Hz, 3H) P-C**H**

3.39 q (J=7.2Hz, 4H) N-C**H**$_2$

6.69 d,d (J=8.7Hz, J=3.0Hz, 2H) P-C-C-C**H**

7.58 d,d (J=13.3Hz, J=8.7Hz, 2H) P-C-C**H**

IR (KBr, cm^{-1}):

3010, 2975 (C-H), 1590, 1480 (aromatic), 1150, 1220 (P-N)

MS (EI, 70eV, in amu):

438 Cl_4 (M^+), 423 Cl_4 (loss of CH_3)

1-methyl-1-(p-methoxyphenyl)-3,3,5,5-tetrachlorocyclotriphospha-zene. **25**:

^{31}P NMR (200MHz, proton decoupled, in ppm, $CDCl_3$ solution):

29.3 t (J=8.8Hz) C-**P**-C

18.6 d (J=8.8Hz) Cl-**P**-Cl

^{1}H NMR (200MHz, in ppm, $CDCl_3$ solution):

1.80 d,t (J=14.8Hz, J=2.5Hz, 3H) P-C**H**

3.80 s (3H) O-C**H**

6.97 d,d (J=9.0Hz, J=3.3Hz, 2H) P-C-C-C**H**

7.72 d,d (J=13.5Hz, J=9.0Hz, 2H) P-C-C**H**

IR (KBr, cm^{-1}):

3020, 2970 (C-H), 1600, 1500, 1460 (aromatic), 1240, 1180 (P-N)

MS (EI, 70eV, in amu):

397 Cl_4 (M^+), 382 Cl_4 (loss of CH_3)

1-methyl-1-(m-methoxyphenyl)-3,3,5,5-tetrachlorocyclotriphospha-zene, **26**:

^{31}P NMR (200MHz, proton decoupled, in ppm, $CDCl_3$ solution):

29.4 t (J=9.8Hz) C-**P**-C

18.5 d (J=9.8Hz) Cl-**P**-Cl

^{1}H NMR (200MHz, in ppm, $CDCl_3$ solution):

1.77 d,t (J=14.7Hz, J=2.4Hz, 3H) P-C**H**

3.80 s (3H) O-C**H**$_3$

7.20 br m (4H) aromatic **H**

IR (KBr, cm^{-1}):

3000, 2950 (C-H), 1585, 1490 (aromatic), 1240, 1170 (P-N)

MS (EI, 70eV, in amu):

397 Cl_4 (M^+), 382 Cl_4 (loss of CH_3)

1-methyl-1-(p-fluorophenyl)-3,3,5,5-tetrachlorocyclotriphospha-zene, **27**:

^{31}P NMR (200MHz, proton decoupled, in ppm, $CDCl_3$ solution):

28.4 t (J=10.3Hz) C-**P**-C

18.7 d (J=10.3Hz) Cl-**P**-Cl

^{1}H NMR (200MHz, in ppm, $CDCl_3$ solution):

1.83 d,t (J=14.5Hz, J=2.4Hz, 3H) P-C**H**

7.06 d,d,d (J=17.4Hz, J=9.0Hz, J=3.0Hz, 2H) P-C-C-C**H**-F

7.72 d,d,d (J=13.2Hz, J=9.0Hz, J=5.4Hz, 2H) P-C-C**H**-C-F

^{19}F NMR (90MHz, in ppm versus CCl_3F, $CDCl_3$ solution):

105.81 d,d (J=17.4Hz, J=5.4Hz) P-C-C-C-C-**F**

IR (KBr, cm^{-1}):

3020, 2950 (C-H), 1600, 1500, 1480, 1450 (aromatic), 1240, 1160 (P-N)

MS (EI, 70eV, in amu):

385 Cl_4 (M^+), 370 Cl_4 (loss of CH_3)

Anal. Calcd: C 21.71, H 1.81, N 10.85, P 24.03, Cl 36.69

Anal. Found: C 21.79, H 2.30, N 10.68, P 24.00, Cl 36.38

1-methyl-1-(m-fluorophenyl)-3,3,5,5-tetrachlorocyclotriphospha-

zene, **28**:

^{31}P NMR (200MHz, proton decoupled, in ppm, $CDCl_3$ solution):

27.7 t (J=11.7Hz) C-**P**-C

18.7 d (J=11.7Hz) Cl-**P**-Cl

^{1}H NMR (200MHz, in ppm, $CDCl_3$ solution):

1.85 d,t (J=14.7Hz, J=2.4Hz, 3H) P-C**H**

7.40 br m (4H) aromatic **H**

^{19}F NMR (90MHz, in ppm versus CCl_3F, $CDCl_3$ solution):

110.35 m P-C-C-C-C-**F**

IR (KBr, cm^{-1}):

