SYNTHESIS AND CARBANION REACTIONS OF METHYLPHOSPHAZENES

by

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# ABSTRACT

The reaction of dimethyltrichlorophosphorane with methylamine hydrochloride provides a novel preparative route to the methylphosphazenes $(NPMe_2)_{3,4}$, the separation of the two compounds being aided by the different solubilities of their salts $(NPMe_2)_3 \cdot RCl$ and $(NPMe_2)_4 \cdot 2RCl$ (R=H, Me) in acetonitrile. A general method for the synthesis of methylphosphazenes of large ring size (i.e. $(NPMe_2)_n$, $n \geqslant 6$) by the methylation of the appropriate fluorophosphazene $(NPF_2)_n$ with methylmagnesium bromide has now been achieved. A variety of quaternary salts $(NPMe_2)_n \cdot RI$ and a number of trimethylphosphinimine derivatives have also been prepared. The differences in the properties of the cyclic and monomeric molecules have been interpreted in terms of their electronic structures.

The methylphosphazenes $(NPMe_2)_{3-10}$ are crystalline solids at room temperature, and the molecular structures of $(NPMe_2)_n$ (n=4,5,7 and 8) suggest that their molecular flexibility is not suppressed by $\pi$-bonding; their conformations can be accounted for in terms of non-bonded and electrostatic interactions, which favour the staggered orientations (GT and CT) of successive ring bonds.

A study has been made of the acidic properties of the P-methyl protons of methylphosphazenes. The multiply-charged carbanions $N_4P_4Me_{8-x}(CH_2^-)_x$ (x=2,4) and the monocarbanion $N_3P_3Ph_4Me(CH_2^-)$ can be prepared by the deprotonation of the neutral methylphosphazenes with alkyllithiums. Their reactions with a variety of electrophiles (e.g. MeI, $Me_3SiCl$, $CO_2$, PhCOOEt, $Br_2$) establish that they are useful intermediates for the synthesis of novel

organophosphazenes. The orientation of the ethyl groups in $N_4P_4Me_6Et_2.2HCl$ shows that the second deprotonation of $N_4P_4Me_8$ occurs trans-antipodally to the first.

The N-methyl quaternary salts $(NPMe_2)_{3,4}.MeI$ and $N_3P_3Ph_4Me_2.MeI$ can also be deprotonated. The products are not the expected exocyclic ylids but the novel azaphosphorins $Me_{2n-1}(NHMe)P_nN_{n-1}CH$ (n=3,4) and $Me(NHMe)Ph_4P_3N_2CH$, formed by a rearrangement in which the methylated nitrogen atom is displaced from the PN ring by the initially produced exocyclic methylene group (Equation 1). The driving force of the reaction is likely to



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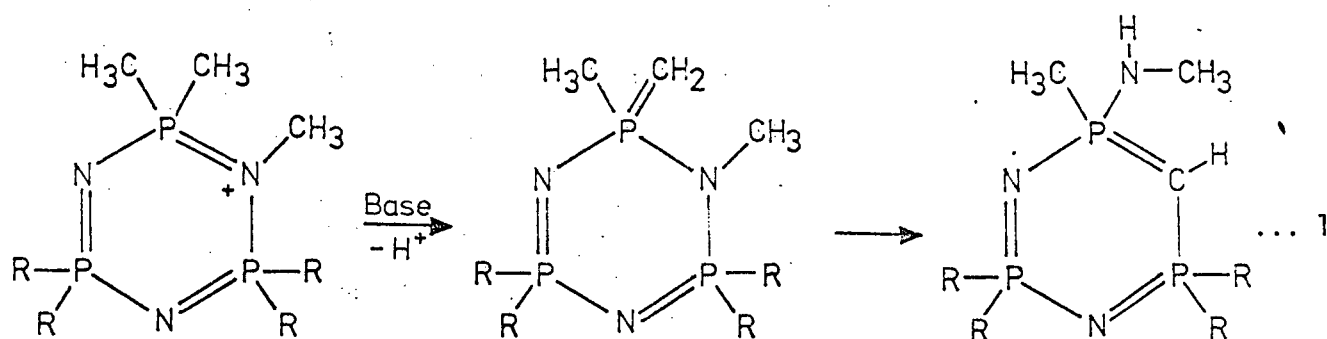
be the attainment of cyclic aromaticity. The $^1H$ n.m.r. spectra of the azaphosphorins indicate a rapid proton exchange between the endocyclic carbon and the exocyclic nitrogen, which can be slowed by the addition of an auxiliary base (e.g. pyridine). When KOtBu is used to deprotonate the quaternary salts, nucleophilic attack competes with proton removal, and the linear oxides $(NHMe)(PMe_2N)_nPMe_2O$ (n=2-4) have been isolated from these reactions.

The azaphosphorins $Me_{2n-1}(NHMe)P_nN_{n-1}CH$ (n=3,4) are hydrolysed in aqueous ethanol to give the cyclic oxides $Me_{2n-1}(O)P_nN_{n-1}CH_2$, and react with methyl iodide by a transylidation reaction to give the hydroiodides $Me_{2n-1}(NHMe)P_nN_{n-1}CH.HI$. Their reaction with benzoyl chloride leads to the

benzoylated derivatives $Me_7(NHMe)P_4N_3CCOPh$ and $Me_5(NMeCCOPh)P_3N_2CCOPh$, the initial substitution on carbon indicating that it is the primary basic centre.

The molecular structures of azaphosphorins are consistent with the delocalization of charge from the endocyclic carbon into the cyclic PN skeleton. Their structural parameters can be accounted for by considering the effect of the replacement of a nitrogen atom with a =CR- group on the two equivalent components of the cyclic $\pi$-system.

## TABLE OF CONTENTS

## LIST OF TABLES

# LIST OF FIGURES

## ACKNOWLEDGEMENT

To, for, and with Marion

CHAPTER 1

GENERAL INTRODUCTION

The fundamental chemical difference between the elements of the first and second row of the periodic table is the property of the latter to possess more than one valence state. Phosphorus, for example, is found in both tri- and pentavalent forms, and sulphur in di-, tetra- and hexavalent states. By contrast, their congeners in the first row, nitrogen and oxygen, are restricted generally to the lowest valency. The interpretation of this difference in terms of molecular binding has long been a central concern of inorganic chemistry, and the potential participation of d-orbitals in bonding has often been suggested to account for the existence of higher valence states[1,2]. In recent years, therefore, much experimental evidence has been gathered with the purpose of determining the role, if any, of d-orbitals in bond formation.

One area of research that has been particularly useful in this regard is the study of phosphazene derivatives. These compounds may be broadly classed as linear or cyclic polymers containing the repeating unit $\{N=PX_2\}$. The importance of phosphazenes to molecular bonding theory lies not so much in their basic chemistry, which is similar in many ways to that of mononuclear phosphoryl compounds, as in their availability for study over a large range of ring sizes and ligand types; the variations in the physical and chemical properties of $(NPX_2)_n$, as a function of X and n, provide a sensitive and specific tool for examining the binding properties of pentavalent phosphorus. The formal structural resemblance of $(NPX_2)_3$

(I) to benzene (II) has been recognised for many years[3], and much work has been devoted to comparing the two types of aromaticity found in these molecules[4].



I                                         II
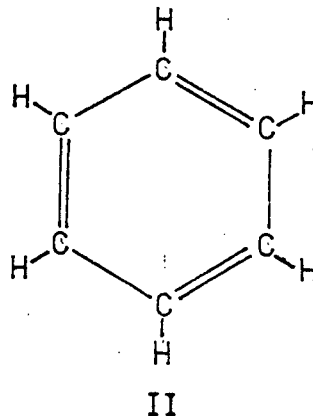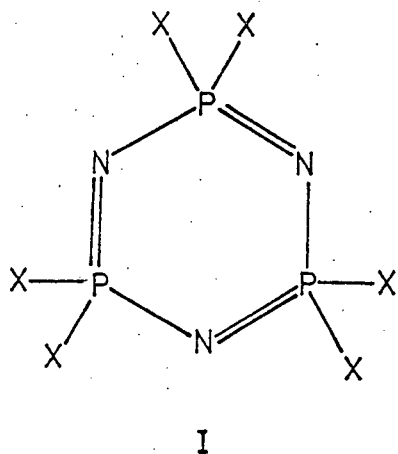
From an historical point of view, chemical knowledge of phosphazenes spans more than a century. The best known phosphazene, the trimeric chloride $(NPCl_2)_3$, was first isolated in 1834[5,6], but it was not until 1896, when Stokes prepared and characterized the chlorophosphazenes $(NPCl_2)_{3-7}$, that a cyclic structure was suggested for them[7]. During the first half of this century, little attention was paid to their physical and chemical properties, and it was not until the 1950's, when the requirements of the aerospace industry stimulated research in inorganic polymer chemistry, that attention was focused on the synthesis and study of phosphazenes. The results of work done in this area in the last 35 years have been the subject of many review articles and several books[8-18].

In the past, research in phosphazene chemistry has generally been directed towards the influence of different ligands on the physical and

chemical properties of the cyclic PN skeleton. The spirit of the work reported in this thesis is somewhat different, in that it is concerned with the effect of the phosphazene ring itself on the chemistry of the attached ligands. More specifically, the thesis deals with the preparation and chemistry of methylphosphazenes $(NPMe_2)_n$, focusing attention on the relationship between the acceptor properties of the phosphazene ring and the chemical reactivity of the methyl groups attached to it. The purpose of this introductory chapter is to summarize certain aspects of phosphorus(V) chemistry in general, and phosphazene chemistry in particular, which relate directly to the results presented in later chapters.

## 1.1 Preparation of Phosphazenes

### 1.1.1 Direct Methods

There exist several methods for preparing phosphazenes, by far the best known of which is the ammonolysis of a phosphorus chloride, according to Equation 1. Usually, the reaction is carried out in a suitably inert

$$X_2PCl_3 \ + \ NH_4Cl \ \longrightarrow \ \frac{1}{n}(NPX_2)_n \ + \ 4HCl \qquad \qquad \dots \ 1$$
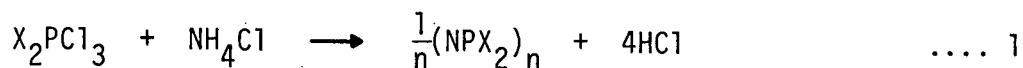
solvent, tetrachloroethane or chlorobenzene being the most commonly used[19]. As well as the chlorophosphazenes $(NPCl_2)_n$[7,19], the bromo $(NPBr_2)_n$[20], alkyl $((NPMe_2)_n$[21] and $(NPEt_2)_n$[22]) and aryl $((NPPh_2)_n$[23,24], $(NPPhCl)_n$[25], $(NPPhBr)_n$[26]) derivatives can be prepared in this way. Usually the cyclic trimer and tetramer are formed, with smaller amounts of the higher ring sizes and linear species of the type $[ClR_2P=N-(PR_2=N)_nPR_2Cl]^+Cl^-$[27-29].

## 1.1.2 Substitution Reactions

The second major synthetic route to phosphazenes is by ligand substitution, starting, usually, from a halophosphazene (Equation 2).
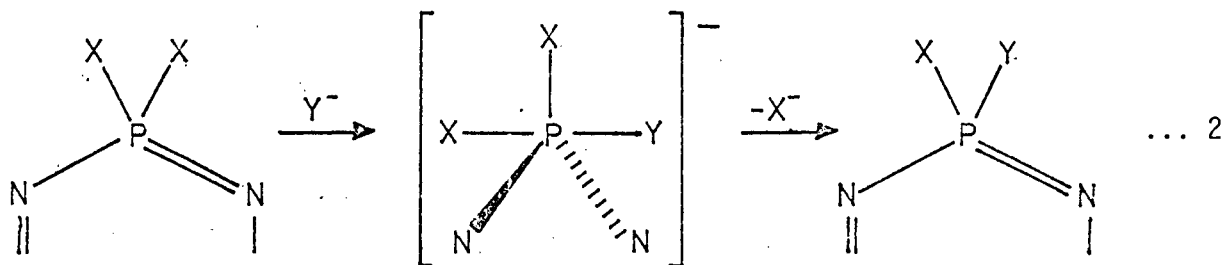


The importance of this type of reaction stems from the fact that the ammonolysis reaction (Equation 1) provides the higher members of the series $(NPX_2)_n$ (n > 5) only in the case of the chlorophosphazenes. Other large ring size phosphazenes must, therefore, be prepared by ligand substitution of the appropriate chlorophosphazene.

The scope and versatility of substitution reactions may be conveniently illustrated by classifying the products according to the periodic group to which the element bound to phosphorus belongs.

## 1.1.2.1 Group VII Derivatives

The reaction of chlorophosphazenes with anionic fluorinating agents such as sodium fluoride[30] and potassium fluorosulphite[31,32] to give mixed fluorochloro- and fully fluorinated phosphazenes has been extensively studied (see reference 18, p. 206). The latter compounds are formed preferentially, since the introduction of one fluorine atom into the PN

ring enhances the reactivity of the ring to further substitution. By contrast, antimony trifluoride reacts with chlorophosphazenes to give partially substituted products[33,34], the reaction depending on the preliminary coordination of antimony to a ring nitrogen atom, the basicity of which is diminished by successive substitution. The effectiveness of both types of reaction appears to be independent of ring size; the fluorophosphazenes $(NPF_2)_n$ (n=3-20), for example, have all been prepared by the action of $KSO_2F$ on the appropriate chlorophosphazene.

### 1.1.2.2 Group VI Derivatives

As in the case of the fluorination of chlorophosphazenes, the reaction of halophosphazenes with a variety of alkoxides and aryloxides (and their mercapto analogues) to yield organosubstituted derivatives (reference 18, p. 150) is successful for a large range of ring sizes. The reaction is carried out using the alcohol itself and an auxiliary base (e.g. triethylamine or sodium carbonate), or the alcoholate anion, which is more reactive. In this way, the phenoxy $[NP(OPh)_2]_{3-8}$[35,36] and methoxy $[NP(OMe)_2]_{3-8}$[36,37] phosphazenes have been prepared in good yield.

### 1.1.2.3 Group V Derivatives

Aminophosphazenes, formed by the action of primary and secondary amines, or their anions, on halophosphazenes, form the largest single class of phosphazene derivatives (reference 18, p. 175). Both fully and partially aminated products can be prepared, the isolation of the latter being aided by the fact that successive amination reduces the reactivity of

the ring to further substitution. The applicability of this reaction, like those outlined above, appears to be independent of ring size; the fully dimethylaminated phosphazenes $[NP(NMe_2)_2]_n$ are known for n = 3 to 9[36,38].

### 1.1.2.4 Group IV Derivatives

The scarcity of aryl and alkyl phosphazenes contrasts sharply with the abundance of amino, alkoxy and aryloxy derivatives, and reflects the greater difficulty of their preparation by substitution reactions.

The introduction of a carbon based ligand into a phosphazene ring can be achieved in two ways. Syntheses of the Friedel and Crafts type can be used to prepare partially phenylated derivatives[39] (Equation 3), but the



$$\text{... 3}$$
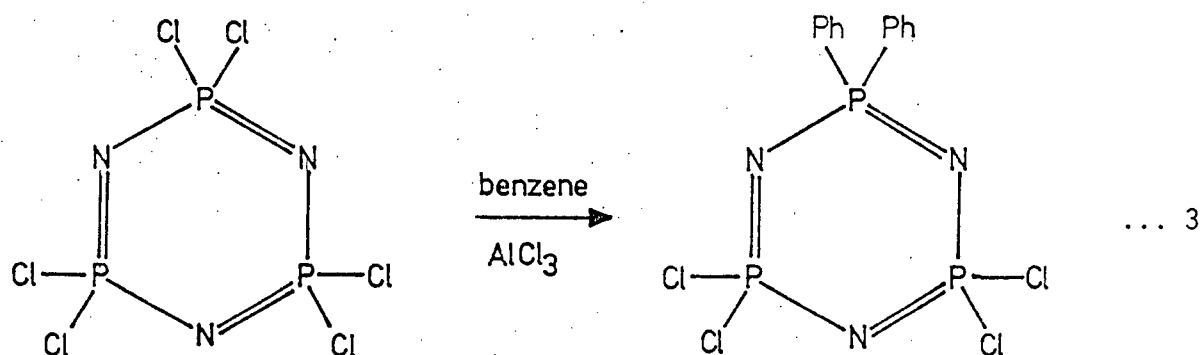
formation of fully phenylated derivatives requires extreme conditions[40,41]. Potentially more productive is the action of organometallic reagents on halophosphazenes, according to Equations 4 and 5. However, the results of

$$2nRLi \ + \ (NPX_2)_n \ \longrightarrow \ (NPR_2)_n \ + \ 2nLiX \qquad \dots 4$$

$$2nRMgBr \ + \ (NPX_2)_n \ \longrightarrow \ (NPR_2)_n \ + \ 2nMgXBr \qquad \dots 5$$
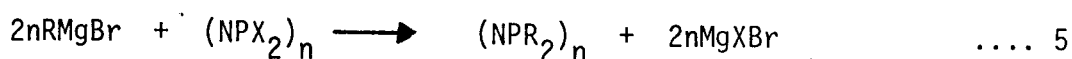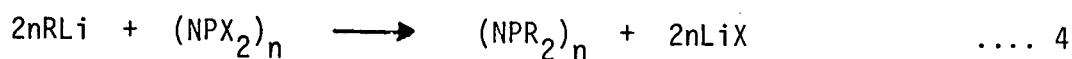
$$(X = \text{halogen, } R = \text{aryl or alkyl})$$

such reactions differ markedly from those obtained from the nucleophilic substitutions already discussed, and it was with the intention of understanding the cause(s) of these differences that the present work was begun.

Early work on the reaction of phenyllithium[39] and phenylmagnesium bromide[42-47] with $(NPCl_2)_3$ has shown that the expected reactions (Equations 4 and 5) are, at best, an alternative to the primary reaction path. Although $(NPPh_2)_3$ can be isolated (in ∿5% yield) from such reactions, the principal products are open chain phenylphosphazenes such as $Ph_3P=N-Ph_2P=N=Ph_2P=N-MgX$, formed, presumably, by the addition of a mole of nucleophile across a PN bond and cleavage of the cyclic phosphazene skeleton (Equation 6)[47].
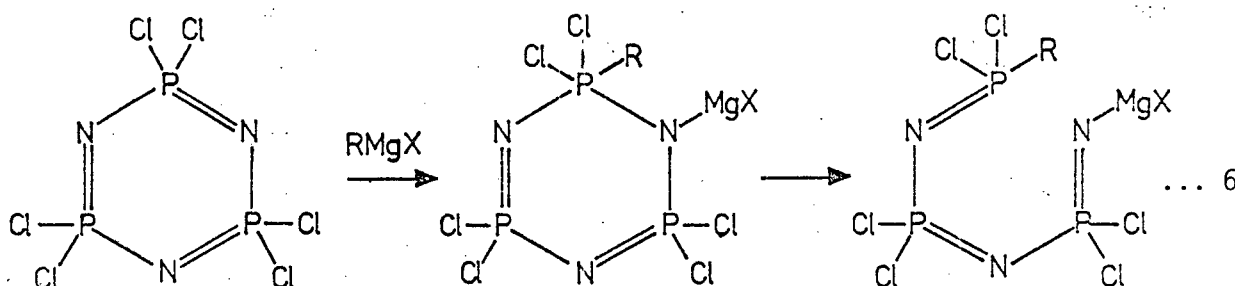


When fluorophosphazenes, rather than chlorophosphazenes, are employed, the substitution reaction is more successful, probably because the PN ring system is strengthened and stabilized by the more electronegative fluorine ligands. Thus, the phenylphosphazenes $(NPPh_2)_n$ (n=4-6) have all been prepared in good yield by the action of phenyllithium on the appropriate fluorophosphazene[48].

The alkylation of halophosphazenes has, to the present time, met with only limited success. The chlorophosphazenes appear to be unsuited to

this type of reaction[‡], and the few reports of the reaction of alkylmetals with chlorophosphazenes that have appeared suggest that addition followed by ring cleavage dominates the course of the reaction[39,49]. As in the case of phenylation reactions, substitution is favoured over addition when fluorophosphazenes are employed. Thus, the reaction of methyllithium with the tetrameric fluoride $(NPF_2)_4$ affords the completely methylated phosphazene $(NPMe_2)_4$ in 70% yield[51]. However, in contrast to this, the complete methylation of $(NPF_2)_3$, to yield $(NPMe_2)_3$, is not possible, and only the monomethyl $(MeF_5P_3N_3)$ and gem-dimethyl $(Me_2F_4P_3N_3)$ derivatives have been isolated from partial substitutions. Complementing the results of the previous two reactions, the pentameric methylphosphazene $(NPMe_2)_5$ can be prepared in 20% yield by the reaction of methyllithium and $(NPF_2)_5$. The oscillating yields in these methylation reactions have been interpreted as being consistent with the competing addition reaction, the influence of which is predicted to be dependent on ring size (vide infra)[51].

The original purpose of the present work was to examine the nature of the addition reaction which competes with substitution during the methylation of fluorophosphazenes, and to find general preparative routes to methylphosphazenes, especially the larger ring sizes. The results of work done in this area are described in Chapter II.

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[‡] By contrast, the alkylation of phosphoryl chlorides leads to moderate yields of trialkyl phosphine oxides (e.g. $Cl_3PO + 3MeMgBr \longrightarrow 3Me_3PO$; yield = 52%[50]).

## 1.2   Electronic Structure of Phosphazenes

### 1.2.1   Endocyclic π-Bonding

The relationship between the molecular structure of phosphazenes and their chemistry has been extensively studied[4]. The stability of halophosphazenes towards hydrolysis (unlike phosphoryl halides) and the fact that, in all phosphazenes, the ring angles at both nitrogen and phosphorus are much greater than the tetrahedral value, both indicate that the simple ionic formulation (III) is inadequate in rationalizing their basic chemical behaviour and structural features.

The existence of delocalized π-system in phosphazenes, based on the use of nitrogen 2p and phosphorus 3d orbitals[3,52] is suggested by many physical and chemical properties, especially the equality and shortness of the ring bonds. In hexachlorotriphosphazene (IV), for example, the PN



III                                    IV                                    V
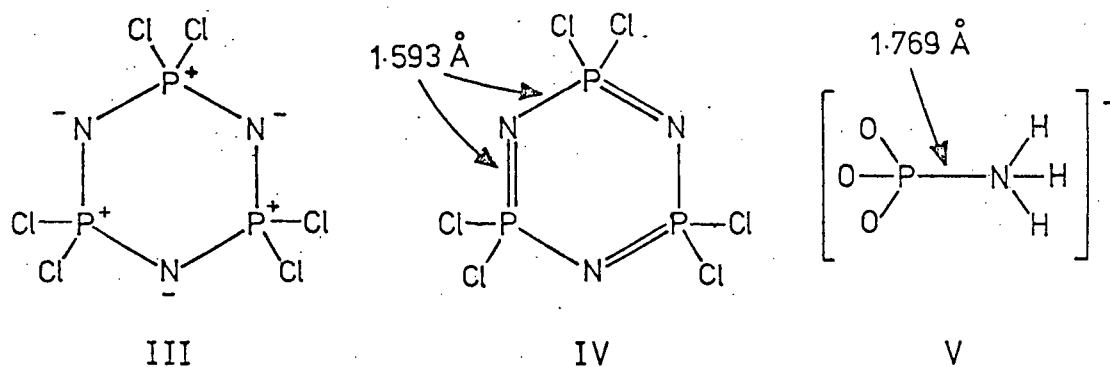
bond length is 1.593 Å[53], considerably shorter than the value of 1.769 Å found in the phosphoramidate ion (V)[54], in which π-bonding is not possible.

Evidence for the existence of π-bonding is also found in the ionization potentials of fluorophosphazenes[55], which indicate the presence

of both heteromorphic[3,56] and homomorphic[3,56] $\pi$-systems. The former is of lower energy and accounts for the general stability of the molecules, whilst the latter is more important chemically. Thus, the dependence on ring size of the relative rates of the first and second substitution of chloride with fluoride ion for the series $(NPCl_2)_{3-5}$[57,58], and of the measured activation energy for the exchange process between $(NPCl_2)_{3-6}$ and chloride ion[59], is believed to originate from homomorphic $\pi$-effects[4]. Figure 1.1 shows, for
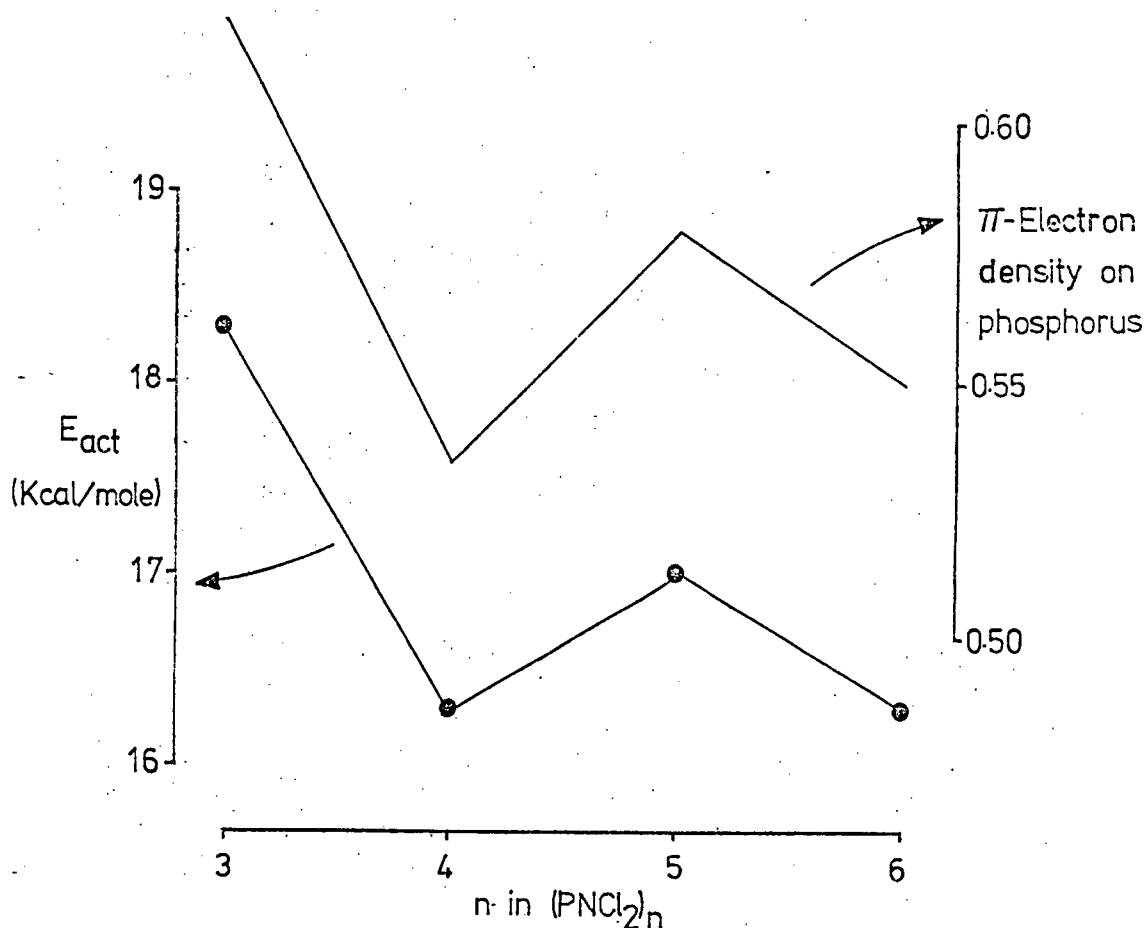


Fig. 1.1  Activation energies for the reaction $Cl^- + (NPCl_2)_n \longrightarrow$ $(NPCl_2)_n + Cl^-$ [from D.B. Sowerby, J. Chem. Soc., 1396 (1965)]. The upper curve shows calculated (HMO) $\pi$-electron densities at phosphorus [from D.P. Craig and N.L. Paddock, in "Nonbenzenoid Aromatics" Vol. 2, p. 273. Academic Press, 1971].

example, how the variation of this latter parameter with ring size is consistent with relative $\pi$-electron densities on phosphorus (as calculated for a homomorphic $\pi$-system). The oscillation in value of these parameters, with change in ring size, suggests that the actual nature of the reaction of phosphazenes with nucleophiles (e.g. substitution versus addition) may also be dependent on ring size. Such an effect has already been noted for the methylation of the fluorophosphazenes $(NPF_2)_{3-5}$ with methyllithium[51] (see Sec. 1.1.4). During the present work, a similar effect was observed in the reactions of the N-methyl methylphosphazenium salts $(Me_2PN)_{3,4}\cdot MeI$ with potassium t-butoxide. The details of these reactions are discussed in Chapter IV.

### 1.2.2 Exocyclic $\pi$-Bonding

The presence of $\pi$-bonding in phosphazenes is not limited to the cyclic framework. Conjugation between the endocyclic $\pi$-system and the exocyclic ligands is also possible. Unlike the conjugation found in aromatic hydrocarbons, the interaction between a ligand on a phosphazene ring and the cyclic $\pi$-system is not restricted to a particular orientation of the ligand about the phosphorus-ligand bond. This is because of the potential availability of more than one phosphorus 3d orbital (rather than the one carbon 2p orbital in benzene) through which conjugation can occur.

In phosphine oxides $R_3PO$, conjugation is strongest when R is an electron releasing group. Consistent with this, the phosphazenes which show structural evidence of exocyclic $\pi$-bonding are those in which the ligand can most readily donate electrons onto phosphorus, i.e., alkoxy and

alkylamino derivatives. In the methoxyphosphazenes $[NP(OMe)_2]_{4,6,8}$[60-62], all the P-O-C angles are close to 120° , as in phosphate esters[63], whereas the C-O-C angle in organic esters is about 112° . Also, the P-O bonds are shorter than expected for a P-O single bond (1.71 Å[64]). The same effects are seen in the dimethylamino phosphazenes $[NP(NMe_2)_2]_{4,6,8}$[65-67], in which the near planarity of the three bonds from the exocyclic nitrogen atoms ($\Sigma$ bond angles at nitrogen $\approx 350°$) indicates substantial electron release to phosphorus.

Exocyclic conjugation has also been studied through its effect on the $^{19}F$ n.m.r. spectrum of a fluorophenyl group attached to a phosphazene ring. The value of $\delta_F^p - \delta_F^m$ (the difference in the chemical shifts of the para and meta fluorine atoms) for the series $N_nP_nF_{2n-1} \cdot C_6F_5$ (n=3-8)[68] shows that, as a group, the fluorophosphazenes are strong $\pi$-acceptors, comparable to a cyano group.

### 1.2.3 Chemical Consequences of Exocyclic $\pi$-Bonding

In contrast to the structural and spectroscopic manifestations of conjugative interactions, the influence of such interactions on the chemistry of phosphazenes is less well documented. The protonation of aminophosphazenes occurs, in general, on an endocyclic nitrogen[69,70], indicative of the lower base strength of the exocyclic nitrogen caused by the drainage of $\pi$-charge from it into the ring. However, there is at least one example of the coordination of an exocyclic amino group to a metal[71] (in $[NP(NMe_2)_2]_4W(CO)_4$), which suggests that the reduction in base strength is not large. Consistent with this, the reaction of $[NP(NMe_2)_2]_3$ with $Me_3O^+BF_4^-$ results in the methylation of both an endocyclic and an exocyclic

nitrogen[72] (although the former is probably quaternized first). In
aminophosphazenes, therefore, the chemical effect of exocyclic conjugation
is small, but, to the extent that it occurs, is such as to reduce the basic
properties of the ligand on phosphorus. This conclusion is crucial, and
provides the link between past work in phosphazene chemistry and the
results reported in this thesis.

During the course of this work, it has been found that the ability
of the phosphazene ring to accept $\pi$-charge from an exocyclic ligand can be
effectively utilized in the synthesis of novel phosphazene derivatives. The
initial experiments that lead to this discovery were concerned with the
reaction of methyllithium with octamethyltetraphosphazene $(NPMe_2)_4$. By
analogy with the addition of methylmagnesium iodide across the Si-O bond of
$(OSiMe_2)_4$[73] (Equation 7), and of alkyllithiums across the C=N bond of
pyridine[74] (Equation 8), it was believed that methyllithium might add across
the P=N bond of methylphosphazenes (Equation 9a). Early work[75] showed that,

$$\dots \text{9a}$$

$$\dots \text{9b}$$
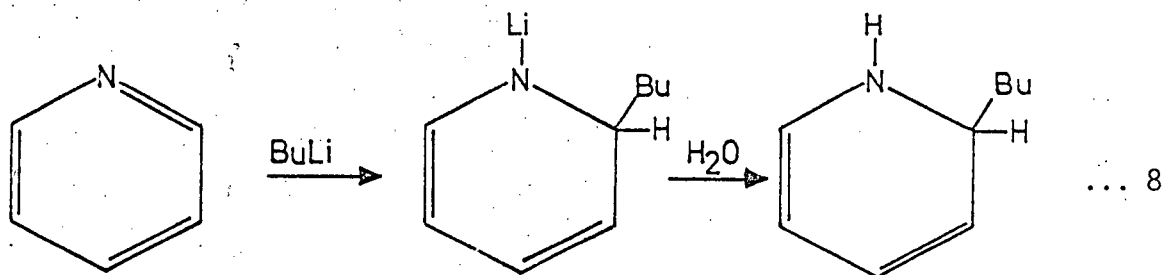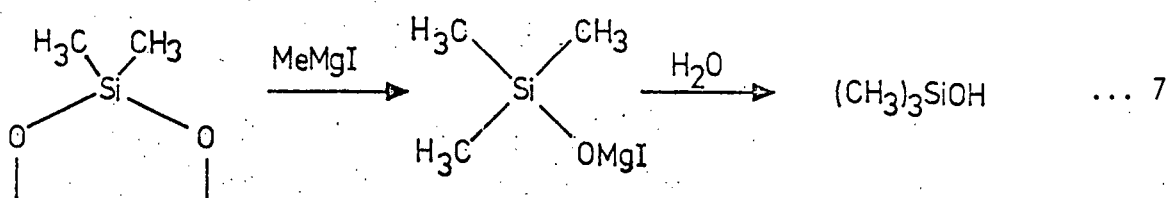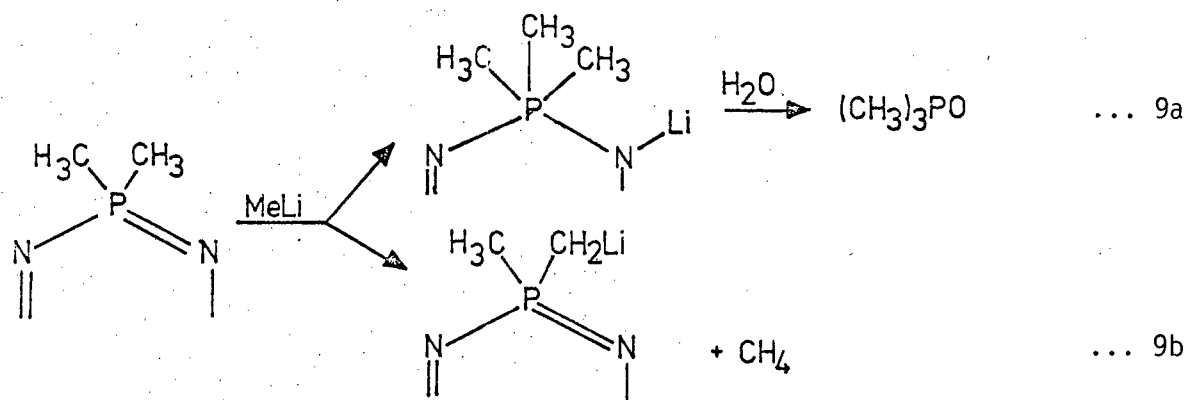
although a reaction did take place, its nature was uncertain. Trimethyl-
phosphine oxide, for example, could not be isolated via the hydrolysis of
the reaction mixture. In fact, it has now been established that
methyllithium reacts with methylphosphazenes as a base (Equation 9b),
rather than as a nucleophile, and deprotonates a methyl group attached to
phosphorus, producing novel phosphazene carbanions. The chemistry of these
carbanions is fully discussed in Chapter III.

The acidity of protons in methylphosphazenes complements the
reported behaviour of the compounds as donors. Both $(NPMe_2)_3$ and $(NPMe_2)_4$
form a variety of simple salts[76], as well as reacting to give complexes
with metal carbonyls[77,78] and metal ions[79,80]. They also react with alkyl



$$\dots \text{10}$$
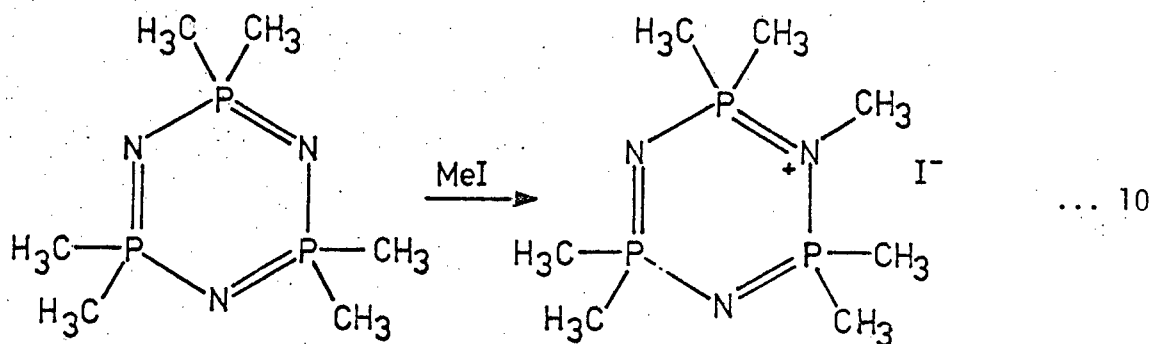
iodides (e.g. Equation 10) to give N-alkyl quaternary salts $(NPMe_2)_{3,4} \cdot RI$

$(R=Me, Et)^{76,81}$. During this work, the potential applications to synthesis of these latter compounds has been explored. This study was encouraged not only by the observed reactivity of the neutral methylphosphazenes towards deprotonation, but by the formal structural resemblance of quaternary phosphazenium salts to more conventional phosphonium salts, whose reaction with bases, to give phosphorus ylids, is well known (vide infra). It was believed that, if the analogy were justified, then the phosphazenium salts $(NPMe_2)_n$.MeI could also be deprotonated with a suitably



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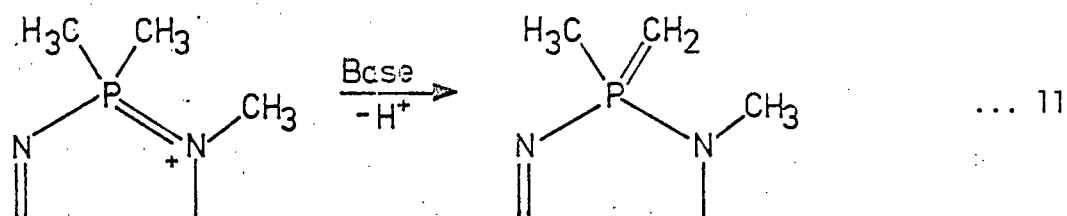
strong base, to yield phosphazene derivatives containing an exocyclic double bond (Equation 11), the physical and chemical properties of which would reflect the extent of conjugation between the ring and ligand. However, the results of this study, as described in Chapter IV, show that although deprotonation of the N-methyl quaternary salts can be effected, the final product of the reaction is quite different from the expected exocyclic ylid.

## 1.3 Carbanion and Ylid Formation in Organophosphorus Chemistry

Although they present many novel features, the reactions of methylphosphazenes and methylphosphazenium ions with bases are related to the formation of carbanions and ylids from mononuclear phosphorus compounds. Because of their greater structural simplicity and ease of preparation, these

latter compounds have been studied extensively, and an outline of their chemistry is helpful in understanding the behaviour of phosphazenes. The present section of this chapter is designed to afford the reader some background information on this topic, thereby facilitating the later comparison of the chemistry of the phosphazene compounds studied in this work with that of the analogous, but more well known, mononuclear phosphorus derivatives.

The acidity of methyl and methylene protons attached to second row elements is well known, and is generally attributed to the influence of d-orbitals[82], the effects of which are vividly demonstrated by the exchange rates (Table 1.1) of the deuteroxide catalysed exchange of tetramethylammonium, tetramethylphosphonium and trimethylsulphonium ions with deuterium oxide (Equations 12a-12c)[83].

$$Me_3\overset{+}{N}-CH_3 \;+\; OD^- \;\rightleftharpoons\; Me_3\overset{+}{N}-\overset{-}{C}H_2 \;+\; HOD \qquad \dots.\ 12a$$

$$Me_3\overset{+}{P}-CH_3 \;+\; OD^- \;\rightleftharpoons\; Me_3\overset{+}{P}-\overset{-}{C}H_2 \;+\; HOD \qquad \dots.\ 12b$$

$$Me_2\overset{+}{S}-CH_3 \;+\; OD^- \;\rightleftharpoons\; Me_3\overset{+}{S}-\overset{-}{C}H_2 \;+\; HOD \qquad \dots.\ 12c$$
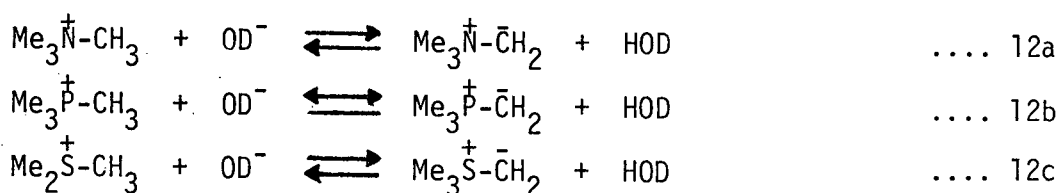
| Compound | Relative Rate | C-X Bond Length (Å) |
|----------|---------------|---------------------|
| $Me_4N^+$ | 1 | 1.47 |
| $Me_4P^+$ | $2.4 \times 10^6$ | 1.87 |
| $Me_3S^+$ | $2.0 \times 10^7$ | 1.81 |

Table 1.1: Relative rates for the deuteroxide catalysed hydrogen-deuterium exchange between ammonium, phosphonium and sulphonium ions and deuterium oxide. From W. von E. Doering and A.K. Hoffman, J. Amer. Chem. Soc., 77, 521 (1955).

In the absence of other factors, the relatively short N-C bond should lead to a more stable intermediate (simple Coulombic stabilization energy being inversely proportional to the charge separation) and hence a faster exchange rate for the $Me_4N^+$ ion. The fact that the observed rates for phosphonium and sulphonium ions are $10^6$ times greater than for the ammonium ion suggests that the dipolar transition state for the former ions is stabilized by the formation of a 3d-2p $\pi$-bond between the two polar centres (e.g. Equation 13).

$$Me_3P^+ - \bar{C}H_2 \quad \rightleftharpoons \quad Me_3P = CH_2 \qquad \text{.... 13a}$$

$$Me_2S^+ - \bar{C}H_2 \quad \rightleftharpoons \quad Me_2S = CH_2 \qquad \text{.... 13b}$$
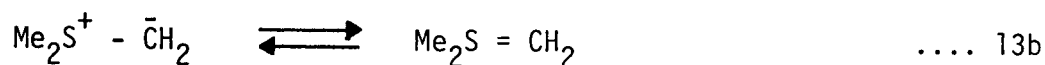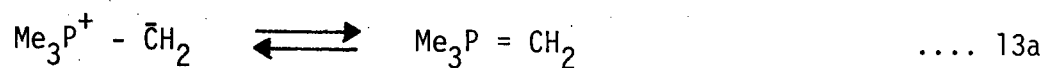
## 1.3.1 Phosphorus Ylids

This pronounced acidity of protons on carbon atoms adjacent to phosphorus and sulphur has many applications in synthesis. Phosphonium salts $[R_3PCH_2R]^+X^-$ can be deprotonated with relative ease to produce phosphorus ylids $R_3PCHR$, the use of which, in the Wittig reaction[84], is well known[85]. By contrast, nitrogen ylids can only be isolated when a sufficiently electron withdrawing group is attached to the $\alpha$-carbon to stabilize the negative charge that it acquires upon deprotonation[86].

The ylids obtainable by the deprotonation of a phosphonium salt are also capable of adding HX (X=halide), thereby regenerating a phosphonium salt. The two compounds may therefore be considered as a conjugate acid-base pair, the equilibrium of which is controlled by the nature of the substituents on phosphorus and carbon (Equation 14). Electron-attracting

$$[R_3^1P-CHR^2R^3]^+X^- \rightleftharpoons R_3^1P-CR^2R^3 + HX \qquad \text{.... } 14$$
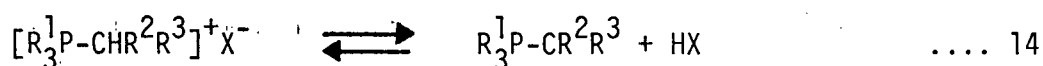
groups on carbon ($R^2$ and $R^3$) enhance the acidity of the phosphonium salt, the polar bond of the corresponding ylid being more effectively stabilized, either by resonance or inductive effects. Thus, $[Ph_3PCH_2COOMe]^+Br^-$ can be deprotonated by a relatively weak base such as sodium carbonate[87,88], the polar P=C bond so obtained being sufficiently stabilized by resonance (Equation 15) so as to render it stable to water. The ligands $R^1$ attached
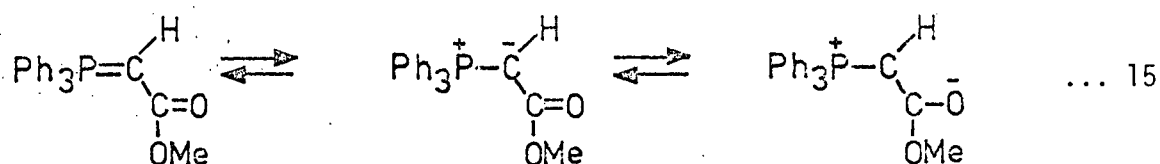


to phosphorus can also influence the acid-base equilibrium. The inductive donating effect of alkyl groups makes alkylphosphonium ions weaker acids than their aryl counterparts. If the three phenyl groups of $[Ph_3PCH_2COOMe]^+Br^-$ are replaced with cyclohexyl groups, sodium hydroxide, rather than sodium carbonate, must be used to induce deprotonation, and the resulting ylid is decomposed on contact with water[87]. In the limit, unsubstituted alkylphosphonium salts are sufficiently weak acids to require alkyl metals to effect proton removal.

The basic nature of phosphorus ylids has led to their use as deprotonating agents for other phosphonium salts, by means of a reaction which is generally referred to as "transylidation"[89]. In Equation 16, the position of the equilibrium is determined by the nature of the ligands $R^1$ and $R^2$, the direction of the reaction being such as to afford the least

$$Ph_3P-CHR^1 + [Ph_3P-CH_2R^2]^+ \rightleftharpoons [Ph_3PCH_2R^1]^+ + Ph_3P=CHR^2 \qquad \dots 16$$
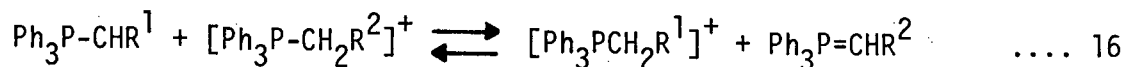
acidic phosphonium salt. For example, the reaction of $Ph_3P=CH_2$ with $[Ph_3PCH_2COPh]^+Br^-$ results in the formation of $[Ph_3PCH_3]^+Br^-$ and $Ph_3PCHCOPh$ in nearly 90% yield[89].

The transylidation reaction renders possible the comparison of the net influence of the inductive and resonance effects exercised by the substituents on carbon on the acidity of phosphonium ions. In agreement with the $pk_a$ values of phosphonium salts $[Ph_3PCH_2R]^+X^-$, the acceptor ability of various R groups increases in the following order[89-91]:

$CH_3 < H < Ph < P(O)Ph_2 \simeq P(S)Ph_2 < COOR < CN < C(O)Ph < \overset{+}{P}Ph_3$. According to this series, the treatment of a phosphonium salt $[Ph_3PCH_2R^1]^+X^-$ with a phosphorus ylid $Ph_3PCHR^2$ results in transylidation if $R^1$ is a better acceptor than $R^2$.

Consistent with their basic character, ylids are methylated on carbon by methyl iodide[91-95] (Equation 17). In agreement with the above

$$R^1_3P=CHR^2 + MeI \longrightarrow [R^1_3P-CHMeR^2]^+I^- \qquad \dots 17$$

series, the phosphonium salts $[R^1_3PCHMeR^2]^+I^-$ ($R^1$=Ph; $R_2$=H[92,93], -P(O)Ph$_2$[91], -COOMe[94]; $R^1$=Me, $R^2$=H[95]) so formed are unreactive to a second mole of ylid. By contrast, the acylation of ylids with acid chlorides results in transylidation of the initially formed salt (Equation (18), the strong acceptor properties of the acyl group making it sufficiently acidic to react with a second mole of starting ylid[96-98]. This difference in behaviour of ylids upon methylation and acylation is an important concept. Its relevance to the present work will be fully discussed in a later chapter.

$$R_3P=CHR^1 + AcCl \longrightarrow [R_3P-CHR^1Ac]Cl$$

$$[R_3P-CHR^1Ac]^+Cl^- + R_3P=CHR^1 \longrightarrow R_3P=CRAc + [R_3P-CH_2R]^+Cl^- \quad \ldots \ldots \text{ 18}$$
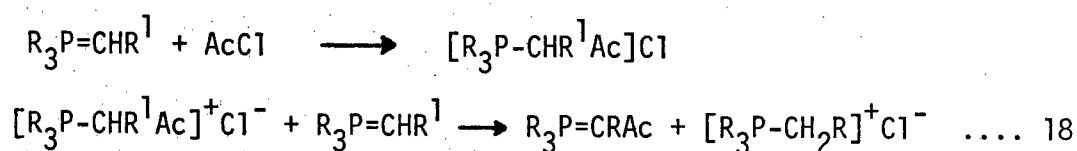
(Ac = acyl)

### 1.3.2 Phosphorus Carbanions

The acidity of phosphonium ions $[R_3PCH_2R]^+$ is enhanced by their charge. However, in formally neutral phosphoryl compounds, the acidity of methyl and methylene protons adjacent to phosphorus is still appreciable. The removal of a proton from such compounds produces a carbanion, the stability of which is attributed to resonance with the phosphoryl group (Equation 19). The potential applications to synthesis of such carbanions are many; accordingly, the preparation and chemistry of the carbanion



$$\ldots \text{ 19}$$
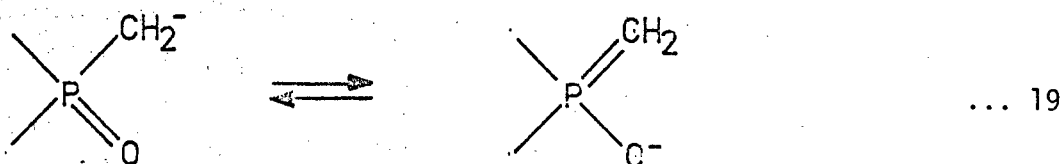
derivatives of phosphonate esters $(RO)_2P(O)CH_2R$[99,100], and phosphine oxides $R_2P(O)CH_2R$[100-108], have been extensively studied. Figure 1.2 shows, for example, a selection of the reactions that the phosphine oxide carbanion $Ph_2P(O)CH_2^-$ undergoes. Its chemical behaviour appears to depend on the nature of the counter cation. With carbonyl compounds, for example, it forms an intermediate betaine $Ph_2P(O)CH_2C(\bar{O})R_2$, which is stable when the cation is lithium[107,108]. However, when a cation other than lithium is present, decomposition of the betaine can occur (as in the Wittig reaction),
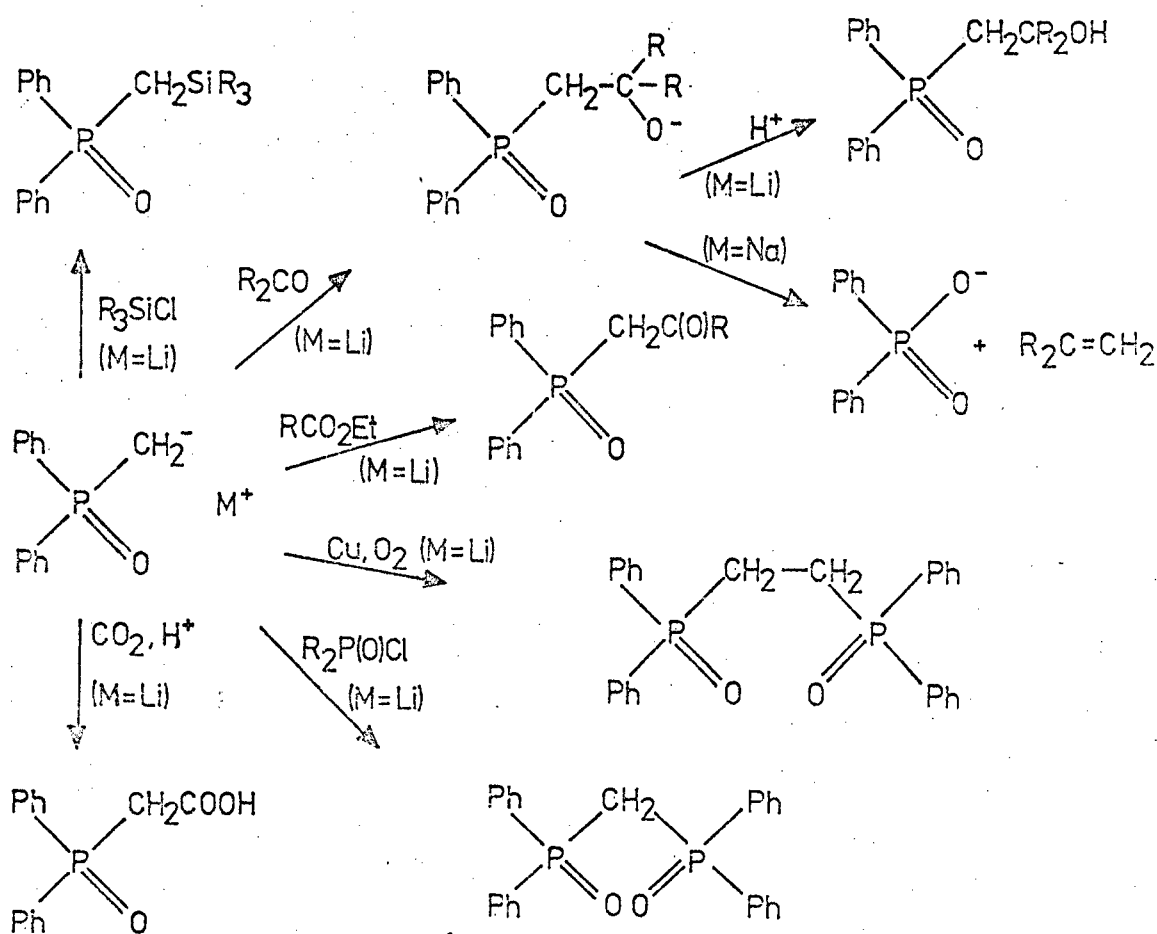
Fig. 1.2  Survey of typical reactions of the methyldiphenylphosphine oxide carbanion $Ph_2P(O)_2CH_2^-M^+$.

with elimination of an alkene and the formation of a phosphinate anion[102].

The chemical similarity between these mononuclear phosphoryl carbanions and the phosphazene carbanions reported in this thesis is discussed in detail in Chapter III.

## 1.4  Summary

As is indicated in the foregoing introduction, this thesis is composed of three related areas of research:  (1) the preparation of

methylphosphazenes, (2) the synthesis and reactions of methylphosphazene carbanions, and (3) the reactions of N-methyl methylphosphazenium quaternary salts with bases. The results obtained from these areas are described and discussed in the following three chapters. The final chapter of the thesis is concerned with the structural aspects of some of the compounds reported in earlier chapters, and relates, where possible, the chemistry of the compounds to their molecular and electronic structures.

CHAPTER II

## PREPARATION OF METHYLPHOSPHAZENES

As was pointed out in the introductory chapter, the principal concern of this work has been the study of the reactivity of the methyl protons in methylphosphazenes $(NPMe_2)_n$ and their quaternary salts $(NPMe_2)_n \cdot MeI$. Such topics will be discussed in later chapters. The purpose of this present chapter (Section 1) is to report the advances that have been made in the preparation of the methylphosphazenes themselves. The preparation of the partially methylated phosphazene $Me_2Ph_4P_3N_3$ and its methiodide salt $Me_2Ph_4P_3N_3 \cdot MeI$ is also described in this chapter. The usefulness of these latter compounds stems from the fact that each contains only one potentially reactive P-methyl group; they therefore provide a simpler model than do the fully methylated phosphazenes for the study of the chemistry of the $-N=PMe_2-$ unit. Section 3 deals with the phosphinimine $Me_3PNMe$ and a number of its derivatives. This molecule constitutes the monomeric counterpart of the cyclic methylphosphazenes, and its preparation and study was undertaken to allow a comparison of the properties of the $-N=PMe_2-$ unit in monomeric and polymeric systems. The final section of the chapter is concerned with the chemical reactivity of the trimeric phosphazene $Cl_2Ph_4P_3N_3$. Although it is not directly related to the other topics covered in the chapter, the reactivity of this compound towards nucleophiles offers an interesting contrast to that of the fully halogenated phosphazenes described in the introduction (Chapter 1, Section 1).

## 2.1 Preparation of Methylphosphazenes

### 2.1.1 Preparation of $(NPMe_2)_n$ (n=3,4)

To date, the most common method for the preparation of the methyl-phosphazenes $(NPMe_2)_{3,4}$ has been by the ammonolysis of dimethyltrichloro-phosphorane[21,76,77,109], according to Equation 1. The phosphazenes are

$$Me_2PCl_3 + NH_4Cl \longrightarrow \frac{1}{n}(NPMe_2)_n + 4HCl \quad (n=3,4) \qquad \ldots 1$$
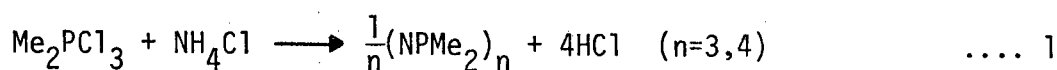
actually produced as their hydrochlorides, which can be converted into the neutral compounds either by a tertiary amine[76,77] or aqueous alkali[109]. When the reaction is carried out in tetrachloroethane, the molar ratio of trimer:tetramer is about 1:4[76]. If the solvent is omitted, the tetramer is the sole product, and the overall yield is diminished[77]. Mixtures of $(NPMe_2)_3$ and $(NPMe_2)_4$ are also formed, in low yield, by heating $Me_2P(NH_2)_2Cl$[77,110], but, however the mixture is produced, the separation of the individual components by fractional crystallization is tedious and time consuming. The tetramer is more easily obtained than the trimer because it is the major product of such reactions and forms much better crystals.

These difficulties prompted the search, in this work, for a new synthetic route to $(NPMe_2)_3$. As a result of this investigation, two useful facts have come to light. (1) By substitution of methylamine hydrochloride for ammonium chloride in reaction 1, the corresponding methyl chloride salts $(NPMe_2)_3 \cdot MeCl$ and $(NPMe_2)_4 \cdot 2MeCl$ are formed instead of the hydrochlorides. Not only is the overall yield of the methylphosphazenes greatly improved, but the ratio of the yields of the two ring sizes favours

the trimeric derivative. (2) The diquaternary chlorides of the tetramer $(NPMe_2)_4 \cdot 2RCl$ (R=Me or H) are insoluble in acetonitrile, whereas the quaternary chlorides of the trimer $(NPMe_2)_3 \cdot RCl$ (R=Me or H) are appreciably soluble in this solvent. Therefore, since the hydrochlorides of the trimer and the tetramer are easily produced from the neutral compounds by their reaction with hydrogen chloride, any mixture of $(NPMe_2)_{3,4}$ can easily be separated.

The procedure for the preparation of $(NPMe_2)_3$ reported here[111] uses chlorobenzene as solvent. An oily intermediate is formed, which has not been characterized but, by analogy with the reactions of $PCl_5$[112] and $PhPCl_4$[113], probably contains the dimeric phosphazane $(MeNPMe_2Cl)_2$[‡]. Pyrolysis of this oil _in vacuo_ then gives a mixture of the quaternary salts $(NPMe_2)_3 \cdot MeCl$ and $(NPMe_2)_4 \cdot 2MeCl$. It is important to note that the ratio of $(NPMe_2)_3 : (NPMe_2)_4$ in the product is very sensitive to the length of time for which the oily intermediate is heated in the presence of solvent. Several preliminary experiments using prolonged heating periods shifted the relative yields of the trimer and tetramer in favour of the latter, and also lowered the overall yield. This may be the result of the polymerization of the dimeric phosphazane, known to occur on prolonged heating of the analogous $(MeNPF_3)_2$[115].

When the reaction conditions outlined above are used in the reaction of $Me_2PCl_3$ with $NH_4Cl$, a high yield of the tetramer (73% compared to

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‡ By contrast, the reaction of $Ph_2PCl_3$ with alkylamine hydrochlorides $RNH_2 \cdot HCl$ gives simple salts $[Ph_2ClP-NHR]^+Cl^-$[114].

literature values of $56\%^{76}$ and $60\%^{77}$) is produced with almost complete exclusion of the trimer. Hence, by the appropriate choice of starting materials and reaction conditions, good yields of trimer or tetramer can be achieved. The two compounds, which are always formed as their salts, can then be separated by virtue of the different solubilities of their salts in acetonitrile. The neutral $(NPMe_2)_3$ is obtained from $(NPMe_2)_3.MeCl$ by heating it $\underline{in\ vacuo}$. There appears to be a similarity, at least in principle, to the formation of $(NPPh_2)_3$ by the dehydrohalogenation of $(HNPPh_2F)_2$ with cesium fluoride[116]. It is also interesting to note a difference from the behaviour of $(MeNPCl_3)_2$, prepared from $PCl_5$ and methylamine hydrochloride[112]. Upon pyrolysis, this compound does not give quaternary salts, presumably because the chlorophosphazenes are too weakly basic; a high polymer of composition $(NPCl_2)_x$ is formed instead[117]. The positive charge on the quaternized methylphosphazenes would tend to prevent such polymerization, an inference which provides a rationale for the absence of larger methylphosphazenes $(NPMe_2)_n$ $(n > 4)$ from such reactions.

## 2.1.2  Preparation of $(NPMe_2)_n$ $(n > 4)$

Although the methylphosphazenes $(NPMe_2)_{3,4}$ have been known for many years[21], studies on the chemical and physical effects of ring size variations within the homologous series $(NPMe_2)_n$ $(n=3,4,5...)$ have always been limited by the difficulty in preparation of the different (more especially the larger) ring sizes. Unlike most phosphazenes $(NPX_2)_n$ (e.g. $X=NMe_2$, OPh, OMe), which have been prepared in a wide variety of ring sizes (from $n=3$ to 8) by the substitution of a halophosphazene,

alkylphosphazenes have been less easily obtained. The varying yields
observed for the methylation of the fluorophosphazenes $(NPF_2)_{3,5}$ (yields,
for n=3, 0%; n=4, 70%; n=5, 20%)[51,76], via Equation 2, have been interpreted
in terms of a competing addition reaction (see Chapter 1, Section 1.1).

$$(NPF_2)_n + 2nMeLi \longrightarrow (NPMe_2)_n + 2nLiF \qquad \text{.... 2}$$
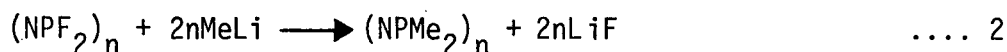
Accordingly, unsuccessful attempts to prepare methylphosphazenes of larger
ring sizes (n $\geqslant$ 6) have been attributed to the increased statistical
difficulty of effectively substituting all the P-F bonds of the
appropriate fluorophosphazene.

During the course of this work, the possibility of using methylmag-
nesium bromide as a methylating agent for the large ring size phosphazenes
was considered. Early attempts[118] to methylate $(NPF_2)_{4,6}$ with MeMgBr were
unsuccessful, and the greater success obtained when methyllithium was
used was attributed to the greater nucleophilicity of the latter, which
would favour complete substitution of all the P-F bonds, and to the lower
Lewis acidity of lithium, which would reduce the possibility of ring
cleavage via coordination of the metal to a ring nitrogen atom. However,
upon re-examination of the reaction of MeMgBr with $(NPF_2)_6$, it was
discovered that a good yield of $(NPMe_2)_6$ could be achieved by suitably
modifying the experimental procedure from that used previously.
Consequently, it has been determined that the reaction of methylmagnesium
bromide with the appropriate fluorophosphazene, according to Equation 3,
offers an efficient and facile preparative route to large ring size
methylphosphazenes, and the derivatives $(NPMe_2)_n$ (n=6-10) have all been

prepared by this method.

$$2n\text{MeMgBr} + (\text{NPF}_2)_n \longrightarrow (\text{NPMe}_2)_n + 2n\text{MgBrF} \qquad \ldots . 3$$

In practice, the reaction of MeMgBr with $(\text{NPF}_2)_n$ is slow. Unlike the immediate exothermic reaction that occurs between methyllithium and fluorophosphazenes, it requires an induction time of 1-2 hours before the precipitation of magnesium halides commences (from ethereal solution). The key to the successful isolation of the product is the work-up procedure, which is similar to that required for the preparation of trimethylphosphine oxide[50]; the reaction mixture is quenched with water, and the magnesium precipitated from the solution by the addition of a base (sodium carbonate and hydroxide have both been used). Evaporation of the solvent from the aqueous extract, and re-extraction of the residue with chloroform, then yields the desired product.