3000, 2960 (C-H), 1585, 1480 (aromatic), 1230, 1150 (P-N)

MS (EI, 70eV, in amu):

385 Cl_4 (M^+), 370 Cl_4 (loss of CH_3)

1-methyl-1-(p-chlorophenyl)-3,3,5,5-tetrachlorocyclotriphospha-

zene, **32**:

^{31}P NMR (200MHz, proton decoupled, in ppm, $CDCl_3$ solution):

28.3 t (J=11.0Hz) C-**P**-C

19.0 d (J=11.0Hz) Cl-**P**-Cl

^{1}H NMR (200MHz, in ppm, $CDCl_3$ solution):

1.70 d,t (J=14.7Hz, J=2.6Hz, 3H) P-C**H**

7.31 d,d (J=8.4Hz, J=3.0Hz, 2H) P-C-C-C**H**

7.63 d,d (J=13.2Hz, J=8.4Hz, 2H) P-C-C**H**

IR (KBr, cm^{-1}):

3010, 2975 (C-H), 1595, 1500, 1450 (aromatic), 1220, 1170 (P-N)

MS (EI, 70eV, in amu):

401 Cl5 (M^+), 386 Cl5 (loss of CH_3)

1-methyl-1-(p-t-butylphenyl)-3,3,5,5-tetrachlorocyclotriphospha-zene, **30**:

^{31}P NMR (200MHz, proton decoupled, in ppm, $CDCl_3$ solution):

29.2 t (J=9.8Hz) C-**P**-C

18.3 d (J=9.8Hz) Cl-**P**-Cl

^{1}H NMR (200MHz, in ppm, $CDCl_3$ solution):

1.34 s (9H) $C(CH_3)_3$

1.82 d,t (J=14.4z, J=2.4Hz, 3H) P-C**H**

7.48 d,d (J=8.7Hz, J=3.9Hz, 2H) P-C-C-C**H**

7.73 d,d (J=13.2Hz, J=8.7Hz, 2H) P-C-C**H**

IR (KBr, cm^{-1}):

3020, 2980 (C-H), 1585, 1470 (aromatic), 1230, 1170 (P-N)

MS (EI, 70eV, in amu):

423 Cl_4 (M^+), 408 Cl_4 (loss of CH_3)

1-methyl-1-(p-methylphenyl)-3,3,5,5-tetrachlorocyclotriphospha-

zene, **29**:

^{31}P NMR (200MHz, proton decoupled, in ppm, $CDCl_3$ solution):

29.4 t (J=9.8Hz) C-**P**-C

18.7 d (J=9.8Hz) Cl-**P**-Cl

^{1}H NMR (200MHz, in ppm, $CDCl_3$ solution):

1.82 d,t (J=14.7z, J=2.7Hz, 3H) P-C**H**

7.33 d,d (J=8.^{1}Hz, J=3.6Hz, 2H) P-C-C-C**H**

7.70 d,d (J=13.5Hz, J=8.^{1}Hz, 2H) P-C-C**H**

IR (KBr, cm^{-1}):

3010, 2940 (C-H), 1600, 1490 (aromatic), 1240, 1180 (P-N)

MS (EI, 70eV, in amu):

381 Cl_4 (M^+), 366 Cl_4 (loss of CH_3)

1-methyl-1-(p-phenylphenyl)-3,3,5,5-tetrachlorocyclotriphospha-

zene, **31**:

^{31}P NMR (200MHz, proton decoupled, in ppm, $CDCl_3$ solution):

29.1 t (J=10.3Hz) C-**P**-C

18.8 d (J=10.3Hz) Cl-**P**-Cl

^{1}H NMR (200MHz, in ppm, $CDCl_3$ solution):

1.82 d,t (J=14.4z, J=2.4Hz, 3H) P-C**H**

7.40 br m (7H) aromatic **H**

7.82 d,d (J=14.0Hz, J=8.0Hz, 2H) P-C-C**H**

IR (KBr, cm^{-1}):

3020, 2950, 2900 (C-H), 1620, 1500, 1480 (aromatic), 1220, 1160 (P-N)

MS (EI, 70eV, in amu):

443 Cl_4 (M^+), 428 Cl_4 (loss of $\dot{C}H_3$)

1-methyl-1-(p-trifluoromethylphenyl)-3,3,5,5-tetrachlorocyclotriphosphazene, **33**:

^{31}P NMR (200MHz, proton decoupled, in ppm, $CDCl_3$ solution):

27.7 t (J=11.7Hz) C-**P**-C

19.1 d (J=11.7Hz) Cl-**P**-Cl

^{1}H NMR (200MHz, in ppm, $CDCl_3$ solution):