The necessity of an aqueous work-up when methylmagnesium bromide is used is consistent with the extent to which complexation of magnesium and lithium ions is known to occur[119]. Because of its greater charge, the magnesium ion is more prone to complex formation than is lithium, and, in the present case, methylphosphazenes appear to be sufficiently strong donors to complex with magnesium bromide, but not with lithium bromide[‡]. The difference in the coordinating ability of the two metals may also affect the mechanism of the reactions of MeMgBr and MeLi with $(\text{NPF}_2)_n$. Such a

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[‡] This assumes that the methyllithium is prepared by the action of methyl bromide on metallic lithium.

belief is supported, for example, by the reactions of PhMgBr[120] and PhLi[121] with $(NPF_2)_3$, which give, respectively, the geminally and non-geminally disubstituted derivatives $Ph_2F_4P_3N_3$.

However, regardless of the actual mechanism of substitution, it is apparent that the difficulties encountered in the preparation of the small ring size methylphosphazenes (especially the trimer), via the substitution of a fluorophosphazene, are not observed during the preparation of the higher members of the series $(NPMe_2)_n$. This conclusion is consistent with many other properties of phosphazenes, which also indicate that the initially significant effects of ring size variation disappear for $n > 6$.

## 2.1.3  Preparation of Methylphosphazenium Quaternary Salts

In agreement with their expected behaviour as donor molecules, the methylphosphazenes $(NPMe_2)_{3-5}$ react with methyl iodide to give simple N-methyl quaternary salts $(NPMe_2)_n \cdot MeI$ $(n=3,4,5)$[76,81]. The synthetic uses of these compounds are discussed in Chapter IV; the purpose of this present section is to report the preparation of several new quaternary salts of this type.

### 2.1.3.1  Preparation of Monoquaternary Salts of $(NPMe_2)_n$

By following the procedure reported for the preparation of the salts $(NPMe_2)_n \cdot MeI$ $(n=3-5)$[76,81], the analogous salts of the hexameric and heptameric methylphosphazenes have now been prepared (Equation 4). In

$$(NPMe_2)_n + MeI \longrightarrow (NPMe_2)_n \cdot MeI \quad (n=3-7) \qquad \dots. 4$$
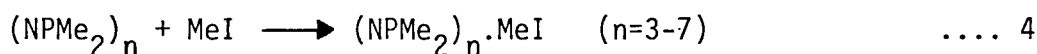
practice, the neutral methyl phosphazene is heated under reflux for several hours in neat methyl iodide. The product, $(NPMe_2)_n \cdot MeI$ (n=3-7) is precipitated from the solution in nearly quantitative yield. To date, apart from the simple N-ethyl and N-methyl derivatives, no other quaternary salts of methylphosphazenes have been prepared. However, during the course of this work, the novel N-ethylacetato quaternary salts $[(NPMe_2)_n \cdot CH_2COOEt]^+I^-$ (n=3,4) have been obtained by heating the appropriate phosphazene in ethyl iodoacetate (Equation 5). As with the

$$(NPMe_2)_n + ICH_2COOEt \longrightarrow [(NPMe_2)_nCH_2COOEt]^+I^- (n=3,4) \quad \dots 5$$
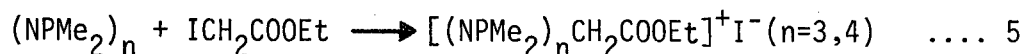
methiodide salts the product is precipitated from the solution and separated by filtration. The reaction is much slower than with methyl iodide, and the yields are only moderate (60-70%).

## 2.1.3.2 Preparation of Diquaternary Phosphazenium Salts

The diquaternary salt $(NPMe_2)_4 \cdot 2MeCl$ can be prepared via the reaction of $Me_2PCl_3$ and methylamine hydrochloride (see Section 2.1.1). However, the dication $[(NPMe_2) \cdot 2Me]^{++}$ can be more conveniently prepared by the diquaternization of neutral $(NPMe_2)_4$ with a sufficiently powerful methylating agent. Similar diquaternizations, of aminophosphazenes[72] and pyrazines[122], have been carried out using trialkyloxonium tetrafluoroborate. However, in this work, the use of methylfluorosulphate ("Magic Methyl") was considered to be preferable. Its strength as an electrophile is well known[123,124], and its ease of handling make it a more convenient choice than $Me_3O^+BF_4^-$. Accordingly, it has been found that $MeSO_3F$ reacts rapidly with

$(NPMe_2)_4$, in acetonitrile solution, to give the diquaternary salt $(NPMe_2)_4 \cdot 2MeSO_3F$. The di-iodide salt $(NPMe_2)_4 \cdot 2MeI$ was prepared from it by ion exchange. It is probable that methyl fluorosulphate is capable of forming polycations from the methylphosphazenes of large ring size (e.g. $[(NPMe_2)_6 \cdot 3Me]^{3+}$ and $[(NPMe_2)_8 \cdot 4Me]^{4+}$).

### 2.1.4 Structure and Spectra of Methylphosphazenes

The preparation of $(NPMe_2)_{6-10}$[‡] extends the series of the known methylphosphazenes from the trimeric to the decameric derivative, and thereby creates the largest single family of phosphazenes other than the halo-derivatives $(NPX)_2$ (X=Cl,F) (see Table 2.1). Their cyclic nature is confirmed by the presence of a single resonance in their $^{31}P$ n.m.r. spectra, and a simple doublet in their $^{1}H$ n.m.r. spectra[‡‡].

Unlike dimethylsiloxanes, and many other phosphazenes of large ring sizes, all the methylphosphazenes $(NPMe_2)_n$ (n=3-10) are crystalline solids at room temperature and, as such, are potentially useful sources of precise structural information. The molecular structures of $[NP(OMe)_2]_{4,6,8}$[60-62] and $[NP(NMe_2)_2]_{4,6,8}$[65-67] all show interesting conformational effects, but their interpretation in terms of non-bonded interactions is complicated by the size and shape of the ligands. In the case of the methylphosphazenes however, the more nearly spherical nature of the methyl ligands and their

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[‡] The author is grateful to Mr. K.D. Gallicano for the preparation of the compounds $(NPMe_2)_{8-10}$.

[‡‡] Because of conformational changes, the exact magnetic equivalence of phosphorus and hydrogen nuclei is probably attained statistically.

Table 2.1:  N.m.r. parameters[a], (P=N) stretching frequencies[b], and melting points of the methylphosphazenes $(NPMe_2)_n$ (n=3-10).

| n | M.pt. (°C) | $\nu_{asym}$ (P=N) ($cm^{-1}$) | $\delta_H$ (ppm) | $\delta_P$ (ppm) |
|---|---|---|---|---|
| 3 | 187-188 | (1185)[c] | 1.46 (13.0) | 90.7 |
| 4 | 161-162 | (1122)[c] | 1.51 (11.5) | 100.3 |
| 5 | 64-65[c] | (1255)[c] | 1.50 (12.0) | 106.7 |
| 6 | 163-165 | 1213, 1255 (1250) | 1.50 (12.3) | 109.3 |
| 7 | 128-130 | 1210, 1255 (1242) | 1.52 (12.5) | 109.7 |
| 8 | 171-173 | 1210, 1268 (1225) | 1.53 (13.0) | 110.4 |
| 9 | 123-125 | 1220 (1220) | 1.54 (13.0) | 109.9 |
| 10 | 100-102 | 1165,1210,1236 (1216) | 1.53 (13.2) | 109.6 |

(a) From dilute solutions, $\delta_H$ (ppm) in $CDCl_3$, reference internal TMS; P-H coupling constants (in Hertz) in parenthesis.  $\delta_P$ (ppm) in $C_6D_6$, reference external $P_4O_6$.  (b) From nujol mull spectra; values in parenthesis from $CCl_4$ solutions.  (c) From H.T. Searle, J. Dyson, N.L. Paddock and T.N. Ranganathan, J. Chem. Soc. Dalton, 203 (1975).

smaller size greatly reduces the number of non-bonded interactions, and conformational trends are therefore more easily understood. Consequently, the crystal structure determinations of several methylphosphazenes of large ring size are currently being carried out; those of the heptamer and octamer have recently been completed (that of $(NPMe_2)_7$ being the first structure analysis of a heptameric phosphazene). The principal structural parameter of these molecules, the P=N bond length, is consistent with the presence of the inductive donating methyl groups on phosphorus. The value of L(P=N) in $(NPMe_2)_n$ (n=4, 1.60Å[126]; n=5, 1.59Å[127]; n=7, 1.59Å[125]; n=8, 1.58Å[125]) is longer than in $(NPF_2)_4$ (1.51Å[128]), $(NPCl_2)_4$ (1.57Å[129a] and 1.56Å[129b]) and $[NP(OMe)_2]_4$ (1.57Å[130]), and indicates the extent to which lone pair delocalization into the ring π-system is suppressed. A more detailed analysis of the structures and conformations of methylphosphazenes is given in Chapter V.

## 2.1.4.1 [31]P Chemical Shifts of $(NPMe_2)_n$ (n=3-10)

The localization of charge on nitrogen is also observed in the [31]P n.m.r. chemical shifts of methylphosphazenes. Figure 2.1(A) shows how the value of $\delta_p$ in the series $(NPX_2)_n$ depends upon the nature of X and the value of n. The phosphorus atoms are effectively deshielded by methyl ligands; not only are the individual values of $\delta_p$ for $(NPMe_2)_n$ lower than when more electronegative groups are present on phosphorus, but the increase in $\delta_p$ along the series n = 3-10, which is usually related to a widening of the ring angle at nitrogen, is least for the methylphosphazenes.
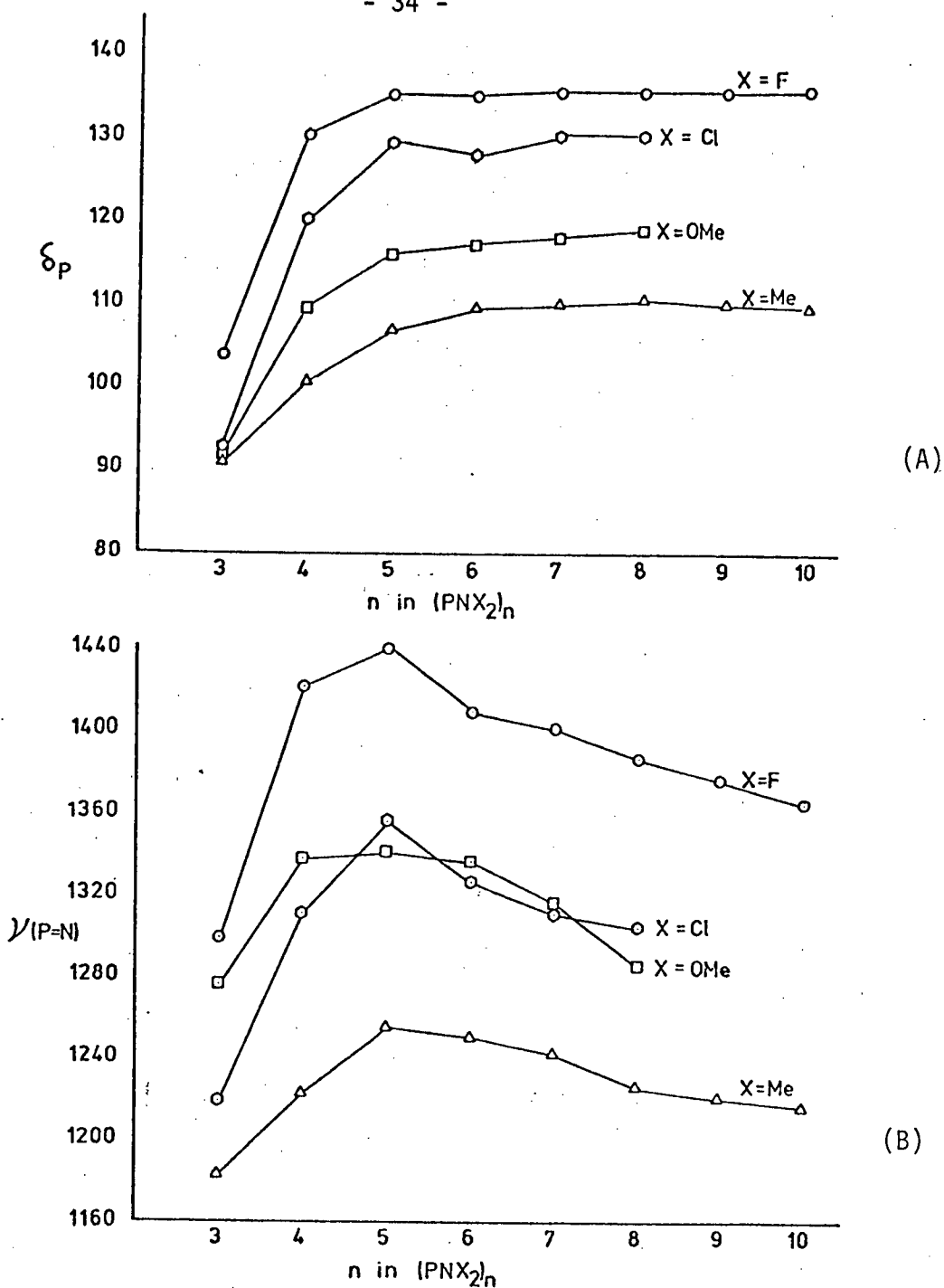
Figure 2.1 (A) $^{31}P$ chemical shifts (ppm, relative to ext. $P_4O_6$) and (B) $\nu(P{=}N)$ frequencies ($cm^{-1}$) of phosphazenes $(NPX_2)_n$ ($X{=}F^a$, $Cl^b$, $OMe^c$, Me) as a function of ring size (n).

(a) A.C. Chapman, N.L. Paddock, D.H. Paine, H.T. Searle and D.R. Smith, J. Chem. Soc., 3608(1960). (b) L.G. Lund, N.L. Paddock, J.E. Proctor and H.T. Searle, J. Chem. Soc., 2542 (1960). (c) R.A. Shaw, Chem. and Ind., 54 (1959); G. Allen, D.J. Oldfield, N.L. Paddock, F. Rallo, J. Serreqi and S.M. Todd, Chem. and Ind., 1032 (1965); N.L. Paddock, unpublished results.

## 2.1.4.2  Infrared Spectra of $(NPMe_2)_n$  (n=3-10)

Although the infrared spectra of the methylphosphazenes $(NPMe_2)_{3-10}$ are, broadly speaking, similar, the detailed analysis and correlation of the spectra of different ring sizes is much more difficult than it is, for instance, in the case of halophosphazenes.  The reason for this difficulty lies in the ambiguity in assignment of skeletal vibrations and those due to the $CH_3$ ligands.  Certain features however, are common to all the spectra.

The antisymmetric ring vibration, $\nu(P=N)$, is easily identified by its position and intensity.  The extent of lone pair delocalization from nitrogen into the ring $\pi$-system, and hence the strength of the P=N bond, is reflected in the magnitude of $\nu(P=N)$; as a group, the values of $\nu(P=N)$ for the series $(NPMe_2)_{3-10}$ are lower than for phosphazenes containing more electronegative ligands (Figure 2.1B).  The variation in $\nu(P=N)$ along the series n = 3-10  is not thought to be related directly to bond strength. The same type of variation is observed for the ring stretching frequency of dimethylsiloxanes[131,132].   In both systems, $(X_2P=N)_n$ and $(X_2Si-O)_n$, the primary effect of an increase in n is to decrease the phase difference between the vibrational motion of ring bonds, and hence to lower the value of the asymmetric ring stretching frequency[4,13,133].

The deformational modes of the $CH_3$ groups are also easily discernible, since they occur in a region which is free of possible interference from skeletal vibrations.  $\delta_{as}(CH_3)$ is found for, all ring sizes, in the region of 1410-1430 $cm^{-1}$.  The symmetric deformation, $\delta_{sym}(CH_3)$, is similarly invariant, and is observed between 1290 and 1305 $cm^{-1}$.

### 2.1.4.3 Mass Spectra of $(NPMe_2)_n$ (n=6-10)

Unlike the series of halophosphazenes $(NPCl_2)_{3-8}$[134] and $(NPF_2)_{3-12}$[135], whose mass spectra can be analysed in reasonable detail, the methylphosphazenes $(NPMe_2)_{3-10}$ are less easily studied by mass spectrometry. The near equivalence in mass of an -NP- unit and three $-CH_3$ units, and the possibility of proton abstractions (which create a problem in the distinction between a $-CH_2-$ group and a nitrogen atom) both make the detailed interpretation of the fragmentation patterns of the methylphosphazenes ambiguous. Thus, the classification of fragments into a cyclic and linear species cannot be made with certainty (as it can be for the halophosphazenes), and the assignment of formulae to small (m/e < 200) fragments is speculative.

Nonetheless, some useful information can be obtained, especially from the higher members of the series, since, above the region m/e ∿ 200, the spectra of $(NPMe_2)_{6-10}$ are relatively simple. Only a few fragments are observed, nearly all of which correspond to ions of formulae $[N_xP_xMe_{2x-y}]^+$ (y=0,1). The relative abundances of these fragments, which are shown in schematic form in Figure 2.3, display several interesting features.

As in the case of the fluorophosphazenes[135], the stability of the parent ion increases with increasing ring size, so that, in $(NPMe_2)_{8-10}$, the parent ion is the most abundant species. When it occurs, fragmentation of the parent ion is a very specific process. The stepwise removal of ligands is not observed; instead, ring cleavage predominates. The same effect is seen in the fluorophosphazenes[135], but in the chlorophosphazenes, where the phosphorus-ligand bond is weaker, ligand abstraction is more common[134].
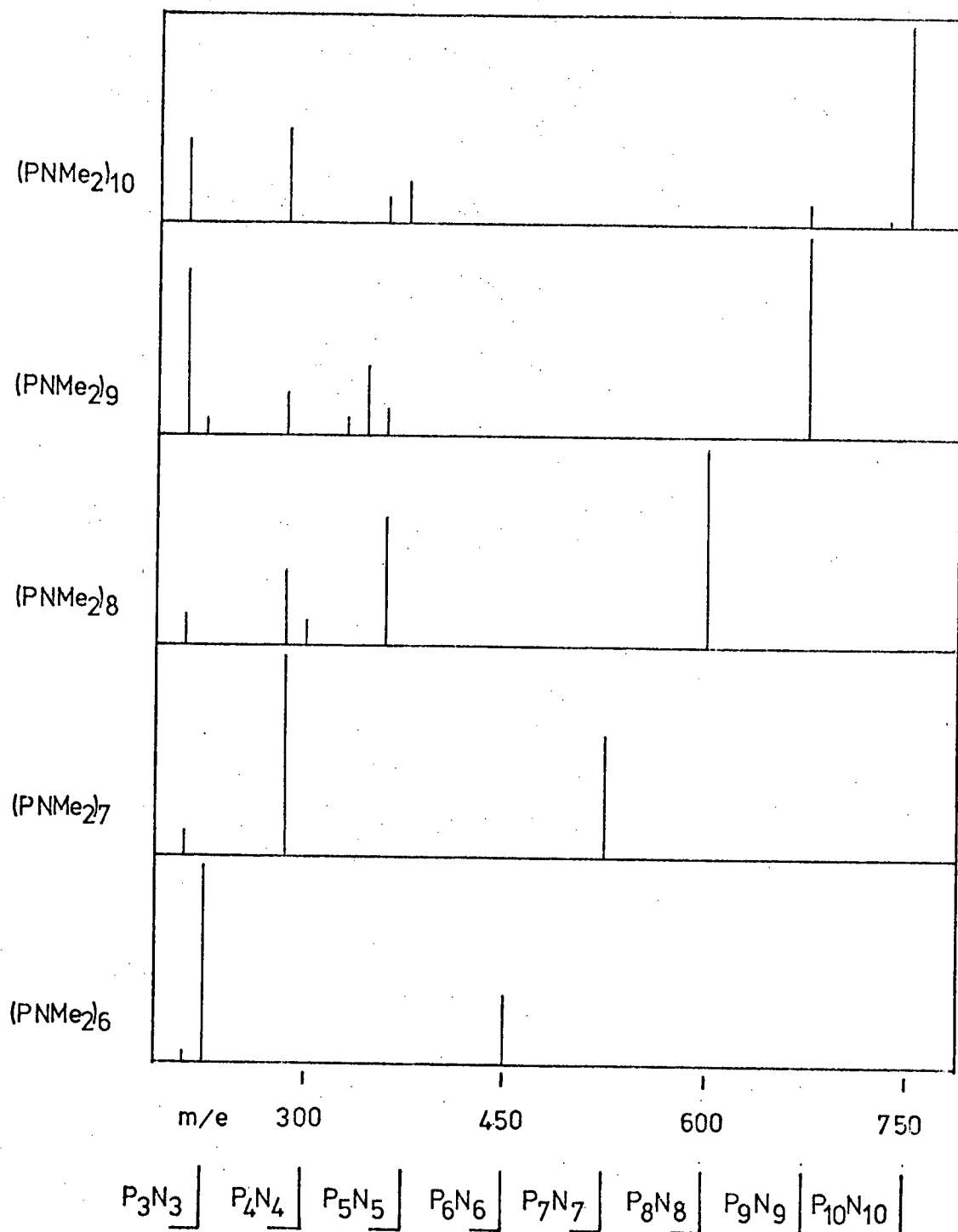
Figure 2.2   The mass spectra of the methylphosphazenes $(NPMe_2)_{6-10}$.   The scales are such that the base peaks of each compound have the same relative intensity.   All fragments with an abundance of less than 5% of the base peak are ignored.

In the fluorophosphazenes, cleavage of the ring occurs in two ways. Abstraction of an $N_3P_3$ unit is the principal reaction path, but, as far as $(NPF_2)_7$, significant quantities of fragments indicating the loss of one and two NP units are still observed. In $(NPMe_2)_{6-10}$, this latter type of degradation is almost non-existent, and the removal of an $N_3P_3$ unit and, to a lesser extent, an $N_4P_4$ unit, from the parent ion is the only route through which fragmentation proceeds; e.g. $N_6P_6Me_{12}$ gives only $N_3P_3$ fragments, $N_7P_7Me_{14}$ gives mainly $N_4P_4$ fragments, and $N_8P_8Me_{16}$ mainly $N_5P_5$ fragments. In the spectrum of $(NPMe_2)_9$, a significantly large quantity of $N_3P_3$ species is observed, suggesting that two $N_3P_3$ units are easily removed from the $N_9P_9$ molecule. As in the case of $(NPF_2)_{10}$, the spectrum of $(NPMe_2)_{10}$ shows little difference in yield between the smaller fragments.

The mass spectra of $(NPMe_2)_{6-10}$ are, therefore, distinguished by the propensity of the phosphazene ring to lose one or more $N_3P_3$ units. The potential importance of transannular interactions as a means to ring cleavage has already been noted for the fluorophosphazenes[135], and their influence in the present system is likely to be augmented by the increased basicity of the nitrogen atoms, which would favour such transition states as I.



I
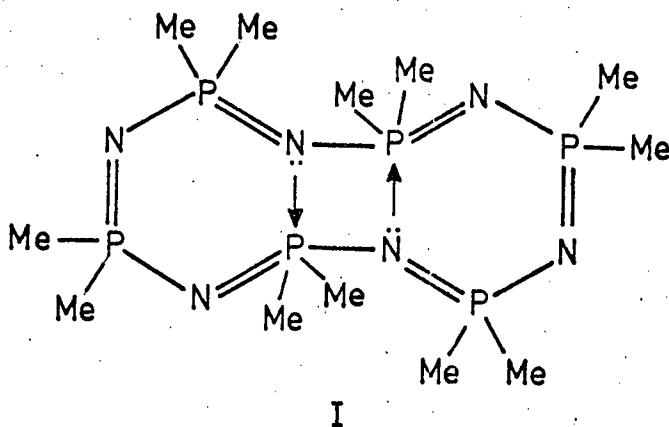
2.1.5 <u>Structure and Spectra of Methylphosphazenium Quaternary Salts</u>

The details of the n.m.r. and infrared spectra of the methylphos-
phazenium quaternary salts prepared in this work are given in Tables 2.2
and 2.3. Both the $^{31}$P and the $^1$H n.m.r. spectra of the methiodides
$(NPMe_2)_n$.MeI (n=3-7) reflect the effects of the perturbation of the cyclic
charge distribution by the quaternization of a ring nitrogen atom, and
allow the classification of the various phosphorus atoms and P-methyl
protons according to their location with respect to this nitrogen. In the
$^{31}$P n.m.r. spectrum of $(NPMe_2)_7$.MeI, for example, the four formally
inequivalent types of phosphorus nuclei are differentiated magnetically,
their chemical shifts indicating their proximity to the positively charged
nitrogen atom. The P-methyl protons are more removed from the asymmetric
charge distribution in the ring, and their magnetic inequivalence is
consequently less marked. Accordingly, as Figure 2.3 shows, the $^1$H n.m.r.

Table 2.2: $^{31}$P n.m.r. parameters[a] of N-methyl methylphosphazenium iodides.

| Compound | $\delta P_A$ | $\delta P_B$ | $\delta P_C$ | $\delta P_D$ |
|---|---|---|---|---|
| $(NPMe_2)_3$.MeI[b] | 64.2 | 76.6 | - | - |
| $(NPMe_2)_4$.MeI[b] | 70.0 | 83.5 | - | - |
| $(NPMe_2)_5$.MeI[b] | 74.1 | 90.4 | 90.4 | - |
| $(NPMe_2)_6$.MeI | 76.4 | 94.5 | 95.7 | - |
| $(NPMe_2)_7$.MeI | 77.0 | 95.8 | 97.2 | 97.8 |
| $(NPMe_2)_4$.2MeI | 65.7 | | | |

(a) Dilute solutions in $D_2O$, $\delta$(ppm) reference external $P_4O_6$. (b) Data from
H.T. Searle, J. Dyson, T.N. Ranganthan and N.L. Paddock, J. Chem. Soc.
Dalton, 203 (1975).

Table 2.3: $^1$H n.m.r. parameters[a], (P=N) and (C-N) stretching frequencies[b] of methylphosphazenium quaternary salts.

| Compound | $\nu$(P=N) cm$^{-1}$ | $\nu$(C-N) cm$^{-1}$ | $\delta$(MeN) | $\delta$(MeP$_A$)[c] | $\delta$(MeP$_B$)[c] | $\delta$(MeP$_C$)[c] |
|---|---|---|---|---|---|---|
| $(NPMe_2)_3 \cdot MeI$[d] | 1196 1242 | 1072 | 3.20 (10.8) | 2.02 (12.8) | 1.64 (13.9)[e] | - |
| $(NPMe_2)_4 \cdot MeI$[d] | 1220 1240 | 1075 | 3.14 (11.2) | 2.05 (13.5) | 1.55 (12.6) | - |
| $(NPMe_2)_5 \cdot MeI$[d] | 1230 1250 | 1071 | 3.05 (11.5) | 2.04 (13.5) | 1.54 (12.4) | 1.43 (11.5) |
| $(NPMe_2)_6 \cdot MeI$ | 1263 | 1075 | 3.08 (11.5) | 2.08 (13.5) | 1.61 (13.5) | 1.51 (12.5) |
| $(NPMe_2)_7 \cdot MeI$ | 1230 1270 | 1040 | 2.99 (11.0) | 2.01 (13.0) | 1.61 (12.5) | 1.51[f] (12.5) |
| $(NPMe_2)_4 \cdot 2MeSO_3F$ | 1275 1330 | 1070 | 2.84 (11.5) | 1.95 (13.7) | - | - |
| $(NPMe_2)_3 \cdot CH_2COOEtI$[‡] | 1200 1240 | g | 4.12[h] (14.5) | 1.81 (13.0) | 1.58[i] (14.5) | - |
| $(NPMe_2)_4 \cdot CH_2COOEtI$[‡] | 1190 1220 | g | 4.08[j] (15.0) | 1.85 (13.5) | 1.51 (13.5) | - |

(a) Dilute solutions in CDCl$_3$, except ‡, in CD$_3$CN. $\delta$(ppm) reference internal TMS. PH coupling constants (in Hertz) in parenthesis. (b) From nujol mull spectra, assignments tentative. (c) Phosphorus atoms in alphabetical order from quaternized nitrogen atom. (d) Data from H.T. Searle, J. Dyson, T.N. Ranganathan and N.L. Paddock; J. Chem. Soc. Dalton, 203 (1975). (e) J(HP$_A$)=1.5Hz. (f) $\delta$(HCP$_C$)=$\delta$(HCP$_D$). (g) Assignment unclear, $\nu$(CO) in trimer = 1740 cm$^{-1}$, and in tetramer = 1737 cm$^{-1}$. (h) For ethyl group, $\delta$(CH$_3$)=1.37 ppm, $\delta$(CH$_2$)=4.22 ppm, J(HH)=7.0Hz. (i) J(HP$_A$)=1.0Hz. (j) For ethyl group, $\delta$(CH$_3$)=1.37 ppm, $\delta$(CH$_2$)=4.22 ppm, J(HH)=7.0Hz.
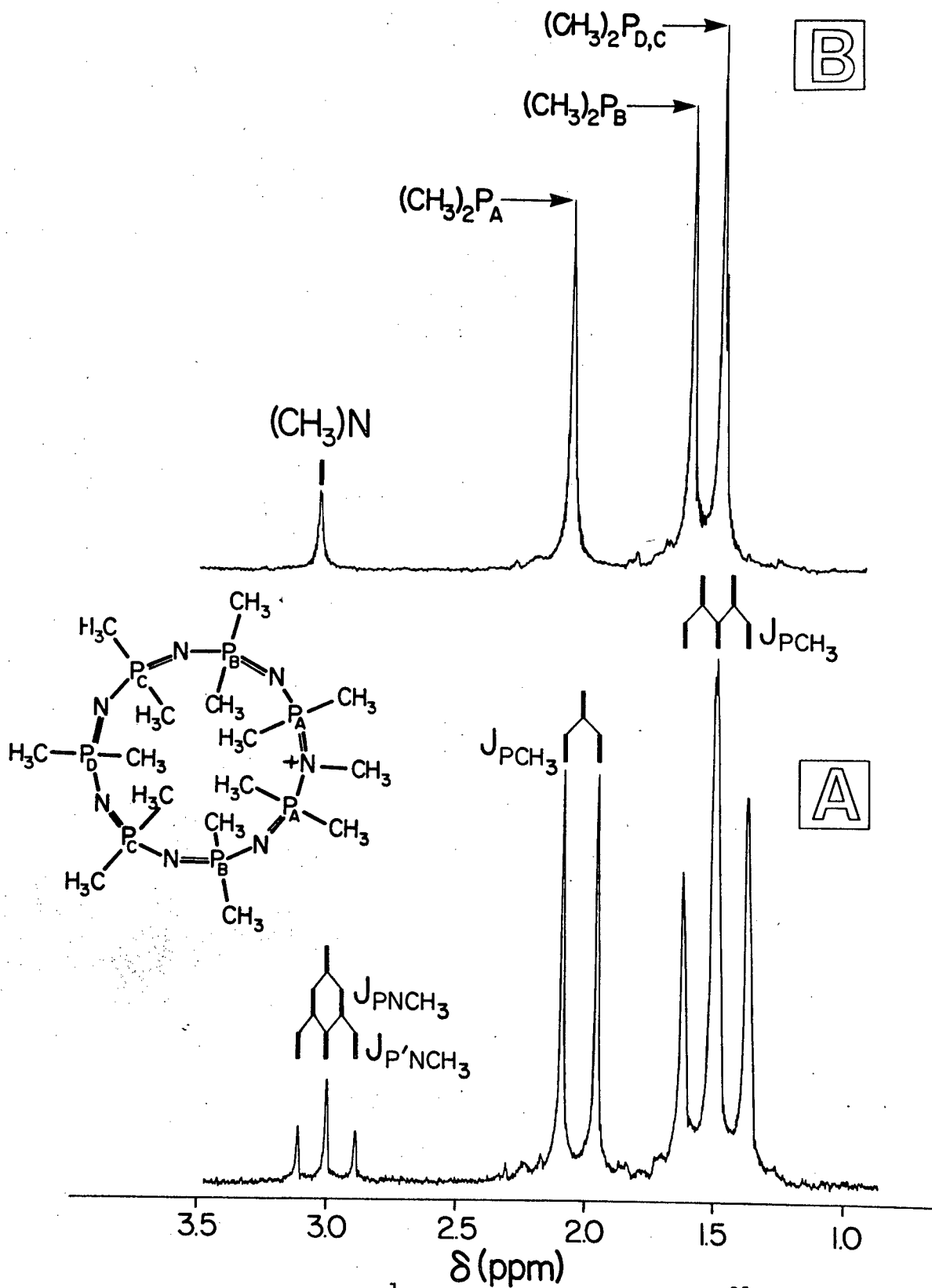
Figure 2.3 Ordinary 100 MHz $^1$H n.m.r. spectrum (A) and $^{31}$P decoupled $^1$H n.m.r. spectrum (B) of $(NPMe_2)_7$.MeI (both on samples in $CDCl_3$ solution).

spectrum of $(NP\overset{\frown}{Me}_2)_7$.MeI does not differentiate between the two types of proton ($P_CMe_2$ and $P_DMe_2$) most remote from the N-methyl group. The single resonances of the $P_AMe_2$ and $P_BMe_2$ protons, however, are easily distinguished, as is the characteristic triplet corresponding to the N-methyl protons.

The $^1$H n.m.r. spectra of the N-ethylacetato salts $[(NPMe_2)_{3,4}CH_2COOEt]^+I^-$ are qualitatively similar to those of the N-methyl salts, the N-methylene resonance being split into a triplet by coupling with the two nearest ring phosphorus atoms. The diquaternary cation $[(NPMe_2)_42Me]^{2+}$ has a centrosymmetric structure, as expected on a simple electrostatic basis. Its $^{31}$P and $^1$H n.m.r. spectra exhibit, therefore, single resonances for both the phosphorus atoms and P-methyl protons.

Apart from the easily identified $\nu$(P=N) vibration, the infrared spectra of the methylphosphazenium salts are largely uninterpretable. In the case of the N-methyl salts, the spectra are characterized by the appearance of a $\nu$(C-N) band at 1040-1075 cm$^{-1}$ (this region is completely clear of absorptions in the neutral compounds). Such a band is less easily assigned in the case of the N-ethylacetato salts, but the $\nu$(C=O) band in them is easily observable near 1740 cm$^{-1}$.

## 2.2 Preparation of gem-Me$_2$Ph$_4$P$_3$N$_3$

To date, three different methods[136-138], all involving ring closure reactions, have been reported for the preparation of $Me_2Ph_4P_3N_3$ (although in two cases[137,138] it was only isolated as its hydrohalide salt $Me_2Ph_4P_3N_3HX$ (X=Cl, I)).

The method used in this work is a modification of that first reported[136], and employs the reaction between dimethyltrichlorophosphorane and the linear phosphazene hydrochloride $[NH_2(Ph_2)PNP(Ph_2)NH_2]^+Cl^-$ (Equation 6). The product is isolated as its hydrochloride, which is
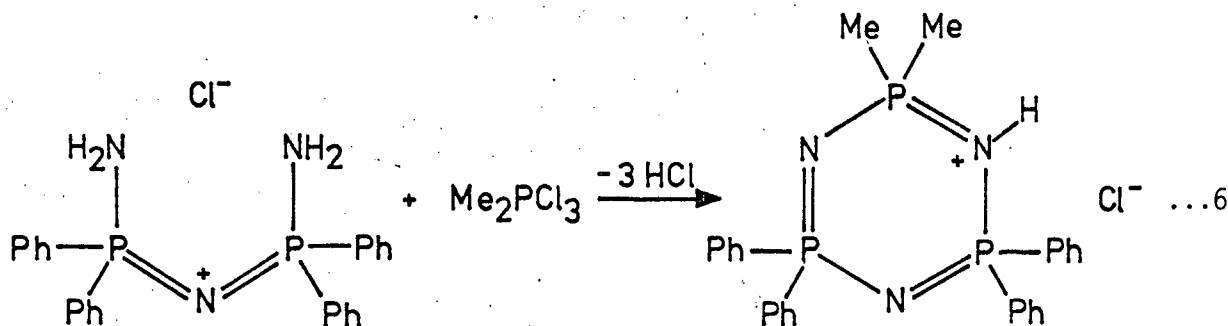


easily converted into the neutral compound by treatment with base (e.g. triethylamine). The reported procedure used benzene as a reaction solvent and the low yield of 4% (calculated in terms of the consumption of $Me_2PCl_3$) can be attributed, in part, to the boiling point of the solvent being insufficiently high to ensure complete reaction. In the present work, a higher boiling point solvent, chlorobenzene, has been used, thereby affording a better (but still not good) yield of ∿20%.

It is apparent from this reaction, and similar ring closure reactions involving $[NH_2(Ph_2)PNP(Ph_2)NH_2]^+Cl^-$ and phosphorus(V) chlorides ($PCl_5$[139,140], $PhPCl_4$ and $Ph_2PCl_3$[140]) that competing reactions play a significant role in lowering the yield of the desired product (usually <35%). The reaction of $[NH_2(Ph_2)PNP(Ph_2)NH_2]^+Cl^-$ and $PCl_5$ in the absence of solvent gives[140] not only the expected product $Cl_3Ph_3P_3N_3$ (in 25% yield) but also the tetrameric derivative $Cl_4Ph_4P_4N_4$ (in 6% yield). Similarly, when the ring closure is attempted using $Ph_2PCl_3$, 24% of the tetrameric phosphazene $(NPPh_2)_4$ is

formed along with the expected trimer $(NPPh_2)_3$[140]. Consistently, it has been found in the present work that the reaction of $Me_2PCl_3$ and $[NH_2(Ph_2)PNP(Ph_2)NH_2]^+Cl^-$ gives significant quantities of $(NPPh_2)_4$ and $(NPMe_2)_4$ as well as the desired product $N_3P_3Ph_4Me_2$.

Although the formation of these anomalous products has been previously recognised[140], its explanation has remained in doubt. The isolation of $(NPMe_2)_4$ from the reaction of $[NH_2P(Ph_2)NP(Ph_2)NH_2]^+Cl$ and $Me_2PCl_3$ does, however, provide a useful insight into the reaction mechanism. It is postulated that the chlorophosphorane $R_2PCl_3$ can act as a chlorinating agent (Equation 7), producing the linear phosphorane

$$[NH_2-(Ph_2)P=N=P(Ph_2)NH_2]^+Cl^- + R_2PCl_3 \rightarrow NH_2-(Ph_2)P=N-P(Ph_2)Cl_2$$
$$+ [R_2P(NH_2)Cl]^+Cl^-$$

$$Ph_8P_4N_4 \quad Ph_4R_2P_3N_3 \quad Ph_4R_4P_4N_4 \quad R_8P_4N_4 \quad \quad \dots 7$$
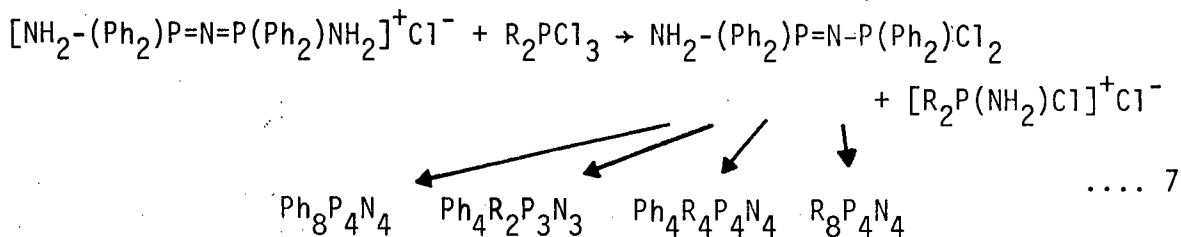
$NH_2P(PH_2)NP(Ph_2)Cl_2$ and the amino salt $[R_2P(NH_2)Cl]^+Cl^-$ [‡]. Cyclization can then occur in a number of ways, producing the observed range of cyclic products.

## 2.2.1 Preparation of $Me_2Ph_4P_3N_3.MeI$

Phenylphosphazenes are much weaker bases than are methylphosphazenes, and do not, for example, react with methyl iodide to give N-methyl quaternary

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[‡] Such a reaction is reminiscent of the preparation of $[R_2P(NH_2)]^+Cl$ from chloramine and $R_2PNH_2$[110,141].

salts(although $(NPPh_2)_3$ can be quaternized by $Me_3OBF_4$[72]). Dimethyltetra-phenylcyclotriphosphazene provides a compromise between the two extremes and can be quaternized by methyl iodide to give the salt $Me_2Ph_4P_3N_3.MeI$. The presence of three distinct phosphorus environments in the $^{31}P$ n.m.r. spectrum of this salt (see Section 2.5.3 of this chapter for details) confirms that, as expected, quaternization takes places on the nitrogen atom adjacent to the $PMe_2$ group (Equation 8).
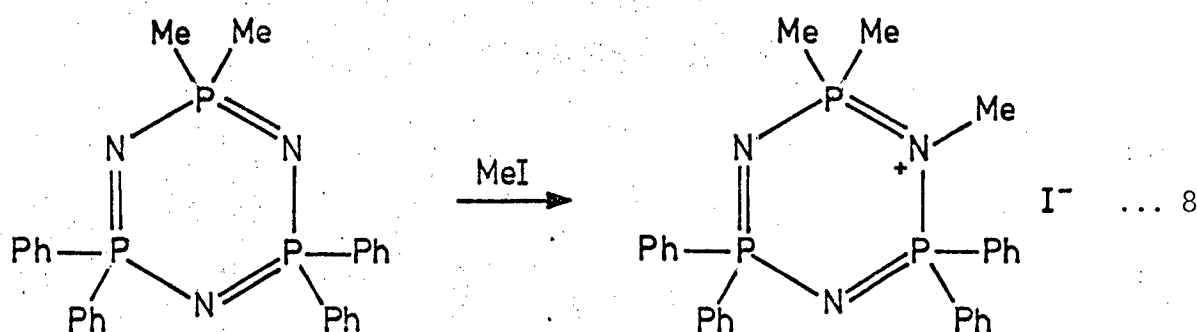


## 2.3   Preparation and Chemistry of Tetramethylphosphinimine

## 2.3.1   Reaction of Trimethylphosphine and Methyl Azide

The classical preparative route to phosphinimines is via the reaction of a tertiary phosphine and an organic azide[142]. Accordingly, the preparation of $Me_3PNMe$ by this method has recently been reported[143] (Equation 9). However, during the present work, the same reaction has been

$$Me_3P + MeN_3 \longrightarrow Me_3P=NMe + N_2\uparrow \qquad \text{.... 9}$$
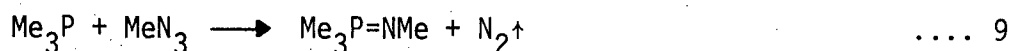
studied independently, and slightly different results were obtained. In the procedure outlined in the literature[143], the reactants were mixed, in the

absence of solvent, at -78°C, producing a 70% yield of $Me_3PNMe$. In this work, the reaction was carried out in pentane solution at 0°C, thereby affording not only the desired product, but also, as a side product, the salt-like compound $[Me_3P=N=PMe_3]^+N_3^-$. The isolation of this latter compound is unexpected, but not without precedent. Similar bis(trialkylphosphine)iminium salts have been isolated during the methanolysis of trialkylphosphinimines[144] and the pyrolysis of aminophosphonium salts[145] (Equations 10 and 11).

$$R_3PNH \xrightarrow{\text{MeOH}} [R_3P=N=PR_3]^+OCH_3^- \qquad \dots \ 10$$

$$[R_3PNH_2]\ Cl^- \xrightarrow{\Delta} [R_3P=N=PR_3]^+Cl^- \qquad \dots \ 11$$
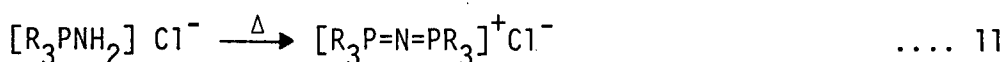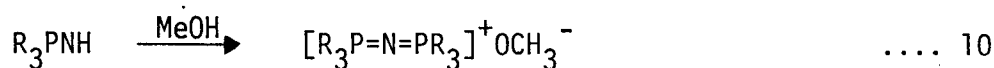
## 2.3.2  Preparation of $[Me_3PNMe_2]^+I^-$

Consistently with its basic character, $Me_3PNMe$ reacts rapidly with methyl iodide to give the expected N-methyl salt $[Me_3PNMe_2]^+I^-$. The isolation of such a compound, via the reaction of methyl iodide and dimethylamino-dimethylphosphine, has already been described[146]. However, its reported melting point of 315-320°C is much higher than that found in the present work (d > 220°C), and its true nature is therefore believed to be uncertain. In the present case, the $^1H$ n.m.r., infrared and mass spectra of the product are all consistent with the proposed structure.

## 2.3.3  Preparation and Deprotonation of $[Me_3PNHMe]^+Cl^-$

The second most common method for the preparation of phosphinimines involves the deprotonation of an aminophosphonium salt (Equation 12), which

$$R_3PCl_2 \xrightarrow{R'NH_2} [R_3PNHR']^+Cl^- \xrightarrow{-HX} R_3P=NR' \qquad \text{.... 12}$$
$$R_3P \xrightarrow{R'NHCl}$$
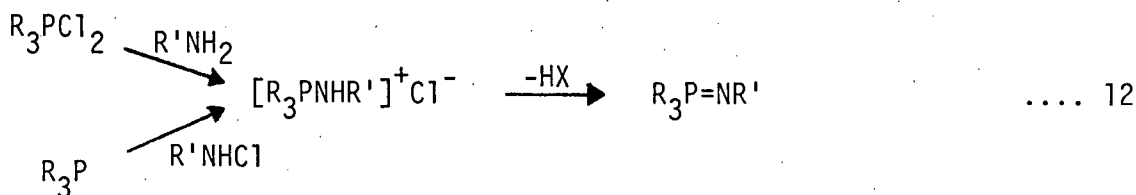
can be prepared by the action of a primary amine on a dihalophosphorane[147] or of a chloramine on a tertiary phosphine[148]. The type of base required for the second step depends (as in the preparation of phosphorus ylids) on the acidity of the phosphonium salt, and varies from triethylamine[147] to sodium amide[149] and sodium[150] in liquid ammonia. In the present work, the aminophosphonium salt $[Me_3PNHMe]^+Cl^-$ was prepared by the reaction of methylamine and $Me_3PCl_2$, and its subsequent deprotonation attempted with (1) sodium amide in liquid ammonia, and (2) potassium t-butoxide (Equation 13). The reaction between $[Me_3PNHMe]^+Cl^-$ and $NaNH_2$ yielded not the expected

$$Me_3PCl_2 \xrightarrow{NH_2Me} [Me_3PNHMe]^+Cl^- \begin{array}{c} \xrightarrow[NH_3(\ell)]{NaNH_2} [Me_3P=N=PMe_3]^+Cl^- \\ \\ \xrightarrow[\phantom{x}]{KOtBu} Me_3PNMe \end{array} \qquad \text{.... 13}$$
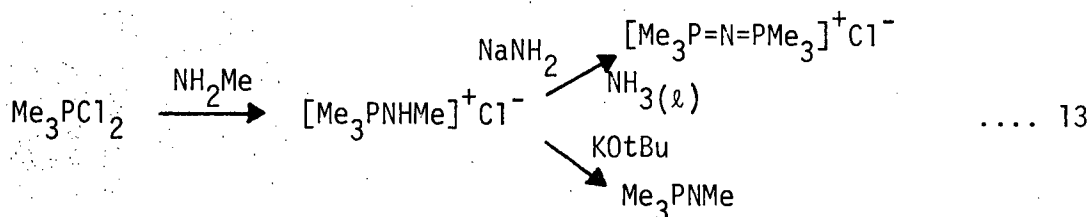
product, but the linear salt $[Me_3P=N=PMe_3]^+Cl^-$. The isolation of the $[\ P=N=P\ ]^+$ cation from this reaction is not easily rationalized. This type of behaviour is not encountered in the reaction of sodium amide with aminotriarylphosphonium salts, but its occurrence is reminiscent of the difficulties alluded to in other work on the preparation of trialkylphosphinimines[144,150]. The reaction of potassium t-butoxide and $[Me_3PNHMe]^+Cl^-$ was more successful, and a good yield of $Me_3PNMe$ was obtained. However, repeated fractional distillation was required to purify the product from the side-product, t-butanol.

## 2.3.4  Reaction of Dihalophosphoranes with $(Me_3Si)_2NMe$

The reaction between fluorophosphoranes $RPF_4$ $(R=Me^{151}, Ph^{161},$ $F^{151,152})$ and heptamethyldisilazane, to give dimeric phosphazanes (Equation 14), is well known.  In this work, the reactions of the

$$RPF_4 + (Me_3Si)_2NMe \longrightarrow \frac{1}{2}(RF_2PNMe)_2 + 2Me_3SiF \qquad \dots\ 14$$
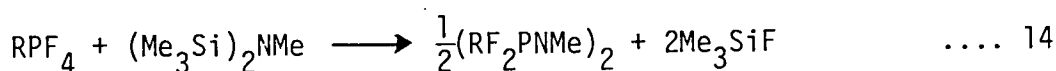
dihalophosphoranes $Me_3PCl_2$ and $Me_3PF_2$ with $(Me_3Si)_2NMe$ have been investigated to see if the phosphinimine $Me_3PNMe$ could be produced. However, in the case of $Me_3PF_2$, it was found that no reaction took place. At first sight, this result is somewhat surprising, but it is consistent with the observed low reactivity of $Me_2PF_3{}^{151}$, $Ph_2PF_3{}^{151}$ and $PF_3{}^{153}$ towards N-alkyl hexamethyldisilazanes.  To account for this, it has been suggested that the reactivity of phosphorus fluorides towards silazanes depends on their Lewis acidity[151].

In the case of $Me_3PCl_2$, a reaction did occur, but the expected product was not isolated.  Instead, the linear salt $[Me_3P=N(Me)-PMe_3]^{2+}2Cl^-$ was formed, according to Equation 15.  This behaviour parallels that of

$$2Me_3PCl_2 + (Me_3Si)_2NMe \longrightarrow [(Me_3P)_2NMe]^{2+}2Cl^- + 2Me_3SiCl \qquad \dots\ 15$$
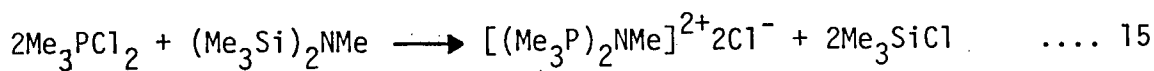
phosphorus trichloride, which, with both $MeNH_2$ and $MeN(SiMe_3)_2$, gives not the cyclic molecule $(MeNPCl)_2{}^{153}$, but the linear species $(Cl_2P)_2NMe^{154}$.

## 2.3.5  Structure and Spectra of Phosphinimine Derivatives

Although there exists a formal structural resemblance between the phosphinimine $Me_3PNMe$ and the methylphosphazenes $(NPMe_2)_n$, the chemical

behaviour of the two types of compound reflect subtle differences in their bonding. Tetramethylphosphinimine is a very strong base, much stronger than are the methylphosphazenes, and is, for example, capable of decomposing chloroform (presumably by proton removal). Consistently, its hydrochloride $[MePNHMe]^+Cl^-$ is a much weaker acid than are the hydrochlorides of methylphosphazenes; whereas $(NPMe_2)_3.HCl$ can be deprotonated with triethylamine, $[Me_3PNHMe]^+Cl^-$ requires potassium t-butoxide. The highly polar nature of the PN bond in $Me_3PNMe$ is also indicated by its rapid hydrolysis in moist air. By contrast, methylphosphazenes are stable in hot aqueous alkali.

The $^1H$ n.m.r. parameters (Table 2.4) of the phosphinimine derivatives described in this section also provide useful information for the comparison of the bonding in phosphinimine and phosphazene derivatives. For example, the resonance of the P-methyl protons of $Me_3PNMe$ is found to high field

Table 2.4: $^1H$ n.m.r. parameters[a] of $Me_3PNMe$ and its derivatives

| Compound | Solvent | $\delta_H$(MeP) | $\delta_H$(MeN) |
|---|---|---|---|
| $Me_3PNMe$ | $C_6D_6$ | 0.98(12.5) | 3.01(27.5)[b] |
| $Me_3PNMe.HCl$ | $CDCl_3$ | 2.11(14.0) | 2.69(14.5)[c] |
| $Me_3PNMe.MeI$ | $CDCl_3$ | 2.23(13.3) | 2.73(10.6)[b] |
| $[(Me_3P)_2NMe]^{2+}2Cl^-$ | $D_2O^\ddagger$ | 2.36(13.0) | 3.24(10.0) |
| $[(Me_3P)_2N]^+Cl^-$ | $CDCl_3$ | 1.93(13.1) | - |
| $[(Me_3P)_2N]^+N_3^-$ | $CD_3CN$ | 1.70(13.7) | - |

(a) Dilute solutions. $\delta$(ppm) reference internal TMS, except $\ddagger$, reference internal DSS. PH coupling constants (in Hertz) in parenthesis. (b) $\delta$(CH$_3$N) in Ph$_3$PNMe=3.01 ppm (24.7Hz), $\delta$(CH$_3$N) in Ph$_3$PNMe.HBr=2.78 ppm (13.8Hz), F. Kaplan, G. Singh and H. Zimmer, J. Phys. Chem., 67, 2509 (1963). (c) J(H-H)=5.8Hz.

of the equivalent signal in $(NPMe_2)_3$ ($\delta$=1.46 ppm, Table 2.1). However, upon quaternization of the two molecules, the order of these chemical shifts is reversed; $\delta(CH_3P)$ in $[Me_3PNMe_2]^+I^-$ is 2.23 ppm, and in $(NPMe_2).MeI$ it is 2.02 ppm (see Table 2.3). Consistent with this order, the N-methyl protons in $[Me_3PNMe_2]^+I^-$ ($\delta$=2.73 ppm) are more effectively shielded than they are in $(NPMe_2)_3.MeI$ ($\delta$=3.20 ppm).

The trends in these chemical shifts suggest that, in the phosphinimine salt $[Me_3PNMe_2]^+I^-$, the positive charge of the cation is located almost completely on phosphorus (Equation 16), with little or no double bond character associated with the PN bond. Consistently, no $\nu(P=N)$ is observed in the infrared spectrum of $[Me_3PNMe_2]^+I^-$. By contrast, the $^1H$ chemical shifts of the $[(NPMe_2)_3.Me]^+$ cation indicate that (in agreement with calculated $\pi$-charge densities[76]) much of the positive charge of the ion is localized on the quaternized nitrogen atom (Equation 17), thereby preserving cyclic aromaticity.



... 16



... 17
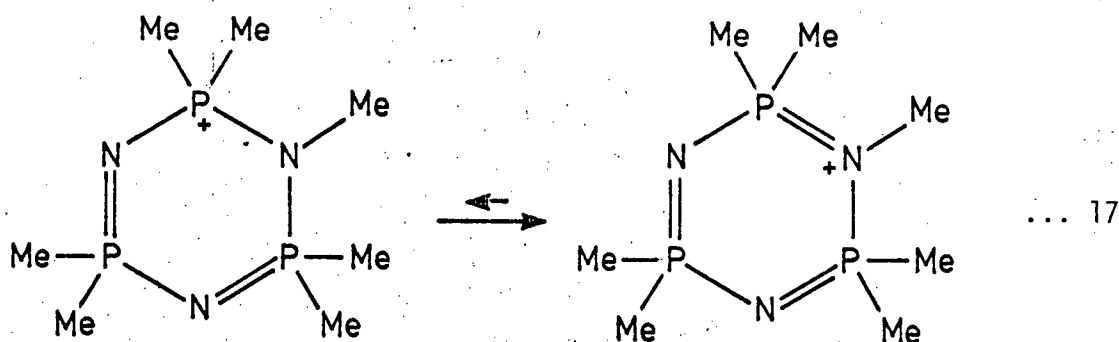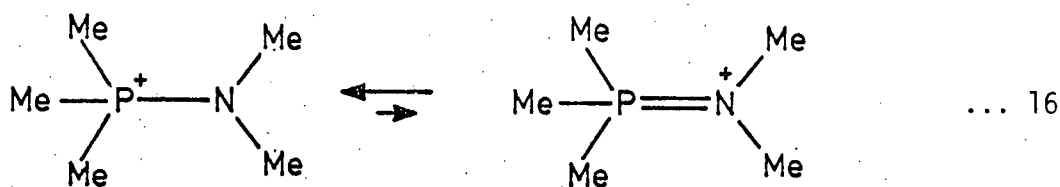
The localization of charge on phosphorus, rather than on nitrogen is again observed in the doubly charged cation $[(Me_3P)_2NMe]^{2+}$, the methyl protons of which resonate at $\delta = 2.36$ ppm. In the cyclic dication $[(NPMe_2)_4 \cdot 2Me]^{2+}$, the analogous signal is observed at $\delta = 1.95$ ppm. Charge delocalization, and the preservation of $\pi$-character for the PN bond, is only possible in the cation $[Me_3P=N=Me_3]^+$; accordingly, the P-methyl protons in $[(Me_3P)_2N]^+Cl^-$ are more shielded ($\delta=1.93$ ppm) than they are in, for instance, $[Me_3PNMe_2]^+I^-$ ($\delta=2.23$ ppm). Consistently, a strong $\nu(P=N)$ band (at 1246 cm$^{-1}$) is observed in the i.r. spectrum of $[(Me_3P)_2N]^+Cl^-$.

As expected, the infrared spectra of the phosphinimine derivatives described here show many similarities. The vibrational spectra of $Me_3PNMe$ itself are described in detail elsewhere[143] (see also Chapter IV). The ionic compounds $[Me_3PNMeR]^+$ (R=H, Me, $PMe_3^+$) and $[(Me_3P)_2N]^+$ all display bands corresponding to $\delta_{sym}CH_3$ (1300-1330 cm$^{-1}$), CH$_3$ rocking (960-980 cm$^{-1}$), CH$_3$ wagging (870-890 cm$^{-1}$) and P-CH$_3$ stretching (720-770 cm$^{-1}$). In addition, the derivatives $[Me_3PNMeR]^+$ (R=H, Me, $PMe_3^+$) all contain a $\nu(C-N)$ band at 1050-1095 cm$^{-1}$.

Summary - The chemical and physical properties of methylphosphinimines and methylphosphazenes indicate a marked difference in the nature of the PN bond in the two systems. The importance of cyclic aromaticity in the latter compounds is clearly evident, the PN bond polarity in them being greatly reduced from that expected from a series of isolated PN units. The presence of a delocalized $\pi$-system within the PN ring of methylphosphazenes has important consequences for the chemistry of the attached ligands. These topics will be fully discussed in the following chapters.

## 2.4  Chemistry of gem-Dichlorotetraphenylcyclotriphosphazene

### 2.4.1  Attempted Methylation of $Cl_2Ph_4P_3N_3$ with MeMgBr

During the course of work on the preparation of $Me_2Ph_4P_3N_3$, the phosphazene $Cl_2Ph_4P_3N_3(II)$ was prepared[139,140] to see if its reaction with MeMgBr, according to Equation 18, would afford a convenient preparative route



II

$$Cl_2Ph_4P_3N_3 + 2MeMgBr \longrightarrow Me_2Ph_4P_3N_3 + 2MgClBr \qquad \dots. 18$$
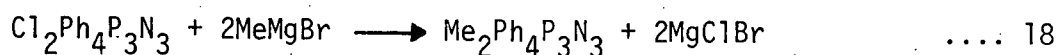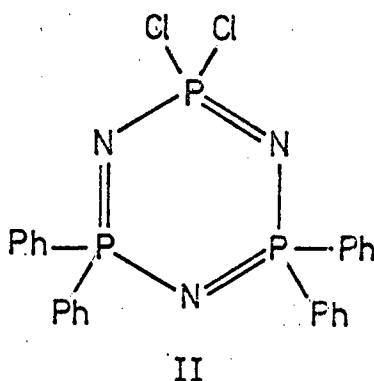
to $Me_2Ph_4P_3N_3$. However, it was found that, unlike $Cl_6P_3N_3$, $Cl_2Ph_4P_3N_3$ does not react at all with MeMgBr. After boiling a solution of $Cl_2Ph_4P_3N_3$ in ether with an excess of MeMgBr for four days, only the starting material was recovered (almost quantitatively). Because of its surprisingly low reactivity towards MeMgBr, a number of other substitution reactions of $Cl_2Ph_4P_3N_3$ were attempted, in order to compare its reactivity with that of $Cl_6P_3N_3$.

### 2.4.2  Dimethylamination of $Cl_2Ph_4P_3N_3$

Consistent with its low reactivity towards MeMgBr, and in contrast to the behaviour of $Cl_6P_3N_3$[155], $Cl_2Ph_4P_3N_3$ reacts only in the presence of an

excess of dimethylamine and/or under extreme conditions (high temperature).

The reaction of $Cl_2Ph_4P_3N_3$ and dimethylamine, in the molar proportion 1:2,

according to Equation 19, has been reported[156] to give a very low yield

($\sim$9%) of $(NMe_2)ClPh_4P_3N_3$. In the present work, the yield has been improved

$$Cl_2Ph_4P_3N_3 + HNMe_2 \longrightarrow (NMe_2)ClPh_4P_3N_3 + HNMe_2.HCl \qquad \dots 19$$
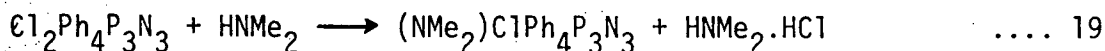
to a nearly quantitative value by bubbling an excess of dimethylamine

through an ethereal solution of $Cl_2Ph_4P_3N_3$ for several hours. Substitution

of the second chlorine, however, cannot be achieved under such mild

conditions, and $(NMe_2)_2Ph_4P_3N_3$ can only be prepared by reacting $Cl_2Ph_4P_3N_3$

with an excess of $HNMe_2$ at 180°C[156].

### 2.4.3 Fluorination of $Cl_2Ph_4P_3N_3$

As was mentioned in the previous chapter, there exist two principal

methods for the preparation of fluorophosphazenes from chlorophosphazenes.

The use of anionic reagents, such as sodium fluoride[30] and potassium

fluorosulphite[31,32], is most useful for the preparation of fully

fluorinated phosphazenes, since the introduction of one fluorine into the

ring activates it to further substitution. Consecutive substitution is,

as expected, predominantly geminal[57,58]. By contrast, the fluorination

of chlorophosphazenes using antimony trifluoride usually takes place

non-geminally[33,157]. Because the effect of $SbF_3$ depends on its

preliminary coordination to a ring nitrogen atom, progressive fluorination

is inhibited by the decreasing donor strength of the phosphazene ring.

By itself, $SbF_3$ is too weak an acceptor to react with $(NPCl_2)_3$[157]. Reaction

occurs when the base strength of the phosphazene is increased by the presence of dimethylamine ligands (e.g. in $(NMe_2)_2Cl_4P_3N_3$[33], $(NMe_2)_3Cl_3P_3N_3$ and $(NMe_2)_4Cl_2P_3N_3$[157]) or when antimony pentachloride is added to the reaction mixture[34,158].

The fluorophenylphosphazene gem-$F_2Ph_4P_3N_3$ has previously been prepared by the phenylation of gem-$F_4Ph_2P_3N_3$ with phenyllithium[159]. In the present work its preparation has been attempted by the fluorination of $Cl_2Ph_4P_3N_3$. As expected from the results of the previous experiments, the use of anionic reagents was ineffectual. Potassium fluorosulphite, in a variety of solvents (boiling heptane, acetonitrile and nitrobenzene) did not react with $Cl_2Ph_4P_3N_3$. Similarly, sodium fluoride, and an (NaF+HF) mixture[158], both failed to fluorinate it. However, the reaction of an $SbF_3/SbCl_5$ mixture with $Cl_2Ph_4P_3N_3$ was more successful, and, in this way, a 27% yield of $F_2Ph_4P_3N_3$ was obtained.

## 2.4.4 Preparation of $(NMe_2)FPh_4P_3N_3$

The comparative ease of fluorination of $Cl_2Ph_4P_3N_3$ with $SbF_3/SbCl_5$ prompted an experiment on the fluorination of the monodimethylamino derivative $(NMe_2)ClPh_4P_3N_3$. Consistent with the activating effect of the amine ligand, it was found that the fluorination of $(NMe_2)ClPh_4P_3N_3$ could be effected using $SbF_3$ alone, without the presence of $SbCl_5$. A high yield of $(NMe_2)FPh_4P_3N_3$ was obtained using this method.

## 2.4.5 Attempted Preparation of a Phosphazenium Cation

The reactions described above indicate an unusually low reactivity of $Cl_2Ph_4P_3N_3$ towards nucleophiles. The cause of this behaviour is thought

to be based upon electronic rather than steric factors, the more electro-
negative chlorine atoms being capable of withdrawing $\pi$-electron density
from the $P(Ph_2)$ phosphorus atoms onto the $P(Cl_2)$ atom.