1.83 d,t (J=14.4z, J=2.5Hz, 3H) P-C**H**

7.73 d,d (J=8.4Hz, J=3.6Hz) P-C-C-C**H**

7.96 d,d (J=13.2Hz, J=8.4Hz, 2H) P-C-C**H**

^{19}F NMR (90MHz, in ppm versus CCl_3F, $CDCl_3$ solution):

63.87 s C**F**

IR (KBr, cm^{-1}):

3010, 2950 (C-H), 1600, 1500, 1470 (aromatic), 1230, 1170 (P-N)

MS (EI, 70eV, in amu):

435 Cl_4 (M^+), 420 Cl_4 (loss of CH_3)

Anal. Calcd: C 21.97, H 1.60, N 9.61, P 21.28, Cl 32.49

Anal. Found: C 21.76, H 1.63, N 9.44, P 21.03, Cl 32.29

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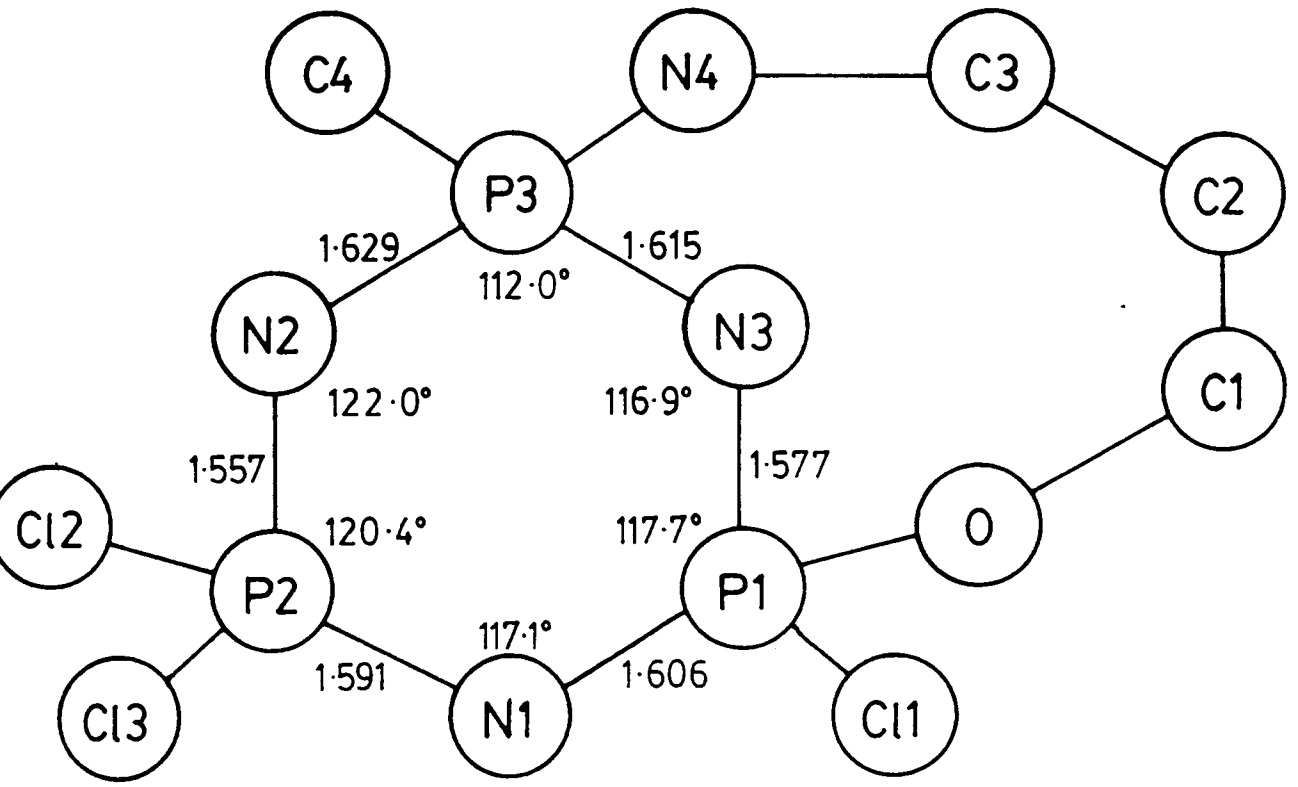
APPENDIX I

Structure of the Ansa Compound **54** as Determined by X-Ray Crystallography



Data collection:

Orthorhombic, space group $P2_12_12_1$, Z = 4

a = 8.033(2), b = 11.534(7), c = 13.450(4)A, V = 1246(1)A^3 at 298 K

a = 7.984(3), b = 11.406(3), c = 13.380(3)A, V = 1218.5(6)A^3 at 123 K

ρ_{exp} = 1.74g.cm^{-3}

ρ_x = 1.76g.cm^{-3}

Graphite monochromated MoKα, λ = 0.71069A

Crystal size : 0.25 mm X 0.40 mm X 0.60 mm

Linear absorption coefficient : μ = 1.030 mm^{-1}

No absorption correction

F(000) = 664

θ range of reflections : 1.5-26°

$\theta/2\theta$ scan technique

Controls of intensity : reflections 2 1 $\bar{4}$, 1 2 7, 2 $\bar{2}$ 0, each 3600s

CAD4 Nonius diffractometer

Take-off angle : 2.5°

25 reflections with $5° < \theta < 13°$ used for measuring lattice parameters

Space group (identified by precession method) verified by rapid measurement of h0l, 0kl, hk0 reflections implying $P2_12_12_1$ space group

$\theta-2\theta$ scan with $\Delta\theta$scan = 1.0 + 0.35 tanθ, prescan speed = 10° min^{-1}

$\sigma(I)/I$ for final scan = 0.018

Maximum time for final scan : 80s

No significant variation during the whole data collection

Structure determination and refinement:

1413 measured reflections, 1246 unique reflections, 1226 utilized reflections with $I>3\sigma(I)$

Use of F magnitudes in least-square refinement

Parameters refined :

Reliability factor : $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.0218$

$Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2} = 0.0250$ w = 1

$S = [\Sigma w(|F_o| - |F_c|)^2/(NO-NV)]^{1/2} = 0.948.$

Fractional atomic coordinates and equivalent temperature factors ($Å^2$ X 100) with e.s.d.'s in parentheses.

Atom	x/a	y/b	z/c	Ueq
P1	0.8795(1)	0.55665(8)	0.23743(6)	1.15(4)
P2	0.6588(1)	0.38767(9)	0.29586(7)	1.27(4)
P3	0.9114(1)	0.46432(8)	0.42392(7)	1.31(4)
Cl1	1.0145(1)	0.56922(9)	0.11168(7)	1.99(5)
Cl2	0.4137(1)	0.42316(9)	0.31996(7)	2.08(5)
Cl3	0.6397(1)	0.22683(8)	0.23422(7)	1.97(5)
N1	0.7222(4)	0.4747(3)	0.2110(2)	1.6(2)
N2	0.7530(4)	0.3798(3)	0.3976(2)	1.8(2)
N3	0.9992(4)	0.5159(3)	0.3245(2)	1.4(2)
N4	0.8586(4)	0.5752(3)	0.4968(2)	1.6(2)
O	0.8115(3)	0.6855(2)	0.2524(2)	1.8(1)
C1	0.8852(5)	0.7612(3)	0.3297(3)	1.7(2)
C2	0.7716(5)	0.7690(3)	0.4198(3)	1.8(2)
C3	0.7188(5)	0.6515(4)	0.4651(3)	1.9(2)
C4	1.0588(6)	0.3822(4)	0.4958(3)	2.2(2)
HN4	0.848(7)	0.560(5)	0.557(4)	4.0
H1C1	0.995(7)	0.734(5)	0.347(4)	4.0
H2C1	0.903(7)	0.829(5)	0.303(4)	4.0
H1C2	0.825(7)	0.813(5)	0.477(4)	4.0
H2C2	0.671(7)	0.810(4)	0.405(4)	4.0
H1C3	0.650(7)	0.613(4)	0.417(4)	4.0
H2C3	0.651(7)	0.666(5)	0.529(4)	4.0
H1C4	1.143(7)	0.426(5)	0.510(4)	4.0
H2C4	1.017(7)	0.363(5)	0.554(4)	4.0
H3C4	1.094(8)	0.327(5)	0.462(4)	4.0

$$Ueq = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \vec{a}_i . \vec{a}_j$$

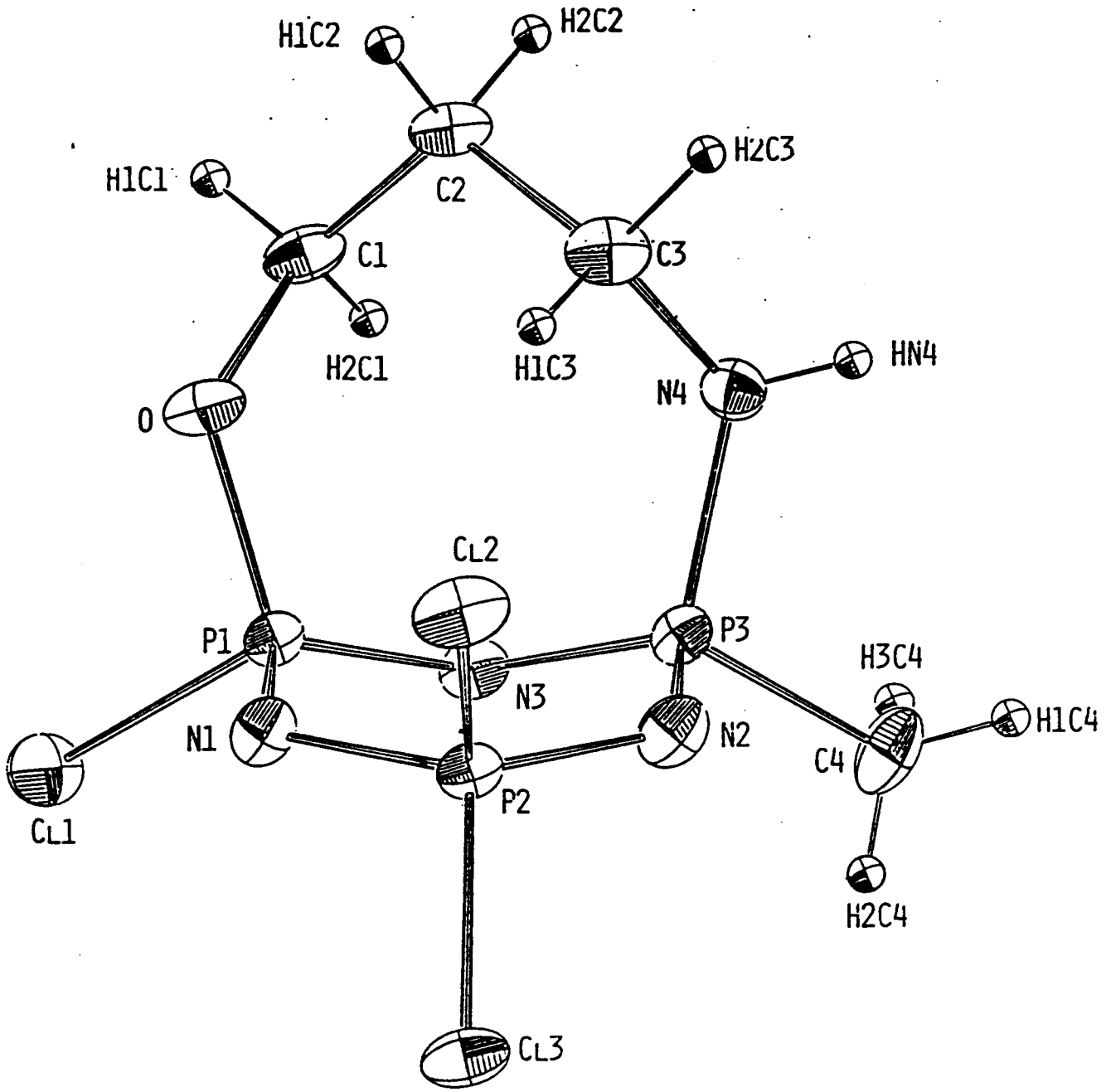
Final anisotropic thermal parameters (Å x 100) with estimated standard deviations in parentheses.

Atom	U11	U22	U33	U12	U13	U23
P1	1.17(5)	1.19(4)	1.08(4)	-0.15(4)	0.03(4)	0.01(4)
P2	1.24(5)	1.27(4)	1.28(4)	-0.28(4)	0.02(4)	-0.07(4)
P3	1.30(4)	1.46(5)	1.17(4)	-0.01(4)	-0.18(4)	0.05(4)
Cl1	2.16(5)	2.27(5)	1.51(4)	-0.32(4)	0.64(4)	0.14(4)
Cl2	1.26(4)	2.21(5)	2.77(5)	-0.16(4)	0.23(4)	-0.25(4)
Cl3	2.21(5)	1.34(4)	2.33(5)	-0.29(4)	-0.06(4)	-0.42(4)
N1	1.7(2)	1.6(2)	1.4(2)	-0.5(1)	-0.4(1)	0.1(1)
N2	1.9(2)	1.6(2)	1.7(2)	-0.6(2)	-0.1(2)	0.2(1)
N3	1.0(2)	1.6(2)	1.4(2)	0.0(1)	-0.1(1)	-0.1(1)
N4	1.9(2)	1.8(2)	1.1(1)	-0.1(2)	-0.1(1)	-0.2(1)
O	1.9(1)	1.4(1)	1.9(1)	0.3(1)	-0.2(1)	-0.3(1)
C1	1.7(2)	1.2(2)	2.0(2)	-0.2(2)	0.0(2)	-0.1(2)
C2	1.8(2)	1.4(2)	1.9(2)	0.1(2)	0.1(2)	-0.4(2)
C3	1.4(2)	2.3(2)	1.9(2)	-0.2(2)	0.3(2)	-0.2(2)
C4	2.2(2)	2.5(2)	1.8(2)	0.3(2)	-0.8(2)	0.8(2)