In the phosphazene $ClPh_5P_3N_3$, the reactivity of the $P(PhCl)$ atom
towards nucleophiles is substantial[160,161]. It is believed that, in this
compound, the PCl bond may be weakened by conjugation of the geminal phenyl
group to phosphorus, in a fashion similar to that postulated to account for
the apparent reactivity of $(NMe_2)ClP_3N_3$[162] (e.g. Equation 20). Consistent
with this, silver perchlorate reacts with $ClPh_5P_3N_3$ in pyridine, yielding
the salt-like compound $Ph_5P_3N_3 \cdot ClO_4 \cdot py$.



$$\ldots 20$$
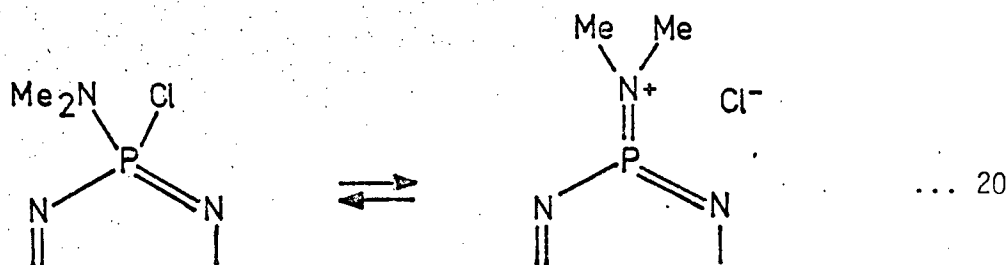
During the present work, an attempt was made to prepare a similar
salt to be the reaction of $BF_3 \cdot Et_2O$ with $(NMe_2)FPh_4P_3N_3$, according to
Equation 21. Unfortunately, the product that was isolated was not the

$$BF_3 \cdot Et_2O + (NMe_2)FPh_4P_3N_3 \longrightarrow [(NMe_2)Ph_4P_3N_3]^+BF_4^- + Et_2O \quad \ldots \ldots 21$$

expected phosphazenium salt(III) but the protonated salt
$[(NMe_2)FPh_4P_3N_3H]^+[BF_3OH]^-$. Although it was not the desired product, this
compound is, nonetheless, informative, since it indicates the relative
effects of dimethylamino and fluorine ligands on the base strengths of the

molecules, i.e., the presence of the electron donating $NMe_2$ group sufficiently offsets the electron withdrawing effect of the fluorine ligand to allow the protonation of the weakly basic ring nitrogen atoms. The $^{31}P$ n.m.r. spectrum of the salt shows that its structure is V rather than IV. Protonation of the $F(NMe_2)Ph_4P_3N_3$ molecule greatly affects the electron distribution in the PN ring. In relation to the neutral molecule ($\delta P(Ph_2)$=94.1 ppm, $\delta PFNMe_2$=95.6 ppm), the $P(Ph_2)$ atoms are considerably deshielded ($\delta$=87.2 ppm), with a consequent transfer of charge onto the $PFNMe_2$ atom ($\delta$=100.6 ppm).

III                         IV                          V
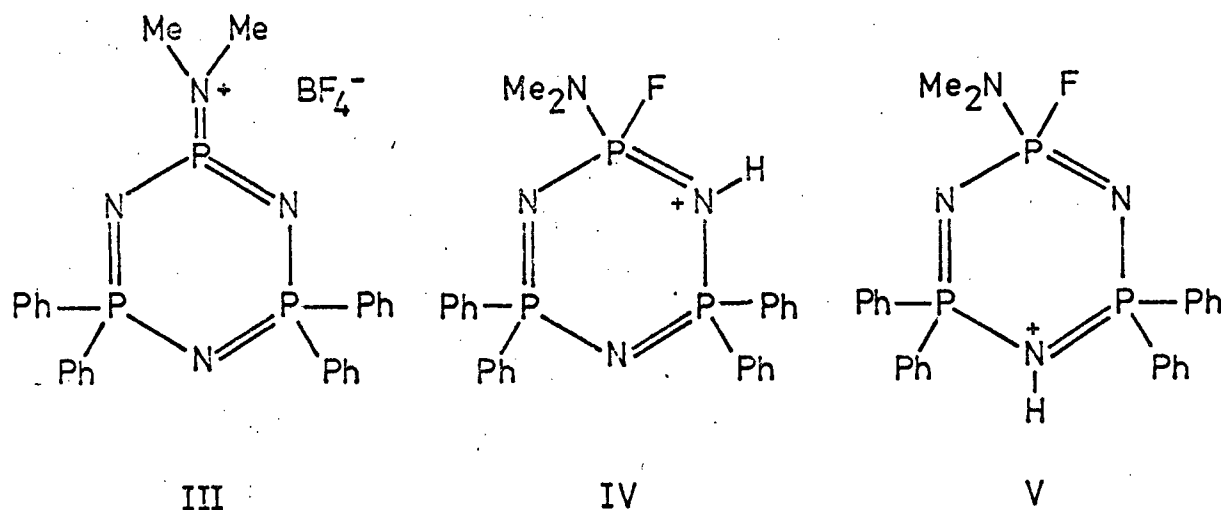
## 2.5 Experimental Section

### 2.5.1 Preparation of Methylphosphazenes

Dimethyltrichlorophosphorane[163] was prepared by the chlorination of tetramethyldiphosphine disulphide[164] in carbon tetrachloride, and dried in vacuo over $P_2O_5$. Methylamine hydrochloride and ammonium chloride were

commercial products, and were oven dried at 120°C for 24 hours before use.

The fluorophosphazenes $(NPF_2)_{6-10}$ were obtained from Prof. N.L. Paddock.

They had been prepared by the fluorination, with $KSO_2F$, of a mixture of

chlorophosphazenes $(NPCl_2)_n$ (n > 5), and separated by v.p.c.[133] Methyl

magnesium bromide was prepared using standard procedures[165] from

commercially obtained magnesium turnings and methyl bromide. Diethyl ether

was dried before use by distillation from lithium aluminium hydride.

## 2.5.1.1 Preparation of $(NPMe_2)_3$

Methylamine hydrochloride (12.0g, 191 mmol) was added to a slurry

of dimethyltrichlorphosphorane (32.0g, 191 mmol) in 125 ml of chlorobenzene,

and the mixture heated to reflux temperature. The evolution of hydrogen

chloride then commenced, and the reactants rapidly fused into a pale yellow

oil which was immiscible with the solvent. After the mixture had been

heated for one hour under reflux, the solvent was distilled off to leave

a viscous oil. (N.B. Prolonged heating under reflux of this mixture

reduces the relative yield of the trimer; it also lowers the overall yield

of methylphosphazenes). The oil was then heated at 165°C/0.05 Torr for

four hours, during which time it gradually solidified into an off-white

mass. This solid was then extracted with 3 x 200 ml of hot acetonitrile.

The extracts were combined and concentrated, whereupon a white, slightly

hygroscopic solid (11.94g) crystallized out. A further 0.84g of the same

solid was obtained by evaporation, under nitrogen, of the mother liquor.

The whole was recrystallized from acetonitrile and identified by

its analysis and [1]H n.m.r. spectrum as the quaternary salt $N_3P_3Me_6$.MeCl;

m.pt. 195-200°C (dec) (yield 12.8g, 46.5 mmol, 73%); [1]H n.m.r. (δ, $CD_3CN$,

internal TMS), 2.94 (3H, triplet, $J_{PH}$=10.5Hz), 1.87 (12H, doublet, $J_{PH}$=13.5Hz), 1.57 (6H, doublet, $J_{PH}$=14.5Hz, long range $J_{PH}$=1.5Hz); i.r. $\nu$(P=N) 1190, 1245 cm$^{-1}$. Anal. calcd. for $C_7H_{21}ClN_3P_3$: C, 30.50; H, 7.68; Cl, 12.86; N, 15.24. Found: C, 30.94; H, 7.75; Cl, 13.00; N, 14.84.

Slow pyrolysis of $N_3P_3Me_6$·MeCl at 200°C/0.1 Torr decomposed the salt, and $N_3P_3Me_6$ was collected, in nearly quantitative yield, by sublimation onto a water-cooled cold-finger. The compound was identified by its infrared spectrum[21], analysis and melting point. Anal. calcd. for $C_6H_{18}N_3P_3$: C, 31.98; H, 8.06; N, 18.66. Found: C, 32.13; H, 7.99; N, 18.80. M.pt. 187-188°C, lit. 195-196°C[21] and 187-190°C (dec)[77].

The insoluble residue from the acetonitrile extraction (2.76g) was recrystallized from hot methanol/chloroform and dried in vacuo. This slightly hygroscopic solid was identified by its analysis and $^1$H n.m.r. spectrum as the diquaternary salt $N_4P_4Me_8$·2MeCl (6.9 mmol, 15%), m.pt. >275°C. $^1$H n.m.r. ($\delta$, $D_2O$, internal DSS), 2.93 (6H, triplet, $J_{PH}$=11.5Hz), 2.03 (24H, doublet, $J_{PH}$=13.5Hz); i.r. $\nu$(P=N) 1350 cm$^{-1}$. Anal. calcd. for $C_{10}H_{30}Cl_2N_4P_4$: C, 29.94; H, 7.54; Cl, 17.67; N, 13.97. Found: C, 29.68; H, 7.70; Cl, 18.00, N, 13.79.

## 2.5.1.2 Preparation of (NPMe$_2$)$_4$

Ammonium chloride (8.8g, 164 mmol) was added to a slurry of dimethyltrichlorphosphorane (27.5g, 164 mmol) in 100ml of chlorobenzene, and the mixture subjected to the same heating cycle as described above (Section 2.5.1.2). The powdery solid so obtained yielded, after extraction

with acetonitrile, 11.2g of an insoluble solid, which was identified by its infrared spectrum[77,109] as the dihydrochloride $(NPMe_2)_4 \cdot 2HCl$. This salt was converted quantitatively into the neutral compound by treating it with an excess of triethylamine in chloroform. Evaporation of the solvent and extraction of the crystalline residue with hot hexane afforded, upon removal of the solvent, the neutral $(NPMe_2)_4$, which was identified by its infrared spectrum[21] and melting point, 161-162°C (lit. 162-163°C[21], 155-156°C[77] and 157-158°C[110]). Evaporation of the acetonitrile extract yielded a yellow oil which, upon treatment with $NEt_3$ and extraction with hexane, yielded a small quantity (∼100mg) of $(NPMe_2)_3$, which was identified by its infrared spectrum and melting point (see Section 2.5.1.1).

### 2.5.1.3  Separation of $(NPMe_2)_3$ and $(NPMe_2)_4$

This experiment demonstrates how a mixture of $(NPMe_2)_3$ and $(NPMe_2)_4$ can be separated via their hydrochlorides[109]. A mixture of $(NPMe_2)_3$ (1.34g, 5.94 mmol) and $(NPMe_2)_4$ (1.41g, 4.71 mmol) was dissolved in 200 ml of diethyl ether. Hydrogen chloride was bubbled through the solution until precipitation of the methylphosphazene hydrochlorides was complete. The resulting white precipitate was filtered off and dried in vacuo (3.36g). This solid was shaken with 100 ml of hot acetonitrile and the mixture filtered. The insoluble $N_4P_4Me_8 \cdot 2HCl$ (1.78g, quantitative) was identified by its infrared spectrum[77,109]. Anal. calcd. for $C_8H_{26}Cl_2N_4P_4$:  C, 25.75; H, 7.02, Cl, 19.00; N, 15.02. Found:  C, 25.61; H, 6.78; Cl, 18.90; N, 15.05. M.pt. > 260°C. Evaporation of the acetonitrile extract gave $N_3P_3Me_6 \cdot HCl$ (1.51g, 97%), m.pt. 247-249°C, i.r. $\nu(P=N)$ 1170, 1230 $cm^{-1}$. Anal. calcd. for $C_6H_{19}ClN_3P_3$:  C, 27.53; H, 7.32; Cl, 13.55; N, 16.07.

Found: C, 37.30; H, 7.39; Cl, 13.27; N, 16.20. The neutral methyl-phosphazenes can be regenerated from their hydrochlorides by treatment with triethylamine[21,76].

### 2.5.1.4 Preparation of $(NPMe_2)_n$ (n=6-10)

The experimental procedure for the preparation of the methylphosphazenes $(NPMe_2)_{6-10}$ is identical. Therefore, only the preparation of one of them (the hexamer) will be described in detail. A solution of $(NPF_2)_6$ (6.77g, 13.6 mmol) in 50 ml of diethyl ether was added, under an atmosphere of nitrogen, to a stirred solution of MeMgBr (from 5.61g, 231 mmol, of magnesium) in 250 ml of ether. No immediate reaction occurred, but, after an induction period of approximately two hours, precipitation of magnesium fluoride slowly commenced. To ensure the completion of the reaction, the mixture was left at reflux temperature, under nitrogen, for a 48 hour period. The solvent was then distilled from the reaction vessel, and the reaction mixture dissolved (carefully!) in 200 ml of water. 300 ml of a 1 molar solution of sodium carbonate was then added to precipitate all the magnesium as its carbonate. The solution was filtered and the solvent evaporated from the filtrate to leave a white solid, which was repeatedly extracted with hot chloroform. The solvent was distilled from the combined chloroform extracts to leave a white crystalline solid (2.52 g). The original water-insoluble precipitate was recombined with the water-soluble residue and the mixture boiled in 300 ml of ∿1M NaOH for one hour. This mixture was then refiltered, the solvent removed from the filtrate, and the residue extracted with hot chloroform, thereby affording a further 1.62g

of material soluble in chloroform. The two fractions of the product (4.14g) were combined and purified by sublimation in vacuo and recrystallization from hot hexane to give colourless blocks of $(NPMe_2)_6$, m.pt. 163-165°C. Anal. calcd. for $C_{12}H_{36}N_6P_6$: C, 32.01, H, 8.06; N, 18.66. Found: C, 32.00; H, 8.06; N, 18.74.

The phosphazenes $(NPMe_2)_{7-10}$ were prepared using a procedure analogous to that just described[‡]. The yields and analytical data obtained from these reactions are given in Table 2.5.

Table 2.5: Yields and analytical data for the reaction
$(NPF_2)_n$ + 2nMeMgBr $\longrightarrow$ $(NPMe_2)_n$ (n=6-10).

| n in $(NPMe_2)_n$ | Yield % | M.pt. °C | Composition[a] | | |
|---|---|---|---|---|---|
| | | | %C | %H | %N |
| 6 | 67 | 163-165 | 32.00 | 8.06 | 18.74 |
| 7 | 40 | 128-130 | 31.90 | 7.90 | 18.80 |
| 8 | 40 | 171-173 | 32.38 | 7.90 | 18.77 |
| 9 | 28 | 123-125 | 32.28 | 8.22 | 18.33 |
| 10 | ∿5 | 100-102 | 31.73 | 8.11 | 18.60 |

(a) Anal. calcd. for $(C_2H_6NP)_n$: C, 32.01; H, 8.06; N, 18.66.

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[‡] The compounds $(NPMe_2)_{8-10}$ were prepared by Mr. K.D. Gallicano.

## 2.5.1.5 Preparation of $Me_2Ph_4P_3N_3$

The acyclic compound $[NH_2(Ph_2)PNP(Ph_2)NH_2]^+Cl^-$ was prepared by the ammonolysis of diphenyltrichlorphosphorane, and purified by recrystallization from acetonitrile[24,139].

Dimethyltrichlorophosphorane (17.14g, 102.3 mmol) and $[NH_2(Ph_2)PNP(Ph_2)NH_2]^+Cl^-$ (46.20g, 102.3 mmol) were heated together, under reflux, in a slurry of 200 ml of chlorobenzene. After one hour, the solvent was removed by distillation, and the residual light brown oil heated at $\sim$165°C/0.1 Torr for a further three hours. On cooling the reaction mixture to room temperature, a glassy off-white solid was obtained. Extraction of this solid with 3 x 300 ml of hot acetonitrile gave 6.26g of a white insoluble solid, the i.r. spectrum of which indicated the presence of the hydrochloride $(NPMe_2)_4$.2HCl. This solid was then heated with $NEt_3$ (as described in section 2.5.1.2) and the product extracted with hot hexane to yield, upon evaporation of the solvent, 2.96g (10.0 mmole, 40%) of $(NPMe_2)_4$, which was identified by its infrared spectrum and melting point (161-162°C). The acetonitrile extracts were concentrated and cooled, whereupon a white crystalline solid precipitated from the solution. This solid was extracted with hot benzene, leaving, as the insoluble part, a white solid whose infrared spectrum showed it to be the hydrochloride $Me_2Ph_4P_3N_3$.HCl[138]. This compound was dissolved in chloroform and the mixture treated with aqueous triethylamine. The organic layer was washed with water, dried over $Na_2SO_4$, and evaporated to leave a white solid, which was purified by recrystallization from ether/hexane to give colourless blocks of $Me_2Ph_4P_3N_3$ (7.2g, 15.2 mmol, 15%), melting point 142-144°C

(lit.[136] 140-142°C).  Anal. calcd. for $C_{26}H_{26}N_3P_3$:  C, 65.96; H, 5.54; N, 8.88.  Found:  C, 65.89; H, 5.66; N, 8.81.

## 2.5.2  Preparation of Methylphosphazenium Quaternary Salts

Methyl iodide and ethyl iodoacetate were obtained from commercial sources, and used without further purification.  Methylfluorosulphate was also a commercial product, but was redistilled, under nitrogen, before use. Acetonitrile was dried by distillation from calcium hydride.  The methylphosphazenes $(NPMe_2)_n$ were all dried by sublimation _in vacuo_ before use.  $Me_2Ph_4P_3N_3$ was oven dried at 100°C for 3 hours.

## 2.5.2.1  Preparation of $(NPMe_2)_6$.MeI

A sample of $(NPMe_2)_6$ (0.366g, 0.813 mmol) was dissolved in 10 ml of methyl iodide and the mixture gently heated under reflux for two hours. Subsequent filtration of the mixture, and recrystallization of the filtered precipitate (0.480g, 0.81 mmol, 100%) from  acetonitrile/toluene yielded colourless, slightly hygroscopic crystals of the adduct $(NPMe_2)_6$.MeI.$(C_6H_5.CH_3)$ (m.pt. 171-173°C).  Heating the powdered crystals at 90°C/0.01 Torr for seven hours freed the product of solvated toluene. Anal. calcd. for $C_{13}H_{39}IN_6P_6$:  C, 26.38; H, 6.64; I, 21.44; N, 14.20. Found:  C, 26.08; H, 6.60; I. 21.20; N, 14.13.  M.pt. 175-178°C.

## 2.5.2.2  Preparation of $(NPMe_2)_7$.MeI

A sample of $(NPMe_2)_7$ (0.215g, 0.409 mmol) was dissolved in 10 ml of methyl iodide and the solution gently refluxed for two hours.  The addition of a large volume (∿250 ml) of diethyl ether to this solution precipitated a

white solid, which was filtered off and recrystallized from a mixture of hot toluene and a few drops of acetonitrile to give air stable crystals of $(NPMe_2)_7 \cdot MeI$ (0.270g, 0.405 mmol, 100%). Anal. calcd. for $C_{15}H_{45}IN_7P_7$: C, 27.00; H, 6.80; I, 19.02; N, 14.69. Found: C, 26.95; H, 6.87; I, 18.91; N, 14.69. M.pt. 153-155°C.

### 2.5.2.3 Preparation of $Me_2Ph_4P_3N_3 \cdot MeI$

A sample of $Me_2Ph_4P_3N_3$ (1.296g, 2.73 mmol) was dissolved in 20 ml of methyl iodide and the mixture heated gently under reflux for 72 hours. The mixture was then filtered and the residue (1.65g, 2.68 mmol, 98%) recrystallized from hot ethanol. The needle-like crystals so obtained contained one mole of solvent per mole of product. Heating the powdered crystals at 60°C/0.01 Torr for seven hours produced an analytically pure sample of $Me_2Ph_4P_3N_3 \cdot MeI$. Anal. calcd. for $C_{27}H_{29}IN_3P_3$: C, 52.70; H, 4.75; I, 20.62; N, 6.83. Found: C, 52.90; H, 5.00; I. 20.40; N, 6.83. M.pt. 226-227°C (dec). $^{31}$P n.m.r. spectrum ($\delta$, $CDCl_3$, external $P_4O_6$); 64.1 (1P, $PMe_2$ atom), 81.0 (1P, $PPh_2$ atom adjacent to N(Me) atom), 93.5 (1P, $PPh_2$ atom remote from N(Me) atom). $^1$H n.m.r. spectrum ($\delta$, $CDCl_3$, internal TMS); 3.07 (3H, triplet, $J_{PH}=11.0Hz$), 2.22 (6H, doublet, $J_{PH}=$ 14.0Hz), 7.0-8.0 (20H, broad unresolved multiplet). i.r. spectrum; $\nu(P=N)$, 1220, 1260 $cm^{-1}$; $\nu(C-N)$, 1070 $cm^{-1}$.

### 2.5.2.4 Preparation of $[(NPMe_2)_3 \cdot CH_2COOEt]^+I^-$

A sample of $(NPMe_2)_3$ (0.633g, 2.81 mmol) was dissolved in 10 ml of ethyl iodoacetate and the mixture stirred, under a nitrogen atmosphere, at

room temperature, for 48 hours. The mixture was then filtered, and the

precipitate recrystallized from acetonitrile/benzene to give colourless

blocks of $[(NPMe_2)_3.CH_2COOEt]^+I^-$ (0.943g, 2.14 mmol, 76%). Anal. calcd.

for $C_{10}H_{25}IN_3O_2P_3$: C, 27.35; H, 5.74; I. 28.90; N, 9.56. Found:

C, 27.63; H, 5.76; I, 28.70; N, 9.64. Dec. >220°C.

## 2.5.2.5 Preparation of $[(NPMe_2)_4.CH_2COOEt]^+I^-$

A sample of $(NPMe_2)_4$ (0.982g, 3.27 mmol) was dissolved in a

solution of 8 ml of $ICH_2COOEt$ and 30 ml of diethyl ether, and the mixture

heated gently under reflux for 96 hours. The white precipitate was then

filtered from the solution and recrystallized from acetonitrile/benzene

to give small, colourless crystals of $[(NPMe_2)_4.CH_2COOEt]^+I^-$ (1.073g, 2.09

mmol, 64%). Anal. calcd. for $C_{12}H_{31}IN_4O_2P_4$: C, 28.14, H, 5.71; I, 24.78;

N, 10.94. Found: C, 28.20; H, 5.80; I, 24.52; N, 10.71. M.pt. 176-178°C.

## 2.5.2.6 Preparation of $[(NPMe_2)_4.2Me]^{2+}$ $2X^-$ $(X=FSO_3, I)$

A solution of $MeSO_3F$ (1.20g, 10.5 mmol) in 10 ml of acetonitrile was

added to a stirred solution of $(NPMe_2)_4$ (1.545g, 5.15 mmol) in 50 ml of

acetonitrile, and the mixture heated under reflux, under an atmosphere

of nitrogen, for two hours. Upon cooling the solution, colourless needles

of $(NPMe_2)_4.2(MeSO_3F)$ appeared. These crystals were removed from the

solution and a further quantity of the product obtained by the addition of

a large volume of ether to the mother liquor. The combined product

(2.703g, 5.12 mmol, 99%) was recrystallized from hot acetonitrile to give

colourless needles of $(NPMe_2)_4.2MeSO_3F$. Anal. calcd. for $C_{10}H_{30}F_2N_4O_6S_2P_4$:

C, 22.73; H, 5.72; N, 10.60. Found: C, 22.90; H, 5.91; N, 10.56. M.pt. 231-233°C. The di-iodide salt $(NPMe_2)_4 \cdot 2MeI$ was prepared, in quantitative yield, by eluting an aqueous solution of $(NPMe_2)_4 \cdot 2MeSO_3F$ through a column packed with Amberlite CG400 anion exchange resin (previously charged with iodide ion). Evaporation of the solvent from the eluant, and recrystallization of the residual solid from acetonitrile, gave colourless blocks of $(NPMe_2)_4 \cdot 2MeI$. Anal. calcd. for $C_{10}H_{30}I_2N_4P_4$: C, 20.56; H, 5.18; I, 43.45; N, 9.59. Found: C, 20.26; H, 5.11; I, 43.29; N, 9.58. M.pt. >250°C.

## 2.5.3 Preparation of Methylphosphinimine Derivatives

Trimethylphosphine was prepared by the methylation of phosphorus trichloride with MeMgBr, using a combination of several literature methods[166-169]. Methyl azide was prepared by the action of dimethylsulphate on sodium azide[170,171], and purified (from $Me_2O$) by trap-to-trap fractionation. Trimethyldichlorophosphorane was prepared by the chlorination of $Me_3PO$[50] with thionyl chloride[172]. Similarly, trimethyldi-fluorophosphorane was prepared by the fluorination of $Me_3PO$ with sulphur tetrafluoride (yield, 73%). $Me_3PF_2$ has not previously been made by this method; it was identified by its infrared spectrum and boiling point (76°C, lit.[173] 76°C). Heptamethyldisilazane was prepared by the reaction of methylamine with chlorotrimethylsilane. Methylamine, sodium amide and methyl iodide were commercial products and used without purification. Potassium t-butoxide was also obtained commercially, but was purified before use by sublimation in vacuo[175].

### 2.5.3.1 Reaction of Me$_3$P and MeN$_3$

A cold solution (0°C) of MeN$_3$ (1.79g, 31.3 mmol) in 10 ml of pentane was slowly added, under an atmosphere of nitrogen, to a stirred solution of trimethylphosphine (2.34g, 30.8 mmol) in 20 ml of pentane at 0°C. Effervescence was immediate, and was accompanied by the formation of a fine white precipitate. When the addition was complete, the mixture was allowed to equilibrate to room temperature, and then stirred overnight under nitrogen. The following day, the mixture was gently heated under reflux, during which time much of the originally formed precipitate redissolved. The mixture was then filtered under nitrogen, and the residue recrystallized from acetonitrile to give air stable crystals of (Me$_3$P)$_2$N$^+$ N$_3^-$ (0.661g, 3.17 mmol). Anal. calcd. for C$_6$H$_{18}$N$_4$P$_2$: C, 34.60; H, 8.72, N, 26.92; P, 29.77. Found: C, 34.42; H, 9.00; N, 22.26[‡]; P, 30.20. M.pt. 211-214°C.

The solvent was distilled from the filtrate to leave a colourless, extremely hygroscopic liquid, which was distilled _in vacuo_ to give Me$_3$PNMe (1.51g, 14.4 mmol). Anal. calcd. for C$_4$H$_{12}$NP: C, 45.68; H, 11.51; N, 13.33. Found: C, 45.38; H, 11.58; N, 13.30. B.pt. 73°C/18 Torr.

### 2.5.3.2 Preparation of [Me$_3$PNMe$_2$]$^+$I$^-$

A solution of methyl iodide (0.296g, 3.08 mmol) in 10 ml of diethyl ether was added, dropwise, under nitrogen, to a stirred solution of Me$_3$PNMe (0.219g, 2.08 mmol) in 5 ml of ether. A white precipitate was

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[‡] No satisfactory nitrogen analysis could be obtained for this compound.

immediately formed. After $\frac{1}{2}$ hour, the solution was filtered and the residue recrystallized from acetonitrile to give air stable crystals of $[Me_3PNMe_2]^+I^-$ (0.512g, 2.06 mmol, 99%). Anal. calcd. for $C_5H_{15}INP$: C, 24.29; H, 6.12; N, 5.67. Found: C, 24.46; H, 6.20; N, 5.44. Dec >220°C.

### 2.5.3.3 Preparation of $[Me_3PNHMe]^+Cl^-$

Methylamine was bubbled through a suspension of $Me_3PCl_2$ (8.46g, 57.6 mmol) in 50 ml of chloroform for $\frac{1}{2}$ hour. The mixture was then heated under reflux for $\frac{1}{2}$ hour to remove the excess methylamine. Filtration of the solution and removal of solvent from the filtrate yielded a white hygroscopic solid, which was recrystallized from acetonitrile/toluene to give $[Me_3PNHMe]^+Cl^-$ (8.06g, 57.0 mmol, 99%). Anal. calcd. for $C_4H_{13}ClNP$: C, 33.91; H, 9.26; Cl, 25.05; N, 9.90. Found: C, 32.67[‡]; H, 9.57; Cl, 25.03; N, 9.80. M.pt. 180-185°C (dec).

### 2.5.3.4 Reaction of $[Me_3PNHMe]^+Cl^-$ with Sodamide in Liquid Ammonia

A sample of $[Me_3PNHMe]^+Cl^-$ (3.43g, 24.2 mmol) was added to a slurry of sodamide (1.01g, 25.9 mmol) in 25 ml of liquid ammonia, and the mixture allowed to react for one hour. The ammonia was then removed and the residual solid extracted with hexane. Evaporation of this extract yielded no product. The reaction residue was then re-extracted with chloroform, and upon slow evaporation, this extract yielded colourless needles of

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[‡] No satisfactory carbon analysis could be obtained for this compound.

$(Me_3P)_2N^+Cl^-$ (1.15g, 5.71 mmol). Anal. calcd. for $C_6H_{18}ClNP_2$: C, 35.72; H, 9.00; Cl, 17.59; N, 6.95. Found: C, 35.37; H, 9.20; Cl, 17.90; N, 6.65. Dec > 210°C.

## 2.5.3.5 Reaction of $[Me_3PNHMe]^+Cl^-$ with Potassium t-Butoxide

A sample of $[Me_3PNHMe]^+Cl$ was added under an atmosphere of nitrogen, to a slurry of KOtBu (3.68g, 32.9 mmol) in 100 ml of hexane, and the mixture heated, under reflux, for 16 hours. The mixture was then filtered and the solvent distilled off to leave a colourless liquid which was then distilled in vacuo. The infrared and $^1H$ n.m.r. spectrum of this product (2.075g) showed it to be $Me_3PNMe$ plus a small quantity (∿20%) of t-BuOH. This crude product was dissolved in 20 ml of heptane and the mixture redistilled. Most of the t-BuOH distilled with the heptane, and the careful fractional distillation in vacuo of the residual liquid yielded, as a final fraction, a small quantity of pure $Me_3PNMe$ (as shown by its boiling point, 73°C/18 Torr, and $^1H$ n.m.r. spectrum).

## 2.5.3.6 Reaction of $Me_3PF_2$ with $(Me_3Si)_2NMe$

Heptamethyldisilazane (2.13g, 12.2 mmol) was sealed in a Carius tube with $Me_3PF_2$ (1.39g, 12.2 mmol) and the resultant mixture heated at 70°C for 48 hours. No visible change had occurred after this time, and the starting materials were recovered by fractional distillation of the reaction mixture.

### 2.5.3.7 Reaction of Me$_3$PCl$_2$ with (Me$_3$Si)$_2$NMe

A solution of (Me$_3$Si)$_2$NMe (5.70g, 32.6 mmol) in 10 ml of chloroform was added to a slurry of Me$_3$PCl$_2$ (4.79g, 32.6 mmol) in 50 ml of chloroform, and the mixture heated under reflux for 24 hours, under an atmosphere of nitrogen. The chloroform insoluble part was filtered from the solution and recrystallized from a methanol/chloroform mixture to give colourless, hygroscopic crystals of [(Me$_3$P)$_2$NMe]$^{2+}$2Cl$^-$ (2.97g, 11.8 mmol, 73%). Anal. calcd. for C$_7$H$_{21}$Cl$_2$NP$_2$: C, 33.32; H, 8.40; Cl, 28.14; N, 5.56. Found: C, 33.18; H, 8.42; Cl, 27.74; N, 5.46. Dec >220°C.

### 2.5.4 Preparation of XYPh$_4$P$_3$N$_3$ Derivatives

Dichlorotetraphenylcyclotriphosphazene was prepared by the reaction of phosphorus pentachloride with [NH$_2$(Ph$_2$)PNP(Ph$_2$)NH$_2$]$^+$Cl$^-$ in benzene[139]. Dimethylamine (lecture bottle), antimony trifluoride and antimony pentachloride were all commercial products and used without further purification. Boron trifluoride etherate, BF$_3$.Et$_2$O, was also obtained commercially, but was distilled, under nitrogen, before use.

### 2.5.4.1 Preparation of (NMe$_2$)ClPh$_4$P$_3$N$_3$

Dimethylamine was bubbled through a solution of Cl$_2$Ph$_4$P$_3$N$_3$ (1.292g, 2.51 mmol) in 150 ml of diethyl ether for four hours. The reaction mixture was then gently heated under reflux to expel the excess dimethylamine. Filtration of the mixture and evaporation of the filtrate yielded a crystalline solid, which was recrystallized from hot hexane and identified by its analysis and melting point (163-165°C, lit.[156] 164-165°C) as (NMe$_2$)ClPh$_4$P$_3$N$_3$ (2.251g, 2.39 mmol, 95%). Anal. calcd. for C$_{26}$H$_{26}$ClN$_4$P$_3$:

C, 59.72; H, 5.01; Cl, 6.78; N, 10.71. Found: C, 59.61; H, 5.07; Cl, 6.58; N, 10.91. $^1$H n.m.r. spectrum ($\delta$, $CDCl_3$, internal TMS); 2.68 (6H, doublet, $J_{PH}$=16.5Hz), 7.0-8.0 (20H, unresolved multiplet).

### 2.5.4.2 Preparation of $F_2Ph_4P_3N_3$

A sample of $Cl_2Ph_4P_3N_3$ (3.024g, 5.79 mmol) was added to a slurry of an excess of $SbF_3$ (~4g) in 25 ml of sym-$C_2H_2Cl_4$ and the mixture brought to reflux temperature under a nitrogen atmosphere. After 1½ hours at this temperature, no visible change was apparent in the reaction mixture. A solution of 2 ml of $SbCl_5$ in 10 ml $C_2H_2Cl_4$ was added to the mixture, producing an immediate exothermic reaction. After 3 hours at the reflux temperature, the mixture was cooled and filtered, the precipitate washed with benzene, and the solvent distilled from the filtrate to leave a dark oil. A few drops of water were added to this oil (to destroy excess antimony halides), and the whole extracted with dichloromethane. This extract was dried over $Na_2SO_4$, and then evaporated to leave a white solid, which was recrystallized from hot octane to give colourless blocks of $F_2Ph_4P_3N_3$ (0.733g, 1.52 mmol, 26%), which was identified by its analysis, melting point (135-136°C, lit.[159] 137-138°C) and infrared spectrum[159]. Anal. calcd. for $C_{24}H_{20}F_2N_3P_3$: C, 59.88; H, 4.19; N, 8.73. Found: C, 59.65; H, 4.28; N, 8.54.

### 2.5.4.3 Preparation of $(NMe_2)FPh_4P_3N_3$

A sample of $(NMe_2)ClPh_4P_3N_3$ (4.31g, 8.26 mmol) was added to a slurry of $SbF_3$ (~4g) in 100 ml of sym - $C_2H_2Cl_4$ and the mixture heated under reflux for 4 hours. The mixture was then cooled and filtered, and the precipitate

washed with a little benzene. The solvent was then distilled from the filtrate to leave a brown paste, which was treated with a few drops of water to destroy the excess of antimony halides. The whole was then extracted with 3 x 50 ml of dichloromethane, and the extract dried over $Na_2SO_4$. Evaporation of the solvent from this extract then yielded a pasty solid, which was recrystallized from hot octane to give colourless flakes of $F(NMe_2)Ph_4P_3N_3$ (2.753g, 5.43 mmol, 67%). Anal. calcd. for $C_{26}H_{26}FN_4P_3$: C, 61.66; H, 5.18; N, 11.06. Found: C, 61.49; H, 5.20; N, 11.10. M.pt. 154-156°C. $^1H$ n.m.r. spectrum ($\delta$, $CDCl_3$, internal TMS); 2.64 (6H, doublet, $J_{PH}$=12.0Hz); 7.0-8.0 (20H, unresolved multiplet).

## 2.5.4.4 Preparation of $[NMe_2)FPh_4P_3N_3.H]^+[BF_3OH]^-$

An excess (1 mmol) of $BF_3.Et_2O$ was added, via a syringe and septum, to a solution of $(Me_2N)FPh_4P_3N_3$ (0.312g, .60 mmol) in 100 ml of diethyl ether. Precipitation slowly commenced after about ½ hour. The mixture was stirred, under nitrogen, for a further 48 hours, and then filtered, to give a white solid, which was recrystallized from chloroform/toluene as the protonated salt $[(Me_2N)FPh_4P_3N_3.H]^+[BF_3OH]^-$ (0.249g, 0.44 mmol). Anal. calcd. for $C_{26}H_{28}F_4N_4OP_3$: C, 52.73; H, 4.76; N, 9.46. Found: C, 52.96; H, 4.80; N, 9.18. M.pt. 184-188°C. $^{31}P$ n.m.r. spectrum ($\delta$, $CDCl_3$, external $P_4O_6$); 87.2 ppm (2P, $P(Ph_2)$ atoms, doublet, $J_{PP}$=15Hz), 100.6 (1P, $P(NMe_2)F$ atom, doublet, $J_{PF}$=935Hz). $^1H$ n.m.r. spectrum ($\delta$, $CDCl_3$, internal TMS); 2.77 (6H, doublet, $J_{PH}$=12.0Hz), 7.0-8.0 (20H, unresolved multiplet).

## CHAPTER III

## REACTIONS OF METHYLPHOSPHAZENES WITH BASES

Although there have been many investigations of the effect of different substituents on the behaviour of cyclic phosphazenes, relatively little work has been directed towards the influence of the phosphazene ring itself on the properties of the substituents. The results reported in this chapter are from a study of the latter type, and are concerned with the reaction of methylphosphazenes(I) with strong bases (e.g. alkyllithiums) to give carbanion derivatives (II) (Equation 1). These in turn can react with a wide variety of electrophiles, yielding novel phosphazenes (III) of synthetic interest.



$$\text{I} \qquad\qquad \text{II} \qquad\qquad \text{III}$$

$$\cdots 1$$
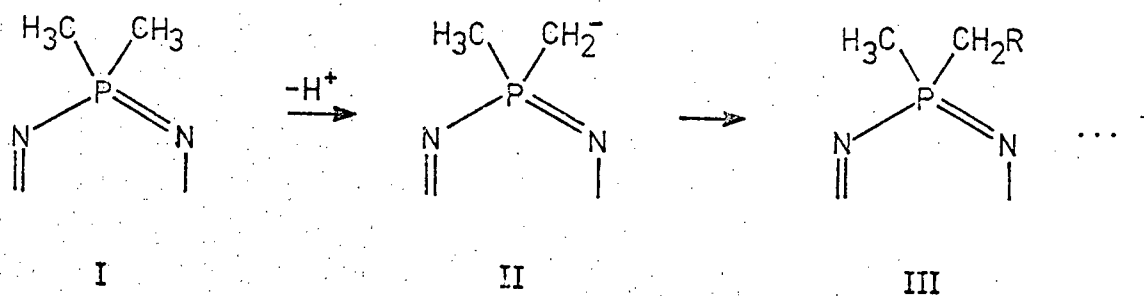
The principal conclusions of this study stem from reactions carried out using two methylphosphazenes, (1) the fully methylated tetrameric phosphazene $(NPMe_2)_4$, and (2) the partially methylated trimeric phosphazene gem-$Me_2Ph_4P_3N_3$. The details of these reactions are given in the following sections.

### 3.1 Preparation and Reactions of $N_4P_4Me_4(CH_2Li)_4$ and $N_4P_4Me_6(CH_2Li)_2$

In diethyl ether solution, methyllithium reacts rapidly and

exothermically with octamethylcyclotetraphosphazene, $N_4P_4Me_8$, to produce the dicarbanion $N_4P_4Me_6(CH_2^-)_2$ and the tetracarbanion $N_4P_4Me_4(CH_2^-)_4$ (equations 2 and 3).

$$2MeLi + N_4P_4Me_8 \longrightarrow N_4P_4Me_6(CH_2Li)_2 + 2CH_4 \qquad \dots 2$$

$$4MeLi + N_4P_4Me_8 \longrightarrow N_4P_4Me_4(CH_2Li)_4 + 4CH_4 \qquad \dots 3$$
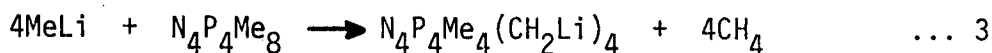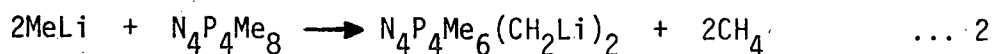
Although these species have not been isolated, their existence, in solution, is confirmed by their reaction with a number of group IV metal chlorides $Me_3MCl$ (M=Si, Ge and Sn) to form di- and tetra-substituted phosphazene derivatives of the type $N_4P_4Me_{8-x}(CH_2MMe_3)_x$ (x=2,4; M=Si, Ge, Sn). They also react with methyl iodide to give the tetraethyltetramethylphosphazene $N_4P_4Me_4Et_4$ and the diethylhexamethylphosphazene $N_4P_4Me_6Et_2$ (isolated as its hydrochloride $N_4P_4Me_6Et_2.2HCl$)[176].

The intermediacy of a mono- and tricarbanion $N_4P_4Me_{8-x}(CH_2Li)_x$ (x=1 and 3) is necessary in the formation of the above mentioned species, but their presence, in ethereal solution, has not been established. Attempts to isolate mono- and tri-substituted derivatives similar to the di- and tetra-substituted phosphazenes already mentioned were unsuccessful. On a simple elestrostatic basis, the introduction of a negative charge onto the phosphazene ring by the primary deprotonation step should retard the removal of a second proton. However, experiments designed to prepare the monocarbanion $N_4P_4Me_7(CH_2^-)$ indicated that the removal of a second proton from the already deprotonated species is favoured over the primary deprotonation of unreacted $N_4P_4Me_8$; i.e. reaction 4b is favoured over reaction 4a.

$$N_4P_4Me_8 + MeLi \begin{cases} N_4P_4Me_7(CH_2Li) + CH_4 & \ldots 4a \\ \frac{1}{2}N_4P_4Me_8 + \frac{1}{2}N_4P_4Me_6(CH_2Li)_2 + CH_4 & \ldots 4b \end{cases}$$
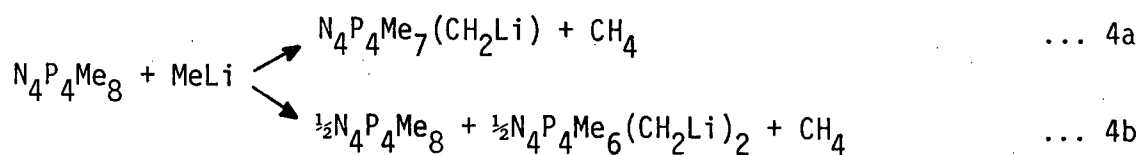
Although these multiply charged carbanions formed from $N_4P_4Me_8$ provide a useful insight into the reactivity of the methylphosphazene ring, their application to the synthesis of novel phosphazenes is somewhat restricted. Their reaction with electrophiles is complicated by the possibility of competing coupling reactions, and a mixture of products is often formed, the successful separation of which depends on the relative solubilities of the different components.

Preliminary attempts to form a monocarbanion from the reaction of $N_3P_3Me_6$ with methyllithium showed that, for this system also, multiple deprotonation is favoured over the removal of a single proton. Attention was therefore focused on the partially substituted methylphosphazene $Me_2Ph_4P_3N_3$, the deprotonation of which leads exclusively to the formation of a monocarbanion.

## 3.2 Preparation and Reactions of $N_3P_3Ph_4Me(CH_2Li)$

Like $N_4P_4Me_8$, gem-dimethyltetraphenylcyclotriphosphazene reacts with methyl- or butyllithium in ethereal solution, resulting in the precipitation of the monocarbanion $N_3P_3Ph_4Me(CH_2Li)$. This intermediate is particularly useful in studying the versatility of phosphazene carbanions in synthesis, since its reaction with electrophiles (Equation 5) leads to a single product.

The chemistry of this carbanion is related to that of phosphine oxide carbanion $Ph_2P(O)CH_2Li$ (see Chapter 1) and the α-picolyl anion

$$R = Br, \ Me_3Sn, \ COOH, \ PhCO$$
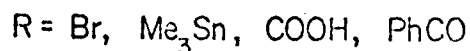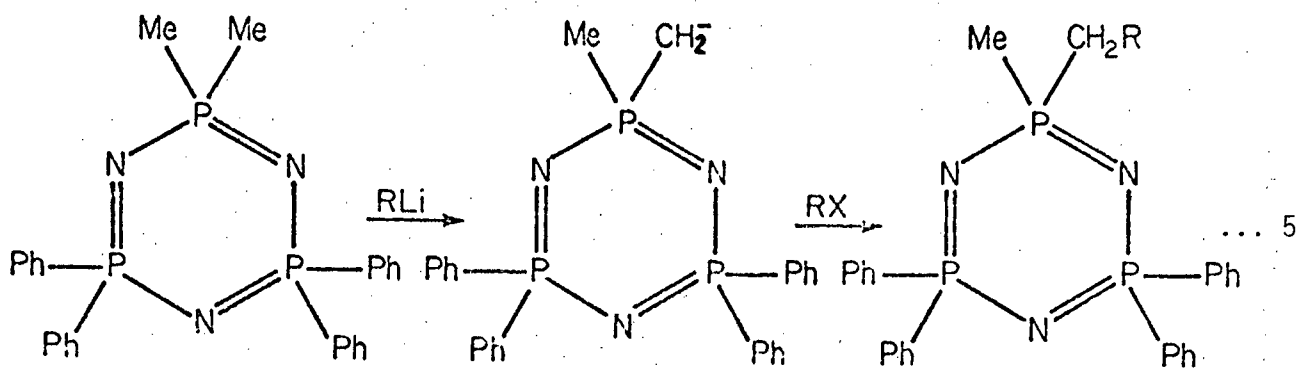
$NC_5H_4(CH_2Li)$. Like the latter two anions[104,177,178], $N_3P_3Ph_4Me(CH_2Li)$ reacts smoothly with carbon dioxide and esters, to give phosphazene derivatives containing carbonyl and carboxyl substituents. Also like phosphine oxide carbanions[106], and the polycarbanions of $N_4P_4Me_8$, $N_3P_3Ph_4Me(CH_2Li)$ reacts with group IV monohalides to give organometallic phosphazene derivatives. The reaction of halogens with phosphine oxide carbanions has not been reported, but their reaction with methylene diphosphonate carbanions, to give halomethylene derivatives, is well known[179]. Consistently, $N_3P_3Ph_4Me(CH_2Li)$ reacts with bromine to give the bromomethyl phosphazene $N_3P_3Ph_4Me(CH_2Br)$. The behaviour of the $\alpha$-picolyl anion is different; it undergoes a coupling reaction with bromine to give 1,2-dipyridylethane[180].

## 3.3 Spectra and Structure of $N_4P_4Me_{8-x}(CH_2R)_x$ (x=2,4) Derivatives

Assuming that the phosphazene carbanions $N_4P_4Me_6(CH_2^-)_2$ and $N_4P_4Me_4(CH_2^-)_4$ do not undergo a charge rearrangement during their reaction with electrophiles, the structures of the di- and tetra-substituted derivatives $N_4P_4Me_{8-x}(CH_2R)_x$ (x=2,4) reflect the structures of their parent

carbanions, and hence the orientation of successive deprotonation of $N_4P_4Me_8$.

### 3.3.1 Disubstituted Derivatives

The determination of the mode of substitution in these compounds has relied on the use of both spectroscopic and crystallographic methods. The presence of two signals, of equal intensity, in their $^{31}P$ n.m.r. spectra is in agreement with both the vicinal (IV) and antipodal (V) arrangements, but only the latter (V) is consistent with the triplet fine structure (P-P coupling) observed for both of the $^{31}P$ signals. The $^1H$ n.m.r.



IV                         V
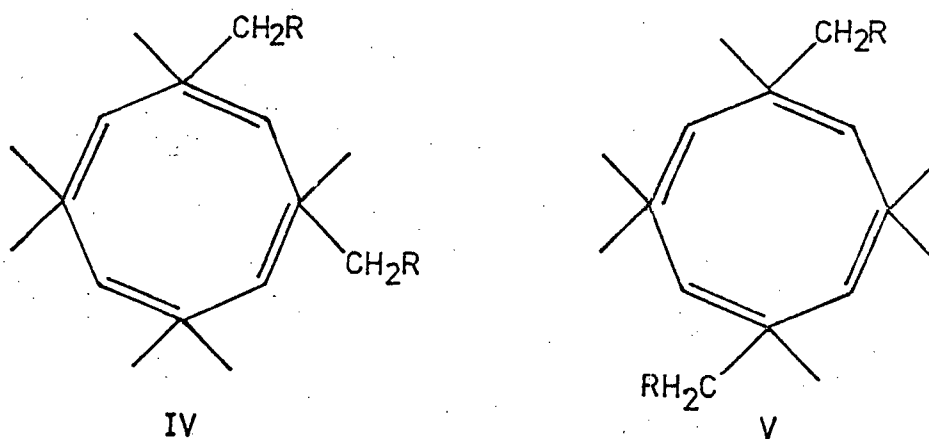
spectra (Table 3.1) of the disubstituted compounds are also consistent with the non-geminal arrangement of the $CH_2R$ groups, showing, typically, the distinct resonances of four equivalent geminally substituted P-methyl groups, two equivalent $P(CH_2R)$-methyl groups, and two equivalent P-methylene groups. However, although the $^{31}P$ and $^1H$ n.m.r. spectra indicate the phosphorus atoms at which successive deprotonations occur, they do not establish the relative orientation of the $-CH_2R$ groups.

This problem has been resolved by the recent crystal structure

Table 3.1 $^1$H[a] and $^{31}$P[b] n.m.r. parameters of $N_4P_4Me_{8-x}(CH_2R)_x$ derivatives

| | $\delta_P(PMe_2)$ | $\delta_P(PMe)$ | $\delta_H(PMe_2)$ | $\delta_H(PMe)$ | $\delta_H(PCH_2R)$ | $\delta_H(R)$ |
|---|---|---|---|---|---|---|
| $N_4P_4Me_6Et_2 \cdot 2HCl$‡ | 75.8 (12) | 71.1 (12) | 2.41 (14.0) | 2.38 (13.0) | 2.62 (12.0) | 1.66 (22.0)[c] |
| $N_4P_4Me_4Et_4 \cdot 2HCl$‡ | - | 71.2 — | - | 2.39 (12.0) | 2.62 (~12.0) | 1.68 (21.0)[d] |
| $N_4P_4Me_4Et_4$ | - | 89.4 — | - | 1.41 (11.5) | 1.65 (~12.0) | 1.10 (17.0)[e] |
| $N_4P_4Me_6(CH_2SiMe_3)_2$ | 95.5 (12) | 99.6 (12) | 1.42 (13.5) | 1.45 (13.0) | 1.18 (18.0) | 0.11 — |
| $N_4P_4Me_4(CH_2SiMe_3)_4$ | - | 100.1 — | - | 1.46 (12.5) | 1.19 (17.0) | 0.24 — |
| $N_4P_4Me_6(CH_2GeMe_3)_2$ | 94.4 (12) | 99.6 (12) | 1.41 (13.5) | 1.42 (13.5) | 1.23 (16.5) | 0.25 — |
| $N_4P_4Me_4(CH_2GeMe_3)_4$ | - | 98.1 — | - | 1.42 (12.0) | 1.23 (17.5) | 0.19 — |
| $N_4P_4Me_6(CH_2SnMe_3)_2$ | 92.8 (12) | 100.0 (12) | 1.45 (13.0) | 1.48 (12.0) | 1.27 (14.0) | 0.14 — |
| $N_4P_4Me_4(CH_2SnMe_3)_4$ | - | 96.5 — | - | 1.40 (12.5) | 1.23 (12.3) | 0.16 — |

(a) $\delta$(ppm), in CDCl$_3$, reference internal TMS, except ‡ in D$_2$O, reference external TMS. J(PH), in Hertz, in parenthesis. (b) $\delta$(ppm) reference external P$_4$O$_6$; all in CDCl$_3$, except ‡ in D$_2$O. J(PP), in Hertz, in parenthesis. $\delta_P$(N$_4$P$_4$Me$_8$) in CDCl$_3$ is 94.4 ppm. (c) J(HH) = 7.5 Hz. (d) J(HH) = 7.1 Hz. (e) J(HH) = 7.3 Hz.

determination of the dihydrochloride of $N_4P_4Me_6Et_2$[181]. The molecular

geometry of this compound (Figure 3.1) shows that the two ethyl groups are

arranged in a trans-antipodal fashion. The centrosymmetrical "chair" –

shaped structure is not uncommon in phosphazene chemistry. Its occurrence



(a)                                    (b)
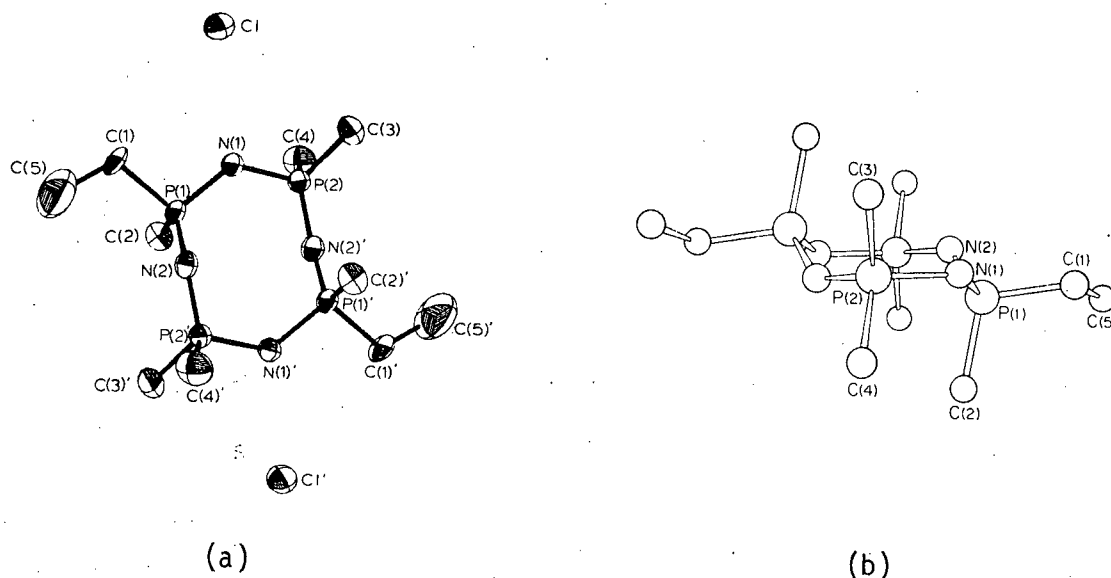
Figure 3.1.   General views of (a) the $N_4P_4Me_6Et_2.2HCl$ structure, and (b)
              the chair conformation of the $N_4P_4Me_6Et_2H_2^{2+}$ cation (from
              H.P. Calhoun, R.T. Oakley, N.L. Paddock and J. Trotter, Can.
              J. Chem., 53, 2413 (1975).

in this molecule can be understood in terms of electrostatic repulsion

between the $CH_2^-$ groups of the carbanion $N_4P_4Me_6(CH_2^-)_2$. Model calculations

on molecules with the conformations found in 8-membered phosphazene rings

(saddle, $D_{2d}$; tub, $S_4$; chair, $C_{2h}$; crown, $C_{4v}$) show that, for normal values

of bond angles, repulsion in the dicarbanion is least in the trans-antipodal

chair conformation, as is found in the diethyl derivatives.  Coordination of

lithium ions to both the methylene groups and the ring nitrogen atoms would

also be especially easy for the chair conformation (e.g. VI).
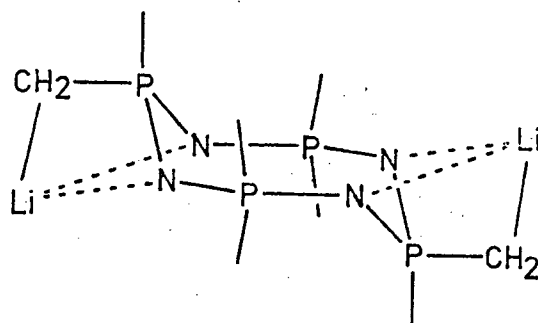
VI

## 3.3.2 Tetrasubstituted Derivatives

The appearance of a single resonance in their $^{31}$P n.m.r. spectra, and of a single P-methyl resonance in their $^{1}$H n.m.r. spectra, indicates that the substitution pattern found in the tetrasubstituted derivatives $N_4P_4Me_4(CH_2R)_4$ is non-geminal, as expected on a simple electrostatic basis. Theoretically, the further reaction of the trans-antipodal dicarbanion to give the non-geminal tetracarbanion can give rise to two possible isomers, the cis,cis,cis,trans (VII), and the cis,cis,trans,trans (VIII). Of the two, the latter is favoured electrostatically, but its existence cannot be confirmed by n.m.r. spectrometry. However, the near mutual exclusion of the Raman and infrared spectra of $N_4P_4Me_4Et_4$ (Table 3.2) is consistent with the centrosymmetric structure VIII, but, because of possible accidental degeneracies of non-skeletal modes, the cis,cis,cis,trans configuration cannot be entirely excluded from consideration.

In general, the infrared spectra of the tetra-substituted derivatives $N_4P_4Me_4(CH_2R)_4$ are, as expected, similar to that of the parent $N_4P_4Me_8$ molecule. All contain a characteristically strong band in the region of 1215-1250 cm$^{-1}$, which is easily assigned to the $\nu_{as}$ (P=N)

Table 3.2 Infrared[a] and Raman[b] absorption frequencies (in $cm^{-1}$) of $Me_8P_4N_4$[c] and $Me_4Et_4P_4N_4$

| $Me_8P_4N_4$ | | $Me_4Et_4P_4N_4$ | |
|---|---|---|---|
| Infrared | Raman | Infrared | Raman |
| 280 w | 251 (6.9) | 435 m (broad) | 185 (1.5) |
| 390 s | 284 (2.4) | 625 m | 256 (6.0) |
| 433 s | 361 (0.6) | 670 w | 355 (0.5) |
| 460 sh | 433 (0.7) | 710 w | 500 (10.0) |
| 505 w | 507 (10.0) | 750 w | 580 (5.0) |
| 630 s | 588 (5.2) | 767 w | 675 (0.4) |
| 736 m | 698 (1.0) | 790 s | 712 (1.0) |
| 760 m | 736 (5.2) | 860 w | 790 (0.6) |
| 787 w | 761 (1.7) | 881 v.s. | |
| 860 s | 767 (3.8) | 940 w | 990 (1.0) |
| 870 s | 860 (0.9) | 1010 w | |
| 920 s | | 1041 m | 1045 (1.2) |
| 980 sh | | 1230 v.s. (broad) | |
| 995 m | | 1270 v.s. | |
| 1040 w | | 1300 v.s. | |
| 1222 v.s. (broad) | | 1379 v.w. | |
| 1240 sh | | 1418 w | 1425 (0.8) |
| 1290 s | | 1461 w | 1465 (0.5) |
| 1300 s | | 2880 w | |
| 1415 w | 1414 (2.8) | 2910 w | 2915 (3.0) |
| 1422 w | 1426 (1.9) | 2940 m | |
| 1430 w | | 2970 m | 2985 (1.0) |

(a) Spectra recorded on nujol and hexachlorobutadiene mulls. (b) Spectra recorded on powdered solid (relative intensities in parenthesis). (c) From T.N. Ranganathan, Ph.D., Brit. Col., 1971.

VIII

VII
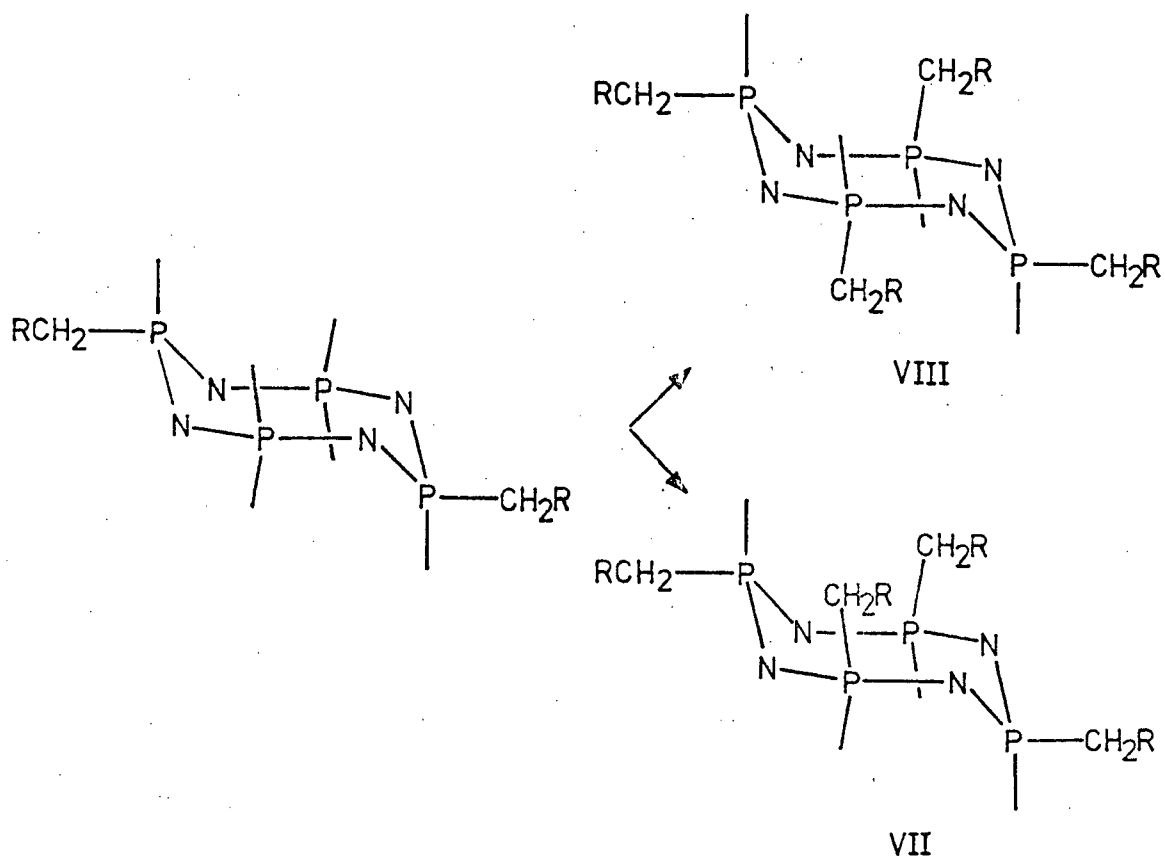
vibration. The $\delta_{as}$ (CH$_3$) vibration at 1414-1427 cm$^{-1}$ is complemented by the deformational mode of the methylene group, the frequency of which is dependent on the mass of the atom bonded to the methylene carbon atom. In N$_4$P$_4$Me$_4$Et$_4$, $\delta$(CH$_2$) is found at 1461 cm$^{-1}$. For the N$_4$P$_4$Me$_4$(CH$_2$MMe$_3$)$_4$ (M=Si, Ge, Sn) derivatives, it occurs in an otherwise clear region of 1040-1110 cm$^{-1}$, within the limits found for this vibration in a variety of XCH$_2$SiMe$_3$ molecules (X=SiMe$_3$[182]; Cl, Cr, Sn, Pb[183]).

## 3.4 Structure and Spectra of N$_3$P$_3$Ph$_4$Me(CH$_2$R) Derivatives

The details of the ^{31}P and [1]H n.m.r. spectra of the N$_3$P$_3$Ph$_4$Me(CH$_2$R) derivatives are given in Table 3.3. The [31]P n.m.r. spectra all consist, as expected, of two signals of relative intensity 1:2

(PMe(CH$_2$R):2PPh$_2$). The proton n.m.r. spectra are also consistent with expectation, and show the effect of substitution of an R group onto one of the P-methyl groups, the chemical shifts of the resulting methylene protons being broadly consistent with the electronegativity of R.

Table 3.3  $^1$H$^a$ and $^{31}$P$^b$ n.m.r. parameters of N$_3$P$_3$Ph$_4$MeCH$_2$R derivatives

| R= | H$^c$ | SnMe$_3$$^d$ | COPh | COOH$^e$ | Br |
|---|---|---|---|---|---|
| $\delta_P$(PMeCH$_2$R) | 85.2 | 80.8 | 87.5 | 86.6 | 89.0 |
| $\delta_P$(PPh$_2$) | 98.2 | 99.3 | 98.3 | 96.8 | 98.2 |
| $\delta_H$(MeP) | 1.58(14.0)$^f$ | 1.52(13.5) | 1.75(15.0) | 1.76(15.0) | 1.72(15.0)$^h$ |
| $\delta_H$(CH$_2$P) | 1.58(14.0)$^f$ | 1.37(14.0)$^g$ | 3.61(18.0) | 2.88(17.0) | 3.20(6.5) |

(a) $\delta$(ppm) in CDCl$_3$, reference internal TMS.  J(PH), in Hertz, in paren-
thesis.  $\delta$(Phenyl) ∿7.0-8.0 ppm.  (b) $\delta$(ppm), in CDCl$_3$ reference external
P$_4$O$_6$.  (c) See also R. Appel and G. Saleh, Chem. Ber., 106, 3455 (1973).
(d) $\delta_H$(Me$_3$Sn) = 0.02 ppm.  (e) $\delta_H$(OH) = 9.38 ppm.  (f) $\overline{J(PH)}$ (long range) =
1.5 Hz.  (g) J(PH) (long range) = 4.0 Hz.  (h) J(PH) (long range) = 2.0 Hz.

The infrared spectra of these compounds are largely uninterpretable, the superposition of phenyl vibrations, and those of the R group, with skeletal modes making detailed assignments speculative.  However, a few definite observations can be made regarding the difference between unsubstituted N$_3$P$_3$Ph$_4$Me$_2$ and its derivatives N$_3$P$_3$Ph$_4$Me(CH$_2$R).

In all the compounds, $\nu_{asym}$ (P=N) occurs at 1160-1200 cm$^{-1}$, near to the value found for (NPPh$_2$)$_3$ (1190 cm$^{-1}$ [24]) and (NPMe$_2$)$_3$ (1180 cm$^{-1}$ [21]). In N$_3$P$_3$Ph$_4$Me$_2$, $\delta_{sym}$ (CH$_3$) appears as a sharp doublet (in-phase and out-of-phase) at 1298 cm$^{-1}$ and 1310 cm$^{-1}$ (in Me$_3$PO[184,185] this band appears at ∿1300 cm$^{-1}$).  Substitution on one of the methyl groups reduces this doublet to a sharp singlet near 1300 cm$^{-1}$.