Selected intramolecular bond lengths and angles

P1 - N1	1.606(4) Å	P1 - N3	1.577(3) Å
P1 - C11	2.003(2)	P1 - O	1.579(3)
P2 - N1	1.591(3)	P2 - N2	1.557(4)
P3 - N2	1.629(4)	P3 - N3	1.615(3)
P3 - C4	1.785(5)	P2 - C12	2.024(2)
P2 - C13	2.017(2)		
P3 - N4	1.651(4)	N4 - C3	1.478(6)
C3 - C2	1.529(6)	C2 - C1	1.512(6)
C1 - O	1.470(5)		
C1 - H1C1	0.96(5)	C1 - H2C1	0.87(5)
C2 - H1C2	1.02(5)	C2 - H2C2	0.95(5)
C3 - H1C3	0.95(5)	C3 - H2C3	1.02(6)
C4 - H1C4	0.86(6)	C4 - H2C4	0.88(5)
C4 - H3C4	0.83(5)		
C11...O	2.816(3)	C12...C13	3.564(2)
P1...P2	2.726(2)	P1...P3	2.720(2)
P2...P3	2.787(2)		
N1 - P1 - N3	117.7(2)°	P1 - N3 - P3	116.9(2)°
N3 - P3 - N2	112.0(2)	P3 - N2 - P2	122.0(2)
N2 - P2 - N1	120.4(2)	P2 - N1 - P1	117.1(2)
O - P1 - C11	103.0(1)	C12 - P2 - C13	100.02(6)
P3 - N4 - C3	118.3(3)	N4 - C3 - C2	114.9(3)
C3 - C2 - C1	115.5(3)	C2 - C1 - O	110.8(3)
C1 - O - P1	119.8(2)	O - P1 - N3	112.9(2)
N3 - P3 - N4	108.5(2)	N4 - P3 - C4	104.6(2)

H - C - H angles are in the range 104(5) - 116(5)°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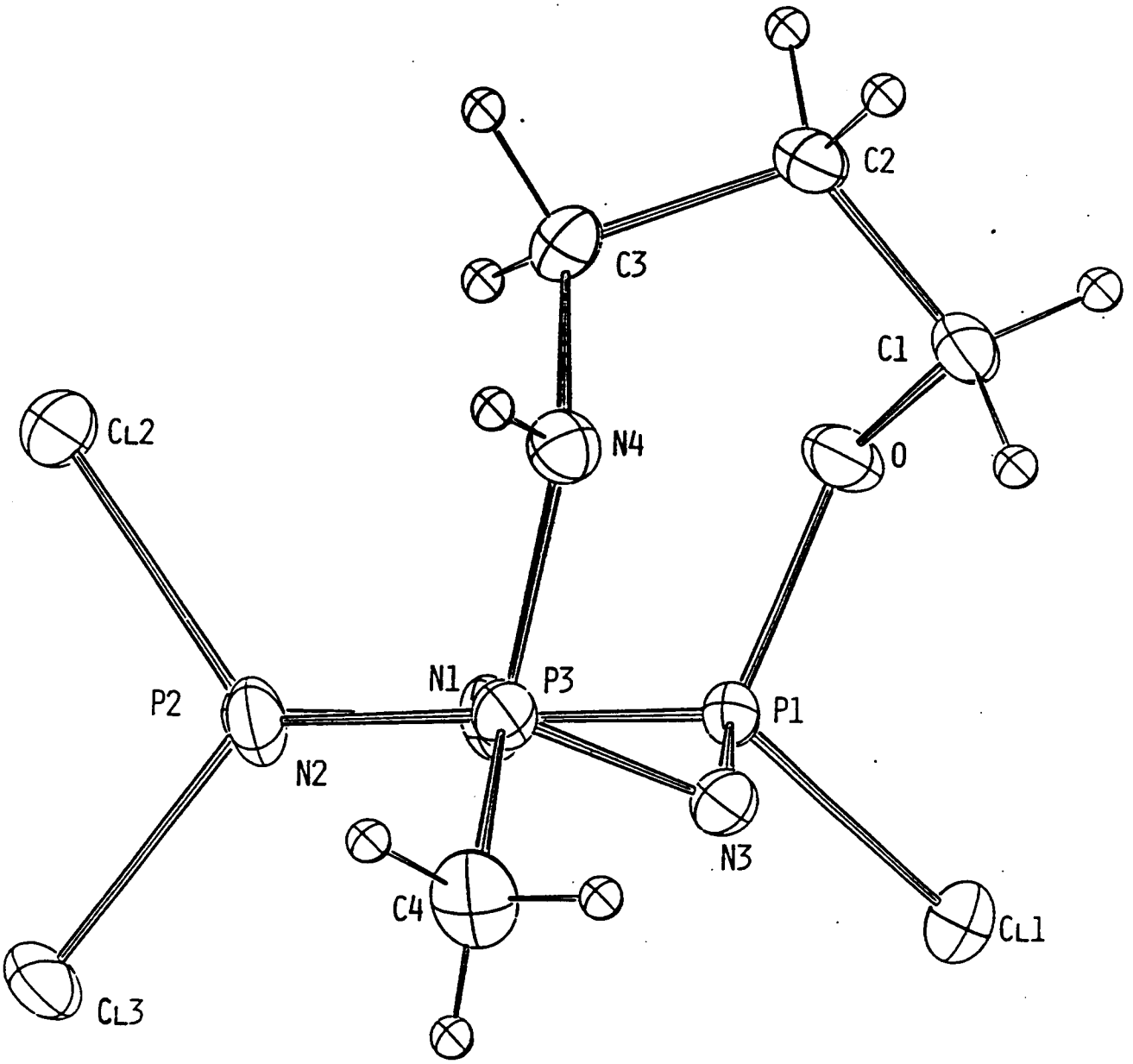
H2C3
H1C1
C2
C1
C3
H2C1
H1C3
HN4
N4
O
CL2
P1
P3
H3C4
N3
N1
N2
H1C4
C4
P2
CL1
H2C4
CL3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P3