In $Me_3PO$, the infrared bands at 950 $cm^{-1}$ and 866 $cm^{-1}$ are assigned, respectively, to the out-of-phase rocking and wagging motions of the P-methyl groups[184,185]. On this basis, the two bands at 955 $cm^{-1}$ and 871 $cm^{-1}$ in $N_3P_3Ph_4Me_2$ may reasonably be assigned to equivalent vibrations. Corroborating this assignment, both these bands disappear upon substitution on one of the methyl groups.

Regarding the R groups themselves, assignments can only be made with certainty for the $\nu(C=O)$ frequency in $N_3P_3Ph_4MeCH_2COPh$ and $N_3P_3Ph_4MeCH_2COOH$; in the former it occurs at 1666 $cm^{-1}$ and, in the latter, at 1695 $cm^{-1}$. For $N_3P_3Ph_4MeCH_2COOH$, the $\nu(OH)$ band is not visible. Intramolecular, as well as intermolecular, hydrogen bonding, to both oxygen and nitrogen, probably accounts for the lack of resolution of this band.

## 3.5 Carbanion Stabilization by Phosphazenes

The formation of carbanions from methylphosphazenes provides a new method for the synthesis of phosphazene derivatives. The ease of successive deprotonation is an unusual and interesting feature of this process, and indicates the importance of conjugative interactions between the ligands and the ring.

The structural similarity between the carbanions formed from methylphosphazenes, methylphosphine oxides, and $\alpha$-picoline is demonstrated by equations 6a-6c. In all three cases, the carbanion is stabilized by conjugation. In the oxide, resonance is restricted to a single phosphoryl group, but in the cyclic phosphazenes and pyridines, the negative charge of the anion can be diffused over the entire aromatic system.

... 6a



... 6b



... 6c

The formation of a tetracarbanion is not unique. Tetrathiane, $(SCH_2)_4$, is deprotonated by butyllithium to yield the tetracarbanion $(SCH^-)_4$[186], the stability of which is attributable to the well known acceptor properties of divalent sulphur. In the present case, the ability of the $P_4N_4$ phosphazene ring to stabilize the negative charge of the $N_4P_4Me_4(CH_2^-)_4$ ion is consistent with the structural features described in chapter 1; viz the apparent loss of electron density from oxygen and nitrogen in $[NP(OMe)_2]_n$ and $[NP(NMe_2)_2]_n$ into the cyclic $\pi$-system. In fact, in the limit of complete delocalization of charge from the methylene groups into the ring, the structure of the $N_4P_4Me_4(CH_2^-)_4$ anion (IX) becomes isoelectronic with the phosphazene $[MeNP(O)OMe]_4$ (X) (formed by the thermal rearrangement of $[NP(OMe)_2]_4$[187]), and the tetrametaphosphate ion $[PO_3^-]_4$ (XI).

The analogy between the tetracarbanion $N_4P_4Me_4(CH_2^-)_4$ and the tetrametaphosphate ion is important, since it allows a comparison between

IX                              X                               XI

the acidic properties of $N_4P_4Me_8$ and tetrametaphosphoric acid, about which more is known. In general, the acidities of the cyclic metaphosphoric acids differ from those of linear phosphoric acids. The tri- and tetra-metaphosphoric acids $[HPO_3]_{3,4}$, for instance, behave as strong acids (their $k_a$ is greater than $k_{a1}$ of orthophosphoric acid), and dissociate in dilute solution according to equation 7[188-191]. By contrast, the

$$[HPO_3]_n \longrightarrow nH^+ + [PO_3]_n^{n-} \qquad (n=3,4) \qquad \ldots 7$$

titration curve of the linear tripolyphosphoric acid $[(HO)_3POP(OH)_2OP(OH)_3]$ exhibits three inflexion points. Not only are the terminal protons less acidic than the central ones, but they display different acidities at each end, the removal of one terminal proton reducing the acidity of those at the other end, presumably by a simple charge accumulation effect. In long chain phosphoric acids, the terminal hydrogen atoms are too greatly separated to have any influence on each other, and their dissociation

constants are the same. The non-terminal protons all display approximately[‡] the same acidity, but are, nonetheless, less acidic than the hydrogen atoms in the cyclic acids.

In the light of this evidence, the behaviour of $N_4P_4Me_8$ as an acid is more easily rationalized. The difficulty in the preparation of mono- and tricarbanions from $N_4P_4Me_8$ has already been noted, the removal of the first proton apparently enhancing, or at least not inhibiting, further deprotonation. This behaviour is entirely consistent with the mono-functionality of metaphosphoric acids, and indicates the effectiveness of the cyclic $\pi$-systems in both the {P-O} and {P=N} rings in accepting charge density from the ligands.

## 3.6   $^{31}P$ Chemical Shifts of Heterogeneously Substituted Phosphazenes

When applied to the study of phosphazene chemistry, $^{31}P$ n.m.r. spectroscopy is a useful tool for establishing the orientation patterns of partially substituted derivatives. However, the interpretation of the $^{31}P$ chemical shifts of phosphazenes, in terms of the charge distribution within them, is not so straightforward, and although there exist simple empirical explanations of the shifts observed in homogeneously substituted phosphazenes, the application of the sample principles to heterogeneously substituted derivatives is not always successful. The importance of angular and steric factors, which have a profound influence on the $^{31}P$ chemical shifts of

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[‡] The apparent weakness, as observed in titration curves, of the fourth proton of $[HPO_3]_4$[188,191], and of successive chain protons in linear acids, is attributed to ion association with the cation[192].

mononuclear phosphorus compounds[193], is simply not known for phosphazenes.

It is generally accepted that, for homogeneously substituted phosphazenes $(NPX_2)_n$, there is an approximate correlation between their $^{31}P$ chemical shifts and the ability of the ligand X to attract electron density from the PN ring onto phosphorus (see Chapter 2, section 2.1.4.1). This trend is not unique to phosphazenes, but is also observed in phosphine oxides and sulphides[194,195], phosphorus ylids[196] and bis(biphenylene)-phosphoranes[197]. In all these compounds the primary influence of the ligand is upon the π-system within the molecule, rather than upon the ligand-phosphorus bond, as is found in tervalent phosphorus compounds[193], and results in the shielding of phosphorus being directly related to the electronegativity of the ligand.

The origin of the effect is illustrated in Figure 3.2, which shows how the perturbation of one phosphorus atom (P*) in a $P_3N_3$ ring by substituents of different electronegativities affects the π-charge density on that phosphorus. The variation in ligand electronegativity is simulated by a change in the Coulomb parameter of the 3d orbital on the P* atom; accordingly, more electronegative substituents give rise to a lower Coulomb parameter, and result in an increase in the π-charge density on the substituted (P*) atom.

This same argument can also be used to rationalize the $^{31}P$ chemical shifts of some heterogeneously substituted phosphazenes. In the series $RCl_5P_3N_3$, for example, the shielding of the substituted phosphorus atom has been shown to increase along the series R = $NMe_2$ < Cl < OMe < $OCH_2CF_3$ < F < OEt < $OPr^i$, this order being broadly consistent with change in electro-negativity of the R group[198].

Figure 3.2. Relative charge densities (P*-P) on phosphorus atoms in a
perturbed $P_3N_3$ ring (assuming homomorphic interactions
between 3d orbitals on phosphorus and 2p orbitals on nitrogen).
Coulomb parameters ($\alpha$) expressed as a function of the resonance
parameter ($\beta$) such that $\alpha_P = \alpha_N - 2\beta$. Coulomb parameter of the
perturbed phosphorus atom (P*) varied such that $\alpha_{P*} = \alpha_P - \delta$.
$(-\beta < \delta < \beta)$.

The influence of different ligands on remote phosphorus atoms is

effectively demonstrated by the series of geminally substituted phenylfluo-

rophosphazenes $F_{2n}Ph_{6-2n}P_3N_3$ (n=0,1,2,3) (Table 3.4). Shielding of the

$P(Ph_2)$ atoms decreases steadily with increasing fluorination of the ring,

indicative of an increasing flow of $\pi$-charge from the phenylated to the

fluorinated phosphorus atoms. Consistently, progressive phenylation of the

ring causes an increase in the shielding of the $P(F_2)$ atoms. An equivalent

effect is observed in the chlorophosphazenes $Cl_{2n}Ph_{6-2n}P_3N_3$ (n=0,1,2,3)

(Table 3.4); it is less marked than in the previous case, the phenyl and chlorine ligands having more nearly equal electronegativities.

Table 3.4  $^{31}P$ chemical shifts[a] of geminally substituted phenylhalophosphazenes $X_{2n}Ph_{6-2n}P_3N_3$.

| n= | | 0 | 1 | 2 | 3 |
|---|---|---|---|---|---|
| X=F | P(Ph$_2$) | 98.2[b] | 85.2[c] | 82.1[c] | - |
| " | P(F$_2$) | - | 106.3[c] | 101.1[c] | 98.6[c] |
| X=Cl | P(Ph$_2$) | 98.2[b] | 95.9[d] | 94.2[d] | - |
| " | P(Cl$_2$) | - | 93.4[d] | 91.9[d] | 92.5[e] |

(a) $\delta$(ppm), relative to external $P_4O_6$.  (b) H.P. Latscha, Z. Anorg. Allgem. Chem., __382__, 7 (1968).  (c) C.W. Allen, F.Y. Tsang and T. Moeller, Inorg. Chem., __7__, 2183 (1968).  (d) B. Grushkin, M.G. Sanchez, M.V. Ernest, J.L. McClanahan, G.E. Ashby and R.G. Rice, Inorg. Chem., __4__, 1538 (1965). (e) L.G. Lund, N.L. Paddock, J.E. Proctor and H.T. Searle, J. Chem. Soc., 2542 (1960).

Simple explanations such as these are not always possible. The anomalous chemical shift of (NPBr$_2$)$_3$ ($\delta_P$ = 157.9 ppm[199], but $\delta_P$ in (NPF$_2$)$_3$ is 98.6 ppm[159] and in (NPCl$_2$)$_3$ is 92.7 ppm[200]) shows that angular effects may be important. Similarly, the decrease in the chemical shift of the P(F$_2$) atoms on moving from $F_8P_4N_4$ to $F_4Me_4P_4N_4$ finds no explanation in terms of a $\pi$-inductive effect. Caution is therefore required in assessing the origins of chemical shift variations between different phosphazenes.

Bearing in mind the above caveat, the purpose of the present section is to report the $^{31}P$ chemical shifts of a variety of heterogeneously substituted phosphazenes prepared during this work, and where possible, to relate these shifts to the $\pi$-electron distribution within the cyclic PN skeleton.

### 3.6.1 $^{31}$P Chemical Shifts of $XYPh_4P_3N_3$ Derivatives

The $^{31}$P n.m.r. parameters of the geminally substituted tetraphenyl-phosphazenes $XYPh_4P_3N_3$ prepared in this work are given in Table 5. For the series $Me(CH_2R)Ph_4P_3N_3$ (R=H, $SnMe_3$, Br, COPh, COOH), it is evident that, as expected, the alkyl groups are more efficient donors than phenyl groups, the greater shielding of the $P(Ph_2)$ atoms indicating a polarization of π-charge onto them. The effect of a change in the nature of R on the remote phosphorus atom is small, but on the $P(CH_2R)$ atom, it is more substantial. The total effect is most easily followed by use of the parameter $\Delta = \delta(PXY) - \delta(PPh_2)$, which provides a measure of the polarization of π-charge from the $P(Ph_2)$ atoms towards the $P(XY)$ atom. For the alkyl derivatives, $\Delta$ is negative, but its value increases along the series $R=SnMe_3 < H < COOPh \sim COOH < Br$. This order is broadly consistent with that observed for the chemical shifts of phosphonate esters $RCH(PO_3Pr^i_2)$[179] (in which $\delta_P$ increases in the order R = Na < Me < H < Br < COOMe), and corresponds approximately to the order of electronegativities of the R group. For the series of compounds $XYPh_4P_3N_3$ (X=F, Cl or $NMe_2$), the variation in $\Delta$ with change in X or Y is more marked than it is in the $Me(CH_2R)Ph_4P_3N_3$ derivatives (with change in R). The sense and magnitude of the variation are such as to provide a useful measure of the combined electronegativities of X and Y (e.g. $E(F + NMe_2) > E(Cl + Cl)$).

### 3.6.2 $^{31}$P Chemical Shifts of $N_4P_4Me_{8-x}(CH_2MMe_3)_x$ Derivatives

The details of the $^{31}$P n.m.r. spectra of these compounds (XII and XIII) are presented in Table 1. As might be expected from the similarity

Table 3.5 $^{31}P$ chemical shifts[a] of $XYPh_4P_3N_3$ derivatives.

| X | Y | $\delta(PXY)$ | $\delta(PPh_2)$ | $\Delta$[b] |
|---|---|---|---|---|
| F | F[c] | 106.3 | 85.2 | 21.1 |
| F | NMe$_2$[d] | 95.6 | 94.1 | 1.5 |
| Ph | Ph[e] | 98.2 | 98.2 | 0 |
| Cl | Cl[f] | 93.4 | 95.9 | - 2.5 |
| Cl | NMe$_2$[g] | 85.2 | 94.4 | - 9.2 |
| Me | CH$_2$Br | 89.0 | 98.2 | - 9.2 |
| Me | CH$_2$COOH | 86.6 | 96.8 | -10.2 |
| Me | CH$_2$COPh | 87.5 | 98.3 | -10.8 |
| Me | Me | 85.2 | 98.2 | -13.0 |
| Me | CH$_2$SnMe$_3$ | 80.8 | 99.3 | -19.3 |

(a) $\delta(ppm)$, reference external $P_4O_6$. All values from $CDCl_3$ solutions.
(b) $\Delta = \delta(PXY) - \delta(PPh_2)$. (c) C.W. Allen, E.Y. Tsang and T. Moeller, Inorg. Chem., 7, 2183 (1968). (d) J(PF) = 893 Hz, J(PP) = 22 Hz. (e) H.P. Latscha, Z. Anorg. Allgem. Chem., 382, 7 (1968). (f) B. Grushkin, M.G. Sanchez, M.V. Ernest, J.L. McClanahan, G.E. Ashby and R.G. Rice, Inorg. Chem., 4, 1538 (1965). (g) J(PP) = 12 Hz.

**XII**          **XIII**

R = Me, MMe$_3$ (M = Si, Ge, Sn)

of the ligands, the differences in chemical shifts between the various compounds is small, and, possibly because of this, the interpretation of the chemical shift variations in terms of a $\pi$-inductive effect is not particularly successful.

For example, the phosphorus atoms in $N_4P_4Me_4Et_4$ are less shielded than in $N_4P_4Me_8$, consistent with the expected greater donating ability of the ethyl groups. However, the chemical shifts of the $N_4P_4Me_4(CH_2MMe_3)_4$ derivatives indicate an unexpectedly high electronegativity for the $(Me_3MCH_2)$ group. Moreover, whereas the $\delta_p$ values in $N_4P_4Me_4(CH_2MMe_3)_4$ suggest the order of electronegativities of the different metals to be E(Sn) < E(Ge) < E(Si), the chemical shifts of the PMe$_2$ atoms in $N_4P_4Me_4(CH_2MeMe_3)_4$ indicate a reverse order[‡].

## 3.7 Experimental

The preparation of the methylphosphazenes used in the following experiments was described in Chapter 2. Each compound was dried before

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[‡] For the series of phosphines $(H_3M)_3P$ (M=C,Si,Ge,Sn). The chemical shifts indicate the order of electronegativities to be E(C) ⩾ E(Ge) > E(Si) > E(Sn)[201].

use; $(NPMe_2)_4$ by sublimation in vacuo and $N_3P_3Ph_4Me_2$ by recrystallization from ether/hexane and heating it at 100°C/24 hours. The various electrophiles (e.g. MeI, $Me_3SiCl$, $Me_3GeCl$, $Me_3SnCl$, $CO_2$, $PhCO_2Et$ and $Br_2$) which were reacted with the phosphazene carbanions were obtained from commercial sources. Methyl iodide and trimethylsilyl chloride were redistilled, and trimethylstannyl chloride sublimed in vacuo before use. Bromine, available commercially in 1 ml vials, was used without further purification, as were carbon dioxide (lecture bottle, "Bone Dry" grade) and ethyl benzoate. Because of the sensitivity of organolithium reagents to oxygen and moisture, the preparations and reactions of the phosphazene carbanions were all carried out under an atmosphere of dry nitrogen.

### 3.7.1 Preparation of Methyllithium

All the reactions described in this section involve the use of methyllithium. Although solutions of it (in ether and THF) are commercially available, accurate work on a small scale requires that such solutions be prepared and used immediately, since decomposition of the solvent occurs on standing. The usual method of preparing methyllithium is by the reaction of methyl bromide and lithium metal (equation 8). However, the different method employed in this work relies on the insolubility of methyllithium in

$$MeBr + 2Li \longrightarrow LiMe + LiBr \qquad \ldots 8$$

hexane, and provides a source of methyllithium that is free from the potential interference of lithium halides.

The method is similar to one that has already been reported[202], and involves the reaction of methyl iodide and butyllithium in hexane at reduced temperatures (equation 9). In a typical preparation, methyl

$$BuLi + MeI \xrightarrow[<0°C]{Hexane} BuI + MeLi\downarrow \qquad \dots 9$$

iodide was added, at -78°C, to a hexane solution containing a slight excess of n-butyllithium (prepared by the dilution with hexane of a commercially available solution from about 2.0 M to 0.5 M). The mixture was stirred under an atmosphere of nitrogen, and allowed to warm slowly to 0°C, whereupon a white precipitate of methyllithium was produced. This precipitate was filtered (under nitrogen!) from the solution and dissolved in diethyl ether (previously dried by distillation from lithium aluminium hydride). The solution so formed was filtered (if necessary) and standardized by quenching an aliquot of it in water and titrating it against normal sulphuric acid. The solutions of methyllithium prepared in this way were used within 24 hours of their preparation.

### 3.7.2 Preparation of $N_4P_4Me_4Et_4$

A solution of methyllithium in ether (56.0 ml, equivalent to 39.2 mmol of MeLi) was added dropwise from a syringe, to a solution of $N_4P_4Me_8$ (2.712g, 9.04 mmol) in 50 ml of ether. Effervescence was observed to occur for about ½ hour following the addition of methyllithium. The mixture was then heated under reflux for 2 hours, when a slight turbidity was apparent in the solution. A large excess (∿25 ml) of methyl iodide was then added to the reaction mixture, and a rapid exothermic reaction ensued.

The mixture was heated under reflux for a further 4 hours, and the solvent and excess methyl iodide distilled off to leave a white paste (10.747 g), which was dissolved in water and neutralized with sulphuric acid (residual alkalinity = 2.15 mmol OH$^-$). Potassium fluoride (2.9 g) was added to the solution to precipitate lithium as its fluoride. After filtration, the solution was distilled to dryness and the residue extracted with 3 x 30 ml of hot chloroform. Triethylamine (10 ml) was added to the chloroform extract, which was then shaken for 5 minutes. Evaporation of the solvent left a crystalline mass which was extracted with 3 x 50 ml of hot hexane. Evaporation of these extracts yielded colourless crystals of $N_4P_4Me_4Et_4$ (2.58 g, 7.2 mmol, 80%), which was purified by sublimation in vacuo and recrystallization from hexane. Anal. calcd. for $C_{12}H_{32}N_4P_4$: C, 40.45; H, 9.05; N, 15.72. Found: C, 40.21; H, 8.89; N, 16.00. Melting point 65-67°C.

### 3.7.2.1  Isolation of $N_4P_4Me_4Et_4 \cdot 2HI$

The treatment of the $CHCl_3$ extract in the above experiment with base is important. If this step is omitted from the procedure, the neutral phosphazene is not obtained. Presumably, the immediate product of the reaction is a complex between the neutral phosphazene and lithium iodide and, upon precipitation of the lithium, the complex is converted into the dihydroiodide $N_4P_4Me_4Et_4 \cdot 2HI$. This hydroiodide was isolated in a preliminary experiment in which triethylamine was not used. It was recrystallized from acetonitrile as colourless cubes. Anal. calcd. for $C_{12}H_{34}I_2N_4P_4$: C, 23.53; H, 5.60; I. 41.47; N, 9.16. Found: C, 23.15; H, 5.68; I, 41.20; N, 9.19. Dec. 188-190°C.

### 3.7.2.2  Isolation of $N_4P_4Me_6Et_2 \cdot 2HCl$

In another preliminary experiment in which the use of triethyl-
amine was omitted, the chloroform extract was evaporated to leave an oil,
which was dissolved in water and eluted through an Amberlite CG400 anion
exchange column (previously charged with chloride ion).  Evaporation of the
eluant gave an oil which, upon standing, yielded a few crystals, which
were recrystallized, under nitrogen, from acetonitrile/benzene as small
hygroscopic cubes of $N_4P_4Me_6Et_2 \cdot 2HCl$.  Anal. calcd. for $C_{10}H_{30}Cl_2N_4P_4$:
C, 29.94; H, 7.54; Cl, 17.67; N, 13.97.  Found:  C, 29.64; H, 7.55;
Cl, 18.05; N, 14.06.  M.pt. 231-234°C.

### 3.7.2.3  Preparation of $N_4P_4Me_4Et_4 \cdot 2HCl \cdot H_2O$

This compound was prepared by saturating a solution of
$N_4P_4Me_4Et_4$ (0.107 g, 0.30 mmol) in carbon tetrachloride with hydrogen
chloride gas.  The resulting precipitate (0.112g) was filtered from the
solution and recrystallized, under nitrogen, from an acetonitrile/benzene
solution as colourless hygroscopic blocks.  Anal. calcd. for $C_{12}H_{36}Cl_2N_4OP_4$:
C, 32.22; H, 8.11; Cl, 15.85; N, 12.53.  Found:  C, 32.29; H, 8.30;
Cl, 15.90; N, 12.68.  M.pt. 180-185°C.

### 3.7.3  Preparation of $N_4P_4Me_4(CH_2SiMe_3)_4$

A solution of methyllithium (15.0 ml, 12.0 mmol of MeLi) in ether
was added. via a syringe, into a solution of $N_4P_4Me_8$(0.758g, 2.52 mmol) in
50 ml of ether, and the mixture heated under reflux for 2 hours under an
atmosphere of nitrogen.  The mixture was then cooled to room temperature,

and an excess of $Me_3SiCl$ (2.0 ml, 15.9 mmol) added slowly to the solution. A vigorous exothermic reaction occurred, and a white precipitate was formed. The mixture was allowed to stir overnight under a nitrogen atmosphere, and then filtered. The solvent was evaporated from the filtrate to leave an oil which was distilled at $\sim$160°C/0.01 Torr to give a colourless liquid which solidified on standing at room temperature. This solid was recrystallized by cooling a concentrated solution of it in hexane to -23°C to give colourless blocks of $N_4P_4Me_4(CH_2SiMe_3)_4$. Anal. calcd. for $C_{20}H_{56}N_4P_4Si_4$: C, 40.79; H, 9.59; N, 9.51. Found: C, 40.49; H, 9.56; N, 9.50. M.pt. 97-102°C.

### 3.7.4 Preparation of $N_4P_4Me_6(CH_2SiMe_3)_2$

A solution of methyllithium in ether (28.0 ml, 18.2 mmol MeLi) was reacted, as described above, with a solution of $N_4P_4Me_8$ (2.348 g, 7.83 mmol) in 150 ml of ether. The mixture was then reacted (as described in Expt. 3.7.2) with a solution of $Me_3SiCl$ (2.06 g, 19.0 mmol) in 20 ml of ether. Subsequent filtration of the reaction mixture and evaporation of the filtrate yielded a colourless oil (3.54 g), which was distilled in vacuo ($\sim$160°C/0.01 Torr). The resulting oil was dissolved in a minimum of pentane and, on cooling it to 0°C, $\sim$0.5 g of unreacted $N_4P_4Me_8$ crystallized from the solution. The remaining solution was then cooled to -23°C and, after several days, a colourless crystalline solid was obtained, which was recrystallized from pentane at -23°C as needles of $N_4P_4Me_6(CH_2SiMe_3)_2$. Anal. calcd. for $C_{14}H_{40}N_4P_4Si_2$: C, 37.82; H, 9.07; N, 12.60. Found: C, 38.15; H, 8.95; N, 12.36. M.pt. 63-65°C.

### 3.7.5  Attempted Preparation of $N_4P_4Me_7(CH_2SiMe_3)$

A solution of methyllithium in ether (3.2 mls, 1.85 mmol MeLi) was reacted, as described above, with a solution of $N_4P_4Me_8$ (0.530 g, 1.76 mmol) in 50 ml of ether. A solution of $Me_3SiCl$ (0.232 g, 2.15 mmol) in 5 ml of ether was then added, as described in Expt. 3.7.3, to the reaction mixture. After filtration of the mixture and evaporation of the solvent from the filtrate, a white pasty solid was obtained. This solid was extracted into hexane, and the solution filtered and allowed to slowly evaporate. A total of 0.321 g of unreacted $N_4P_4Me_8$ (identified by its infrared spectrum and melting point, 161-162°C) crystallized from the solution, leaving an oily residue (0.244 g). No monosubstituted derivative could be isolated from this oil; in fact, its $^1$H n.m.r. spectrum showed it to be a mixture of polysubstituted products of formulae $N_4P_4Me_{8-x}(CH_2SiMe_3)_x$ (x=2∿3). The following mass balances demonstrate the probable course of the reaction (see Text).

(a) Observed:

$$N_4P_4Me_8 \longrightarrow N_4P_4Me_8 + N_4P_4Me_{8-x}(CH_2SiMe_3)_x$$

Mass balance  0.530g,1.76mmol  0.321g,1.07mmol      0.244g

(b) Calculated for the reaction:

$$N_4P_4Me_8 \longrightarrow N_4P_4Me_8 + \tfrac{1}{2}N_4P_4Me_6(CH_2SiMe_3)_2$$

Mass balance  0.530g,1.76mmol    0.265g,0.88mmol      0.390g,0.88mmol

(c) Calculated for the reaction:

$$N_4P_4Me_8 \longrightarrow N_4P_4Me_8 + \tfrac{1}{4}N_4P_4Me_4(CH_2SiMe_3)_4$$

Mass balance    0.530g,1.76mmol      0.396g, 1.32mmol      0.259g,0.44mmol

### 3.7.6   Preparation of $N_4P_4Me_{8-x}(CH_2MMe_3)_x$ (x=2,4, M=Ge, Sn)

The preparation of these compounds[‡] is similar to that of the derivatives $N_4P_4Me_{8-x}(CH_2SiMe_3)_x$ (x=2,4) and has been described elsewhere[203].

### 3.7.7   Preparation and Reactions of $N_3P_3Ph_4Me(CH_2Li)$

### 3.7.7.1   Preparation of $N_3P_3Ph_4Me(CH_2Li)$

In a typical preparation, a slight molar excess (~10%) of a freshly prepared solution of methyllithium in ether[‡‡] was added, via a syringe, to a solution of $N_3P_3Ph_4Me_2$ in ether. After an induction period of a few minutes, a heavy white precipitate of $N_3P_3Ph_4Me(CH_2Li)$ was formed. To ensure completion of the reaction, the mixture was gently heated under reflux for 2 hours before reacting it with an electrophile.

### 3.7.7.2   Preparation of $N_3P_3Ph_4Me(CH_2SnMe_3)$

A solution of $Me_3SnCl$ (0.300g, 1.50 mmol) in 20 ml of ether was

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[‡] The author is grateful to Mr. R.H. Lindstrom for the preparation of these compounds.

[‡‡] n-Butyllithium in hexane has also been used.

added to a slurry of $N_3P_3Ph_4Me(CH_2Li)$ prepared from the reaction of

$N_3P_3Ph_4Me_2$ (0.651, 1.38 mmol) and methyllithium (1.5 mmol) in 100 ml of

ether. The turbidity of the mixture became less intense following the

addition. The mixture was then left to stir overnight in order to ensure

completion of the reaction. Subsequent filtration of the mixture and

evaporation of the filtrate yielded a colourless crystalline solid, which

was recrystallized from ether/hexane to give needles of $N_3P_3Ph_4Me(CH_2SnMe_3)$

(0.861g, 1.35 mmol, 97%). An analytically pure sample was obtained by

recrystallization three times from hot hexane. Anal. calcd. for

$C_{29}H_{34}N_3P_3Sn$: C, 54.75; H, 5.39; N, 6.60. Found: C, 54.88; H, 5.47;

N, 6.46. M.pt. 146-148°C.

### 3.7.7.3 Preparation of $N_3P_3Ph_4MeCH_2COOH$

Anhydrous carbon dioxide was bubbled for 15 minutes through a

slurry of $N_3P_3Ph_4MeCH_2Li$ prepared from the reaction of $N_3P_3Ph_4Me_2$ (0.408 g,

0.863 mmol) and methyllithium (1.00 mmol) in 100 ml of ether. All turbidity

rapidly disappeared. 50 ml of 0.1N sulphuric acid was then added to the

mixture and the whole thoroughly shaken. The organic layer was extracted

and dried over anhydrous sodium sulphate. Subsequent evaporation of

the solvent yielded a white solid, which was recrystallized from acetone

as white flakes of $N_3P_3Ph_4Me(CH_2COOH)$ (0.390 g, 0.754 mmol, 87%). Anal.

calcd. for $C_{28}H_{26}N_3O_2P_3$: C, 62.67; H, 5.06; N, 8.12. Found: C, 62.85;

H, 5.15; N, 7.98. M.pt. 185-186°C (dec).

### 3.7.7.4  Preparation of $N_3P_3Ph_4MeCH_2COPh$

A solution of ethyl benzoate (0.525 g, 3.5 mmol) in 30 ml of ether was added, dropwise, to a slurry of $N_3P_3Ph_4Me(CH_2Li)$ prepared from the reaction of $N_3P_3Ph_4Me_2$ (1.50 g, 3.17 mmol) and methyllithium (3.5 mmol) in 100 ml of ether.  An immediate lessening of turbidity was noted in the reaction mixture, which was then left to stir at room temperature until the following day.  50 ml of 0.1N sulphuric acid was then added to the mixture, and the whole thoroughly shaken.  The organic layer was extracted and dried over anhydrous sodium sulphate.  Subsequent evaporation of the solvent yielded a white solid, which was recrystallized from benzene/toluene and ether/hexane to give a microcrystalline mass of $N_3P_3Ph_4Me(CH_2COPh)$.  Anal. calcd. for $C_{31}H_{30}N_3OP$:  C, 68.48; H, 5.26; N, 7.31.  Found:  C, 68.66; H, 5.39; N, 7.13.  M.pt. 144-146°C.

### 3.7.7.5  Preparation of $N_3P_3Ph_4MeCH_2Br$

An excess of bromine (∼0.5 g, 3.0 mmol) in 10 ml of ether was added to a cold slurry (-78°C) of $N_3P_3Ph_4Me(CH_2Li)$ prepared from the reaction $N_3P_3Ph_4Me_2$ (0.787 g, 1.66 mmol) with a solution of methyllithium (1.75 mmol) in 100 ml of ether.  The mixture was then allowed to warm to room temperature and 50 ml of dilute NaOH added to it.  The organic layer was separated and the aqueous layer washed with 50 ml of $CH_2Cl_2$ (this step was necessary because the product was not overly soluble in ether).  The organic extracts were combined and dried over anhydrous sodium sulphate.  Evaporation of the solvent then yielded a white crystalline solid (0.92 g).  The [1]H n.m.r. spectrum of this crude product showed it to be a ∼4:1 mixture

of product ($N_3P_3Ph_4MeCH_2Br$) and starting material ($N_3P_3Ph_4Me_2$). Repeated recrystallization of this solid from benzene/octane and chloroform/octane produced analytically pure crystals of $N_3P_3Ph_4MeCH_2Br$. Anal. calcd. for $C_{26}H_{25}BrN_3P_3$: C, 56.54; H, 4.56; Br, 14.47; N, 7.61. Found: C, 56.88; H, 4.45; Br, 14.10; N, 7.70. M.pt. 176-178°C.

CHAPTER IV

PREPARATION AND REACTIONS OF AZAPHOSPHORIN DERIVATIVES

The acidic properties of methylphosphazenes described in the previous chapter reflect the similarity in behaviour between cyclic phosphazenes and simple phosphoryl compounds.  In view of this analogy, and the structural resemblance of mononuclear phosphonium salts to the quaternary salts of methylphosphazenes, a study of the reactions of bases with the latter compounds was undertaken during the present work to determine if they could be deprotonated, like phosphonium salts, to give phosphazene derivatives containing a formal exocyclic double bond (I) (Equation 1).

However, whilst the results of this study, as reported in the present chapter, confirm that deprotonation can be achieved, they also show that the final products of such reactions are not the expected ylids (I), but novel azaphosphorin derivatives (II).  The structural rearrangement required for the formation of these compounds is hitherto unknown in phosphazene chemistry, and its occurrence here is significant, since it illustrates the fact that although many properties of phosphazenes do correspond to those of mononuclear phosphorus compounds, certain features of their chemistry are unique to them alone.