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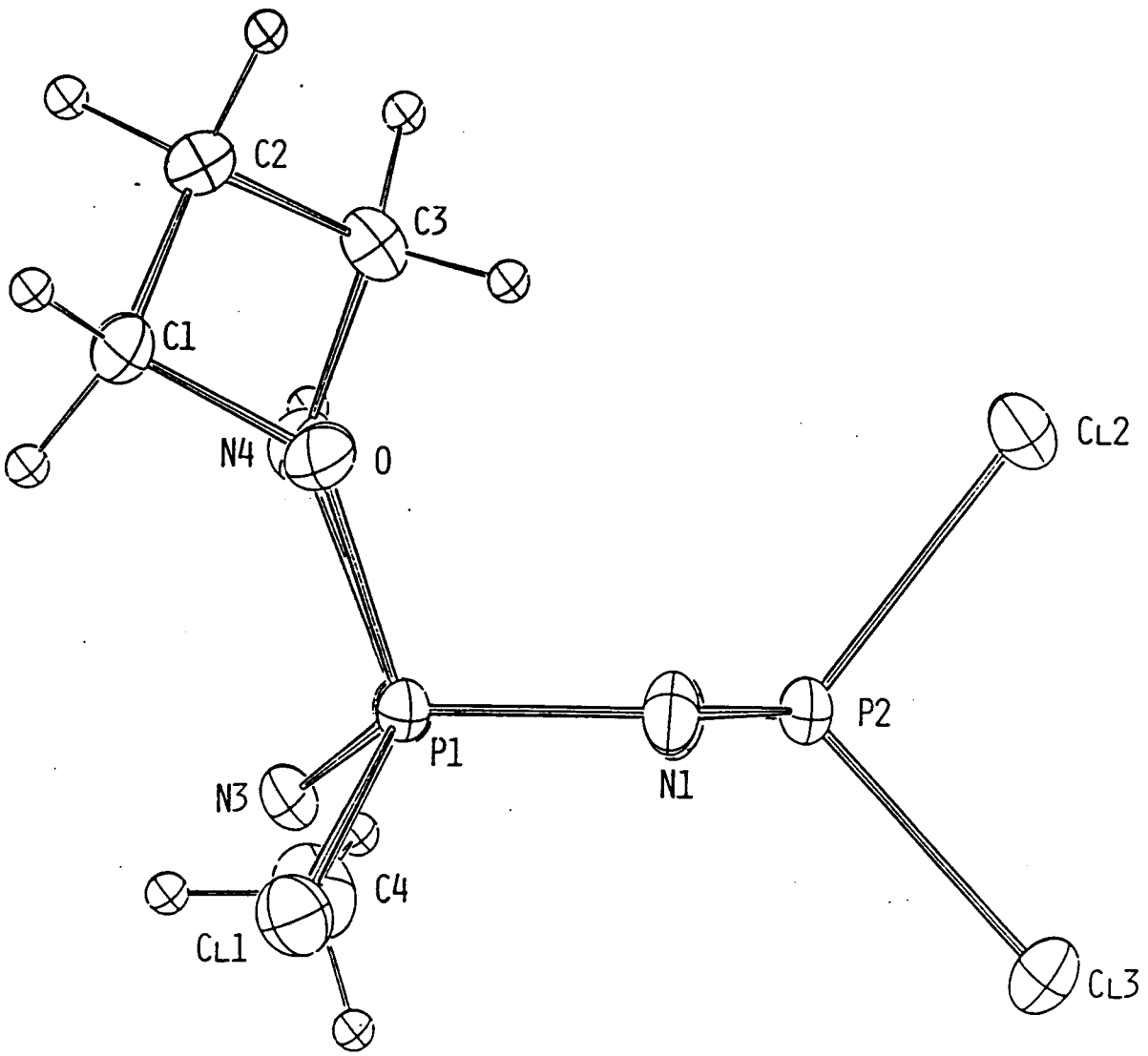
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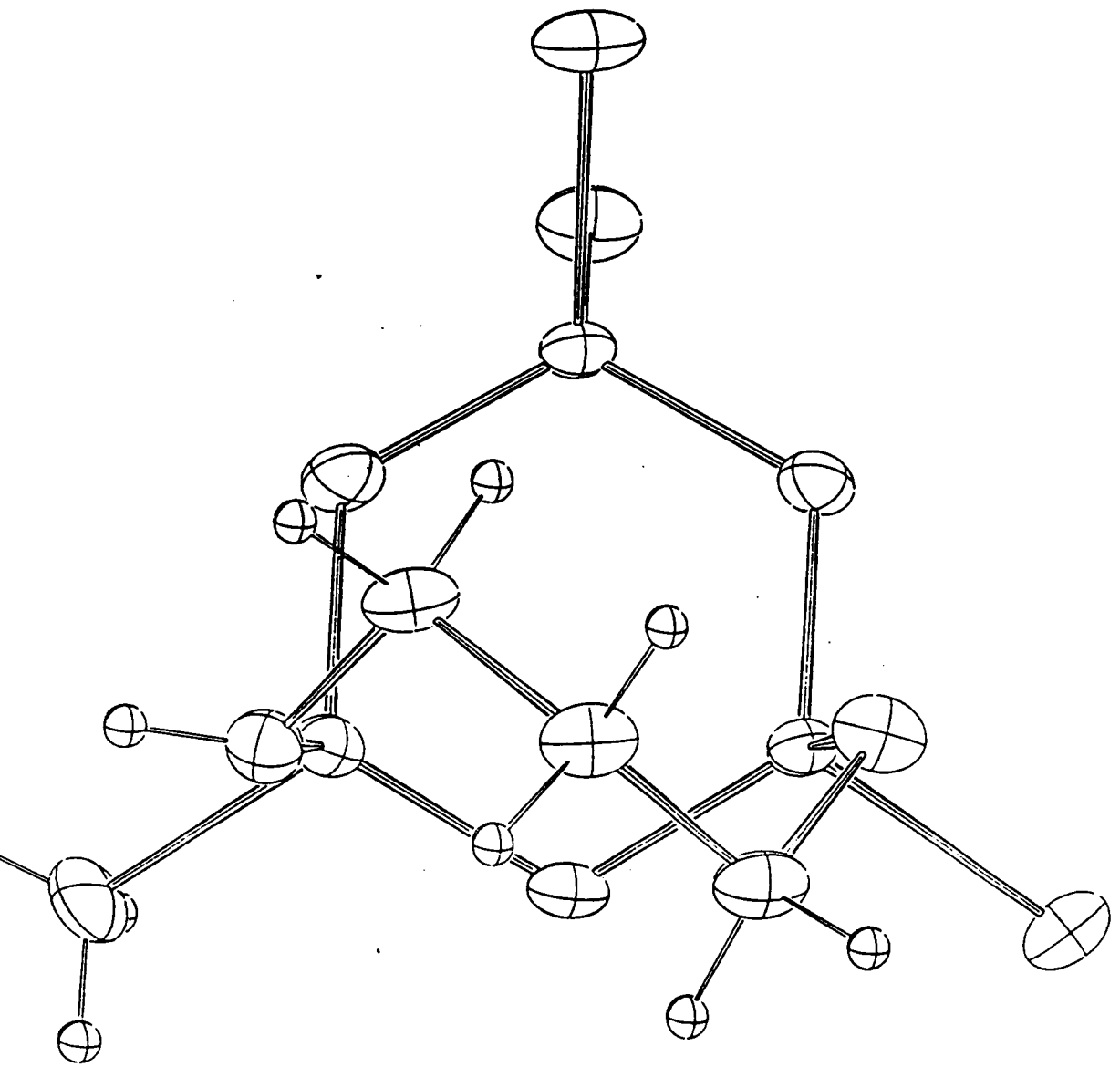
C1
N4
O
CL2
P2
P1
N1
N3
C4
CL1
CL3



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