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## 4.1 Reaction of N-methyl Methylphosphazenium Salts with Bases

The formal similarity of methylphosphazenium quaternary salts to phosphonium salts led initially to the use of a variety of bases commonly used for the preparation of phosphorus ylids as reagents for the deprotonation of the phosphazenium salts. Because of their sensitivity to oxygen and water, phosphorus ylids are usually prepared and used in situ (e.g. in the Wittig reaction). When the ylid itself is to be isolated organolithium bases, usually the reagents of choice, cannot be used, since lithium salts form complexes with ylids. In spite of this complication, a few deprotonation experiments using methyllithium have been carried out.

The two bases most extensively used in this work have been potassium t-butoxide and sodium bis-(trimethylsilyl)amide. Both have been used successfully in the Wittig reaction (KOtBu[204-206] and $NaN(SiMe_3)_2$[207]) and have an appreciable solubility in hydrocarbon solvents, which are the most convenient media for achieving a clean separation of the products. However, as will be described in the following sections, the reactions of these two bases with N-methyl methylphosphazenium salts indicates that there is a profound difference in the behaviour of oxygen and non-oxygen bases with phosphazenium compounds.

### 4.1.1 Reaction of $NaN(SiMe_3)_2$ with N-methyl Methylphosphazenium Salts

In boiling octane or toluene, $NaN(SiMe_3)_2$ reacts smoothly with the monoquaternary phosphazenium iodides $(NPMe_2)_{3,4}$.MeI and $N_3P_3Ph_4Me_2$.MeI, removing a proton from an exocyclic P-methyl group. However, the final products isolated from the reactions are not the expected ylids III and V (Figure 4.1);

Figure 4.1. Deprotonation of N-methyl methylphosphazenium quaternary salts to give exocyclic ylids, which then rearrange in situ to give azaphosphorin derivatives containing an endocyclic carbon atom.

instead, the initially formed ylids rearrange <u>in situ</u> displacing the methylated nitrogen atom from the ring, and forming the novel azaphosphorin derivatives IV and VI (Figure 4.1).

The analogous reaction between the diquaternary salt $(NPMe_2)_4 \cdot 2MeX$ (X=FSO$_3$, I) and NaN(SiMe$_3$)$_2$ is less successful. Although a reaction does take place, no characterizable materials have been isolated.

## 4.1.2 <u>Reaction of KOtBu with N-methyl Methylphosphazenium Salts</u>

Potassium t-butoxide can react with methylphosphazenium salts in at least two ways. It can act (a) as a base, removing a proton from an exocyclic methyl group, resulting, as above, in the formation of an azaphosphorin (i.e. IV (R=Me), VI), or (b) as a nucleophile, attacking directly at a phosphorus atom adjacent to the quaternized nitrogen. The products obtained from the reactions of $(NPMe_2)_{3,4} \cdot MeI$ and $(NPMe_2)_4 \cdot 2MeSO_3F$ with KOtBu demonstrate the occurrence of both possibilities, and indicate that their relative importance is strongly dependent on the size and charge of the phosphazenium cation.

The reaction of $(NPMe_2)_3 \cdot MeI$ with KOtBu illustrates one possible reaction pathway. Abstraction of a proton does not occur; instead, t-butoxide ion effects a nucleophilic attack on the phosphorus atom adjacent to the quaternized nitrogen cleaving the PN skeleton (Equation 2). The subsequent



$$(NHMe)(PMe_2N)_2 PMe_2O \quad \cdots 2$$
$$+$$
$$O(tBu)_2 \text{ or } Me_2CCH_2$$

elimination of isobutene (as in the reaction of chlorophosphazenes with NaOtBu[208]) or di-(t-butyl)ether (as in the reaction of phosphonium salts with t-butoxide ion[209]) then produces the novel linear phosphine oxide $(NHMe)(PMe_2N)_2PMe_2O$ in high yield (92%).

The reaction of the tetrameric quaternary salt $(NPMe_2)_4$.MeI with KOtBu (Equation 3) shows a marked contrast to the one just described. Nucleophilic attack of t-butoxide ion still occurs, to give the linear oxide $(NHMe)(PMe_2N)_3PMe_2O$, but the yield of this product is low (∼5%). The principal product (80%) is the cyclic triazatetraphosphorin $Me_7(NHMe)P_4N_3CH$, formed



(80%)

... 3

(NHMe)(PMe₂N)₃PMe₂O (~5%)
+
O(tBu)₂ or Me₂CCH₂

presumably by a deprotonation reaction and a phosphazene-phosphorin rearrangement (Figure 4.1).

The reaction of the diquaternary ion $[NPMe_2)_4.2Me]^{2+}$ with KOtBu

reflects the effect of an increase in charge on the tetrameric ring. Nucleophilic attack at phosphorus now predominates, the only product of the reaction, the linear oxide $(NHMe)PMe_2NPMe_2O$, indicating that ring cleavage has occurred in two places (Equation 4).

$$\text{[cyclic phosphazene structure]} \xrightarrow{\text{KOtBu}} \begin{array}{c} (NHMe)PMe_2NPMe_2O \\ + \\ O(tBu)_2 \text{ or } Me_2CCH_2 \end{array} \quad \ldots 4$$

### 4.1.3  Reaction of Methyllithium with N-methyl Methylphosphazenium Salts

The formation of complexes between lithium halides and phosphorus ylids is well known, and for this reason salt-free solutions of ylids cannot be obtained when alkyllithiums are used to deprotonate phosphonium salts. On the basis of n.m.r. measurements, a tetrahedral coordination of the ylid carbon atom has been proposed, the carbon-lithium bond being substantially covalent[210]. It can be inferred, therefore, that lithium salts can effectively reduce the nucleophilic character of an ylidic carbon atom. Accordingly, two deprotonation experiments using methyllithium as base have been carried out in order to determine if the presence of lithium ions, complexed to the initial product of the reaction (e.g. III and V, Figure 1), will sufficiently stabilize the latter to prevent its rearrangement into an

azaphosphorin. However, the results of these two reactions (see below) indicate that the presence of lithium does not interfere with the rearrangement step, since the azaphosphorins (e.g. IV and VI, Figure 4.1) are still produced.

The two experiments, involving the reaction of methyllithium with (a) $N_3P_3Ph_4Me_2$.MeI and (b) $(NPMe_2)_4$.MeI, both required an aqueous work-up in order to remove lithium ions from the reaction mixture. In experiment (a), the azaphosphorin (IV, R=Ph, Figure 1) itself was not obtained; instead, its hydroiodide $Me(NHMe)Ph_4P_3N_2CH$.HI was isolated[‡]. In experiment (b), hydrolysis of the initial product (VI, Figure 4.1) occurred during the aqueous extraction, yielding the linear phosphazene oxide $HO(PMe_2N)_3PMe_2O$. This hydrolysis reaction will be discussed in more detail in a later section.

## 4.1.4 Discussion

Simple Huckel M.O. calculations have shown[76] that, in quaternary phosphazenium salts, much of the positive charge of the cation is localized on nitrogen, as in N-alkyl pyridinium ions. However, for both types of system, their reaction with anionic reagents also depends on other factors.

For example, the reaction of N-alkyl pyridinium salts with base can occur in different ways[86,211]. (1) When a methyl group is present in the 2-position, deprotonation of that group takes place, to give a methide VII (which alkylates on carbon rather than on nitrogen, thereby conserving ring

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[‡] The formation of this salt, rather than the neutral compound, parallels the reaction of $N_4P_4Me_4(CH_2Li)_4$ and methyl iodide to give the dihydroiodide $N_4P_4Me_4Et_4$.2HI, and not the neutral $N_4P_4Me_4Et_4$.

aromaticity)[212]. (2) When an electron withdrawing substituent (e.g. a halogen) is present in the 2- (or 4-) position, the susceptibility of the molecule to nucleophilic attack at these positions is increased, and, in basic solution, such salts are hydrolysed to pyridones VIII[211]. If the alkyl group on nitrogen is such that the acidity of the $\alpha$-protons is enhanced by an electron withdrawal (as in the phenacyl salt $[C_5H_5NCH_2COPh]^+Br^-$), then deprotonation of the $\alpha$-carbon can occur, yielding a nitrogen ylid IX[86,213].

VII                     VIII                     IX

In the reactions of N-alkyl phosphazenium salts with bases, similar variations are observed. Deprotonation of a methyl group in the 2-position can occur, but so, also, can nucleophilic attack at phosphorus (when oxygen containing bases, such as KOtBu, are used). The dependence of these two alternatives on ring size is an interesting feature of these reactions, and reflects the importance of ring size variations in influencing the chemistry of phosphazenes (see Chapter 1). The $N_3P_3Me_7^+$ ion is apparently more susceptible to nucleophilic attack and ring opening than is $N_4P_4Me_9^+$, and it is believed that this tendency of the trimeric ring to cleavage may be related to the difficulties encountered in preparing trimeric alkylphosphazenes by substitution reactions.

In the case of N-methyl methylphosphazenium salts, deprotonation of the N-methyl group does not occur. When an N-ethyl group is present, reaction of the salt with base (Equation 5) eliminates ethylene and yields the neutral methylphosphazene (a Hofmann elimination). Attempts to prepare

$$[(NPMe_2)_4Et]^+I^- \xrightarrow[- HI]{Ag_2O} (NPMe_2)_4 + C_2H_4 \qquad \dots 5$$

nitrogen ylids from methylphosphazenium salts, using the N-ethylacetato derivatives $[(NPMe_2)_{3,4}CH_2COOEt]^+I^-$, have been unsuccessful. A reaction does take place, but no characterizable materials have been isolated.

The mechanism of the formation of azaphosphorins via the deprotonation of methylphosphazenium quaternary salts is not completely understood. As mentioned earlier, it seems likely that the initial step in the reaction (Equation 6) is the formation of an exocyclic ylid (X). The subsequent rearrangement of this intermediate into the final structure probably involves the nucleophilic attack of the exocyclic methylene group on an endocyclic phosphorus atom (XI), with the displacement of the quaternized nitrogen from the ring[‡].

The resulting azaphosphorin can then exist in two possible tautomeric forms, containing either an exocyclic methylimino (XII) or methylamino (XIII) group. In the absence of other effects, a P=N double bond can be considered stronger than a P=C double bond. This statement is

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[‡] Such a 4-centre mechanism is reminiscent of that proposed for the Wittig reaction[85].

supported by the structures of azaphospholes[214], which, in solution, exist
completely in the P=N form (XIV) rather than the P=C form (XV). However,
in the present system, the P=C bonded structure (XIII) is favoured (vide infra)

over the P=N bonded structure (XII), since it is only in that form that cyclic aromaticity is attained. However, in solution, proton transfer from the endocyclic carbon to the exocyclic nitrogen is sufficiently rapid to cause the collapse of $^1H$-$^1H$ coupling (see the following section).

Rearrangements of this type are not uncommon in phosphorus chemistry. For example, the ylid XVI (Equation 7) isomerizes (slowly at 25°C, rapidly at 120°C) into the six membered ring XIX[215]. The conversion is similar to that of the present reaction, and is suggested to be initiated by catalytic amounts of base, which produce the carbanion XVII. Nucleophilic



XVI                                    XVII                              .... 7

XIX                                    XVIII

attack of this carbanion on a silicon atom, followed by ring cleavage, then generates a new carbanion XVIII, which yields the final product XIX by reprotonation.

A 4-centre mechanism has also been suggested for the reaction of ammonia with bis-(diphenylphosphino)methane in carbon tetrachloride[216], to yield not the expected product $[NH_2P(Ph_2)=CH-P(Ph_2)NH_2]^+Cl^-$ but $[NH_2P(Ph_2)=N=P(Ph_2)CH_3]^+Cl^-$ (Equation 8). This same mechanism may also have a



... 8

bearing on the reaction of bis(diphenylphosphino)methylamine with chloramine and ammonia (Equation 9)[217]. Here also, a rearrangement occurs, the N-methyl group ostensibly migrating from the central nitrogen to a terminal nitrogen atom. As before, the driving force of the reaction is the formation of the resonance stabilized $[P=N=P]^+$ cation (cf. Chapter II, section 2.3), but whether it is the methyl group alone that migrates (as in the Stevens rearrangement[218]), or the entire -NMe- unit, has not been established.

$$MeN(PPh_2)_2 \xrightarrow[NH_2Cl]{NH_3} [(NHMe)P(Ph_2)NP(Ph_2)NH_2]^+Cl^- + NH_4Cl \qquad ... 9$$

In summary, the novel phosphazene-azaphosphorin rearrangement reported here is unique in phosphazene chemistry. The presence of sterically bulky groups on phosphorus (e.g. R=Ph, Equation 6), and the torsional restrictions of a six-membered PN ring do not impede the conversion, which is thought to occur in order to reestablish an aromatic $\pi$-system in the cyclic framework. The results of simple Huckel M.O. calculations (see Chapter V) on the exocyclic ylid (X) and azaphosphorin (XIII) structures support this argument.

## 4.2 $^1$H n.m.r. and Infrared Spectra of Azaphosphorins

### 4.2.1 $^1$H n.m.r. Spectra

The numerical details of the $^1$H n.m.r. spectra of the azaphosphorins $Me_{2n-1}(NHMe)P_nN_{n-1}CH$ (n=3,4) and $Me(NHMe)Ph_4P_3N_2CH$ are given in Table 4.1. The deceptively simple appearance of these spectra, run at ambient temperature on samples in deuterobenzene solution, reveals little resolution of the P-methyl signals, indicating that the perturbation of the charge distribution within the phosphazene skeleton, caused by the replacement of a nitrogen atom with a carbon atom, is small. In $Me_7(NHMe)P_4N_3CH$, for example, the P-methyl signals appear as an unresolved multiplet. In the case of $Me_5(NHMe)P_3N_2CH$, however, three closely spaced doublets, corresponding to the methyl groups on the three different phosphorus atoms, can be distinguished (Figure 4.2).

The chemical shift of the N-methyl protons ($\delta$=2.28-2.47 ppm) is similar to that found in $N_3P_3(NHMe)_6$ ($\delta_H(NMe)$=2.57 ppm[219]) and N-methylaniline ($\delta_H(NMe)$=2.67 ppm[220]). In all three types of molecule, $^1$H-$^1$H coupling between

Figure 4.2. $^{31}P$ decoupled 100 MHz $^1H$ n.m.r. spectrum (A) and ordinary 100 MHz $^1H$ n.m.r. spectrum (B) of $Me_5(NHMe)P_3N_2CH$. Spectra run on samples in benzene-$d_6$ solution.

Table 4.1 $^1$H n.m.r. parameters[a] and selected vibrational frequencies[b] of azaphosphorin derivatives.

| | $Me_5(NHMe)P_3N_2CH$ | $Me_7(NHMe)P_4N_3CH$ | $Me(NHMe)Ph_4P_3N_2CH$[f] |
|---|---|---|---|
| $\delta$(MeN) | 2.47 (14.0)[c] | 2.46 (13.0)[c] | 2.28 (14.0)[c] |
| $\delta$(MeP) | 1.45 (14.0) | ~1.42[e] | 1.43 (14.5) |
| $\delta$(Me$_2$P) | 1.32 (12.5) 1.39 (13.5) | ~1.42[e] | _ [d] |
| $\nu$(N-H) | 3180 | 3210 | 3195 |
| $\nu$(C-N) | 1081 | 1082 | 1067 |
| $\nu$(P=N) | 1159, 1187 | 1153, 1185 1209 | 1144, 1170 1191 |

(a) $\delta$(ppm), in $C_6D_6$, reference internal TMS.  J(PH) (in Hertz) in parenthesis.
(b) $\nu$(cm$^{-1}$) from nujol mull spectra, assignments tentative.  (c) No $^1$H-$^1$H coupling observed (at ambient temperature).  (d) $\delta$(Phenyl) $\sim$ 7.0-8.0 ppm.
(e) Unresolved multiplet.  (f) $\delta_H$(CH) = 1.23 ppm, $\delta_H$(NH) = 1.76 ppm.

the N-methyl and NH protons is not observed, but in the case of the azaphos-phorins $Me_{2n-1}(NHMe)P_nN_{n-1}CH$ (n=3,4), the actual resonance of the NH proton is also absent.  For $N_3P_3(NHMe)_6$ and $(NHMe)C_6H_5$, this phenomenon is similar, in origin, to the lack of coupling of OH protons in alcohols, and is accounted for by assuming a rapid intermolecular exchange of the NH protons.  For the present azaphosphorin system an exchange process is also postulated, but its explanation is more complicated.

The chemical shift of the protons attached to ylidic carbon atoms varies with the nature of the other groups on carbon.  In simple ylids

(e.g. $Me_3P=CHR^{210}$ and $Ph_3P=CH_2^{221}$) the anionic nature of the carbon atom has

a large shielding effect on the CH proton ($\delta_H$(CH)=-0.5 to -1.0 ppm). When

an electron withdrawing group is present on carbon the CH proton is less

shielded (e.g. $\delta_H$(CH) in $Ph_3P=CHC(O)Me$ is 6.32 ppm[222]). In phosphorins,

electron withdrawal also occurs, but to a lesser extent, and the CH resonance

is usually found in the region $\delta$ = 1.5-2.0 ppm[216,222]. Accordingly, the CH

signal of $Me(NHMe)Ph_4P_3N_2CH$ (in benzene solution) appears as a broadened singlet

(not the expected triplet) at $\delta$ = 1.23 ppm (Figure 4.3). For $Me_{2n-1}(NHMe)P_nN_{n-1}CH$

(n=3,4), no CH resonance is observed (although the possibility that it is

obscured by the P-methyl resonances cannot be entirely excluded).



Figure 4.3.    100 MHz $^1$H n.m.r. spectrum of $Me(NHMe)Ph_4P_3N_2CH$ ($C_6D_6$ solution). Phenyl region is not shown.

The absence of the CH (and NH) resonance from the $^1$H n.m.r. spectra of $Me_{2n-1}(NHMe)P_nN_{n-1}CH$ (n=3,4), its presence (as a broadened singlet) in the spectrum of $Me(NHMe)Ph_4P_3N_2CH$, and the lack of $^1$H-$^1$H coupling from the NH proton in all three molecules, can all be rationalized in terms of an intramolecular proton exchange between the exocyclic nitrogen and the endocyclic carbon (Equation 10). Proton exchange between nitrogen and carbon has already been reported for methylene diphosphine dioxides in the presence of aniline[223], and, in the present system, corresponds to the equilibrium between the amino and imino tautomeric forms referred to earlier (i.e. XII and XIII, Equation 6).

$$ \cdots 10 $$

This equilibrium is similar to that proposed for the sulphur ylid 3-dimethylsulphonioindole (XX), which rapidly incorporates deuterium into the S-methyl group when dissolved in deuterochloroform[224]. It is suggested that such an exchange requires (a) the intermediacy of the tautomer XXI (Equation 11),

$$ \cdots 11 $$

XX                    XXI

and (b) a sufficiently strong basic character to enable the compound to
deprotonate chloroform[‡].

The azaphosphorin $MeS(N_2P_2Ph_4)CH$[222,225] (XXII) provides a
combination of the structural features found in the previous two systems. The
CH resonance of this compound, as a broad singlet at $\delta = 1.6$ ppm, is similar
to that found in $Me(NHMe)Ph_4P_3N_2CH$, and its resolution into the expected
triplet cannot be achieved even at -30°C. As before, proton exchange
(Equation 12) between the two possible tautomers XXII and XXIII is believed to
account for this lack of resolution.



XXII                                        XXIII                    ... 12

In simple phosphorus ylids, the sensitivity of $^{31}P-^{1}H$ coupling to
traces of acid is well known[210,221,226]. For example, a rapid reversible
proton exchange, caused by the addition of methanol to a solution of
$Me_3P=CH_2$ in benzene results in the collapse of $^{31}P-^{1}H$ coupling to the methyl
groups, and the complete disappearance of the methylene signal[210]. A similar

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[‡] The azaphosphorins $Me_{2n-1}(NHMe)P_nN_{n-1}CH$ (n=3,4) decompose chloroform on
contact. $Me(NHMe)Ph_4P_3N_2CH$ is less basic, and is stable in chloroform solution
(but proton exchange may still occur).

effect can be produced, in the absence of acid, by warming the solution to 100°C.

Several workers[221,226,227] have found that the addition of base (e.g. aluminium oxide, butyllithium) to solutions of ylids suppresses such exchanges and aids in the enhancement of the otherwise unobserved fine structure of the resonances of ylidic protons. This effect has also been observed in the present work. Specifically, it has been found that the $^1$H n.m.r. spectrum of Me(NHMe)Ph$_4$P$_3$N$_2$CH in pyridine (Figure 4.4) displays much more resolution of fine structure than does the corresponding spectrum in benzene (Figure 4.3); $^1$H-$^1$H coupling is observed between the NH and N-methyl protons, and the triplet structure of the CH proton is clearly visible. As in the case of Me$_3$P=CH$_2$[210], an increase in temperature accelerates proton transfer; at 60°C, the spectrum of Me(NHMe)Ph$_4$P$_3$N$_2$CH shows the collapse of $^1$H-$^1$H coupling for the N-methyl group and of $^{31}$P-$^1$H coupling for the ylidic hydrogen. The temperature and solvent dependence of $\delta$(NH) is noteworthy; more detailed study of this phenomenon may provide more quantitative information on the exchange process.

The use of pyridine as solvent has no significant effect on the $^1$H n.m.r. spectra of methylated azaphosphorins Me$_{2n-1}$(NHMe)P$_n$N$_{n-1}$CH (n=3,4). These derivatives are much more basic than pyridine, and will compete successfully with it for traces of acid. Proton exchange between the two tautomeric forms XII and XIII is not, therefore, inhibited.

In summary, the $^1$H n.m.r. spectra of the azaphosphorins prepared in this work are consistent with the existence, in solution, of an acid-catalysed proton exchange between two tautomeric forms. In the strongly basic methylated

Figure 4.4. 220 MHz $^1$H n.m.r. spectrum of Me(NHMe)Ph$_4$P$_3$N$_2$CH in pyridine-d$_5$ solution, (A) at 20°C and (B) at 60°C.

compounds $Me_{2n-1}(NHMe)P_nN_{n-1}CH$ (N=3,4), the exchange is fast enough to prevent the observation of the NH and CH resonances. The phenylated derivative $Me(NHMe)Ph_4P_3N_2CH$ is less basic, and the exchange is consequently slower; the NH and CH resonances are therefore observed as broad unresolved singlets (in benzene). The use of pyridine as solvent further slows the exchange, and allows the resolution of all the expected coupling of the CH and NH protons.

## 4.2.2. Infrared Spectra

Because of the low molecular symmetry of the azaphosphorin derivatives, their infrared spectra (on samples in nujol mulls) are complex, and the detailed assignment of vibrational modes is difficult and speculative. However, some vibrations (Table 4.1) can be assigned with reasonable certainty.

For all the compounds, the degeneracy of the $\nu(P=N)$ vibration is removed by the replacement of a ring nitrogen atom with a carbon atom. Consequently, the single $\nu(P=N)$ vibration observed in the parent phosphazene appears as a number of bands in the corresponding azaphosphorin.

The observation of a $\nu(N-H)$ vibration is an important feature of all the spectra. The frequency of this band at $\sim$3180 cm$^{-1}$ is similar to that found in N-alkyl phosphoramidates $R_2P(O)NHR$[228], and indicates the existence, in the solid state, of the amino tautomer (P-NHMe) rather than the imino structure (P=NMe). This conclusion is also supported by the frequency of the $\nu(N-C)$ vibration, which appears, in all the azaphosphorin derivatives, in the region 1067-1082 cm$^{-1}$. The validity of this assignment is confirmed by the infrared spectrum of the deuterated compound $Me_7(NHCD_3)P_4N_3CH$, in which the $\nu(N-C)$

frequency is lowered to 1037 cm$^{-1}$ [‡].

In N-alkyl phosphoramidates, the $\nu$(N-C) vibration is observed between 1020-1220[228,231], but in N-methyl phosphinimines, it occurs at much lower frequencies (e.g., 848 cm$^{-1}$ in $Ph_3PNMe$[232]), because of coupling with $\delta$(P=N). Hence the high value of $\nu$(N-C) found for the azaphosphorins confirms the existence of an exocyclic methylamino group (e.g. XIII) rather than an exocyclic methylimine.

## 4.3  Linear Phosphazene Oxides $X(PR_2N)_nPR_2O$:  Their Preparation, Structure and Spectra

Phosphazenes of formula $X(Ph_2PN)_nPPh_2O$ have been known for some time. The compound $ClPh_2PNPPh_2O$ was first prepared by the oxidation of diphenylchloro-phosphine with diphenylphosphinyl azide[236]. Various attempts to lengthen the chain in this molecule by the inclusion of more $(Ph_2PN)$ units have led not to the next member, $Cl(PPh_2N)_2PPh_2O$, but to the salt-like compound $Cl(PPh_2N)_3PPh_2O$[236,237]. The $^{31}P$ n.m.r. spectrum of this molecule displays only two signals, suggestive of the cyclic (XXIV) rather than the linear (XXV) structure. Its ionic nature is also apparent from the fact that the chlorine atom can be replaced by another anion without changing the i.r. spectrum

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[‡] $\nu$(C-N) in $MeNH_2$ is at 1044 cm$^{-1}$[229,230], and is reduced to 973 cm$^{-1}$ upon deuteration of the methyl group.

[‡‡] This is equivalent to the coupling found in simpler molecules, e.g. $\nu$(N-C) in $MeNH_2$ is at 1044 cm$^{-1}$[229,230], but is reduced to 910 cm$^{-1}$ in $MeN_3$[233], 921 cm$^{-1}$ in $MeNO_2$[234], and 928 cm$^{-1}$ in $MeNCO$[235].

XXIV

XXV

of the cation[237]. However, the reaction of $Cl(Ph_2PN)_3PPh_2O$ with amines and phenoxide ion leads to cleavage of the cyclic skeleton and the formation of the covalent linear oxides $X(PPh_2N)_3PPh_2O$ ($X=NH_2$, NHMe, $NMe_2$, OPh), the structures of which are confirmed by the presence of four distinct resonances in their $^{31}P$ n.m.r. spectra[237]. Hydrolysis of the chloro-compound leads to the corresponding hydroxy derivative $HO(PPh_2N)_3PPh_2O$[236,237]. This compound, and its congeners $HO(PPh_2N)_nPPh_2O$ (n=1,2) have also been isolated (in low yield) from other reactions[236,238]. Linear structures have also been proposed for these compounds, but no spectroscopic data has been reported to support this belief.

In the present work, the preparation of the oxides $MeHN(PMe_2N)_nPMe_2O$ (n=1,2,3), by the ring cleavage of N-methyl methylphosphazenium salts, is described. The hydroxy derivative $HO(PMe_2N)_3PMe_2O$ has also been isolated. This is the first report concerning fully methylated oxides of this type, possibly because, unlike their phenylated analogues, the compounds $X(PMe_2N)_nPMe_2O$ are all extremely hygroscopic, and therefore more difficult to handle. However, the presence in them of methyl rather than phenyl ligands makes them potentially more informative from a spectroscopic point of view. The details of their n.m.r. and infrared spectra are given in Table 4.2.

Table 4.2. $^{31}P^a$ and $^1H^b$ n.m.r. parameters, and selected infrared frequencies$^c$ of phosphazene oxides $X(PMe_2N)_nPMe_2O$.

| X= | HNMe | HNMe | HNMe | OH[‡] |
|---|---|---|---|---|
| n= | 1 | 2 | 3 | 3 |
| $\delta_P P_A$ | 81.7 | 98.0 | 101.8 | d |
| $\delta_P P_B$ | 81.2 | 85.3 | 98.3 | d |
| $\delta_P P_C$ | - | 80.9 | 87.28 | - |
| $\delta_P P_D$ | - | - | 80.7 | - |
| $\delta_H(Me_2P_A)$ | 1.22(13.5)$^e$ | 1.20(13.5)$^e$ | 1.18(13.0)$^e$ | 1.50(14.0) |
| $\delta_H(Me_2P_B)$ | 1.48(14.0) | 1.37(12.0)$^e$ | 1.36(13.0)$^e$ | 1.66(13.5) |
| $\delta_H(Me_2P_C)$ | - | 1.51(12.5) | 1.41(15.0)$^e$ | - |
| $\delta_H(Me_2P_D)$ | - | - | 1.50(15.0) | - |
| $\delta_H(MeN)$ | 2.51(13.0) | 2.47(14.0) | 2.49(14.0) | - |
| J(HH) | 7.0 | 8.5 | 6.0 | - |
| $\nu(P=N)$ | 1205 | 1220 | 1190,1220,1260 | 1202,1260 |
| $\nu(P=O)$ | 1150 | 1135 | 1135 | 1108 |
| $\nu(NH)$ | 3110 | 3130 | 3103 | f |

(a) $\delta$(ppm), in $CDCl_3$, reference external $P_4O_6$. Phosphorus atoms lettered alphabetically from the oxygen atom. (b) $\delta$(ppm), in $CD_3CN$, except ‡ in $CDCl_3$, reference internal TMS. J(PH), in Hertz, in parenthesis. (c) From nujol mulls, assignments tentative. (d) $\delta_P$ values unavailable. (e) J(PH) (long range) $\simeq 1.0$ Hz. (f) $\nu(OH) \simeq 2500$ cm$^{-1}$ (broad).

For the compounds $NHMe(PMe_2N)_nPMe_2O$ (n=1,2,3) a linear structure is indicated, since all the phosphorus atoms, and the $PMe_2$ protons, are inequivalent ($^1H$ n.m.r. assignments are consistent with the results of a single frequency $^{31}P$ decoupling experiment on $NHMe(PMe_2N)_2PMe_2O$). The shielding of the P-methyl protons increases with their proximity to the terminal oxygen atom, consistent with a polarization of charge through the molecule towards the more electronegative end, an effect which has already been suggested to account for the $^{31}P$ chemical shift variations in the phenylated oxides $X(PPh_2N)_3PPh_2O$[237]. The $\delta_p$ values of the methylated oxides $NHMe(PMe_2N)_nPMe_2O$ are therefore assigned by analogy with the above trends.

The $^1H$ n.m.r. spectrum of $HO(PMe_2N)_3PMe_2O$ differs from those of the other oxides. The presence of only two P-methyl signals indicates a rapid inter- or intramolecular hydrogen transfer between the terminal oxygens. The effect of such hydrogen bonding is also observed in $NH_2P(Ph_2)NP(Ph_2)NH$, which exhibits only one $^{31}P$ n.m.r. signal[239], and in $NHMePMe_2NPMe_2O$, where the two $^{31}P$ n.m.r. signals are almost coincident. Hydrogen bonding is also indicated, for all the compounds listed in Table 4.2, by the low value of $\nu(P=O)$ (1160 cm$^{-1}$ in $Me_3PO$[184,185]), the effect being greatest in the hydroxy derivative ($\nu(P=O)$=1108 cm$^{-1}$), as expected.

## 4.4 Reactions of Azaphosphorins

The chemical properties of the azaphosphorins prepared in this work are primarily those of a strong base. However, in order to understand the details of their behaviour as bases, the equilibrium between their imine and amine tautomeric forms must be considered, since, depending on the position

of this equilibrium, the reaction of the compounds can take place using either carbon or nitrogen as the primary basic centre. Hence, although their chemistry is related to that of simple ylids $R_3PCH_2$ and phosphorins (e.g. XXVI), it also displays features which are reminiscent of the behaviour of phosphinimines.



XXVI

For example, unlike simple phosphorus ylids, which are easily oxidized to phosphine oxides[240,241], the azaphosphorins do not react with molecular oxygen. Also in contrast to simple ylids, but like other phosphorins (e.g. XXVI)[242], they do not undergo the Wittig reaction, the P=C bond being insufficiently polar.

A number of reactions of the azaphosphorins have been studied in detail, and these are discussed in the following sections.

4.4.1 <u>Hydrolysis of Me$_{2n-1}$(NHMe)P$_n$N$_{n-1}$CH (n=3,4)</u>

The hydrolysis of the azaphosphorins Me$_{2n-1}$(NHMe)P$_n$N$_{n-1}$CH (n=3,4) in aqueous ethanol produces the corresponding cyclic phosphazene oxides XXVII and XXVIII. The ready loss of the exocyclic methylamino group from the molecules is in contrast to the hydrolytic stability of aminophosphazenes, and indicates the increased susceptibility of the aminated phosphorus atom in the

XXVII                    XXVIII

azaphosphorins to nucleophilic attack (e.g. by hydroxide ion). By analogy with the hydrolysis of simple phosphinimines[240,241], the reaction (Equation 13) probably proceeds by the preliminary protonation of either the imine or amine form. The intermediate hydroxide then decomposes, with the elimination of methylamine, to yield the exocyclic phosphoryl group.



... 13

It is interesting that the hydrolysis of these azaphosphorins leads to the rupture of the exocyclic P-N bond rather than the endocyclic P=C bond. By contrast, the hydrolysis of the phosphorin XXIX (Equation 14) leads to

cleavage of the cyclic skeleton, both a P=C and P=N bond being broken[216].
A similar mechanism may account for the anomalous hydrolysis of the lithium
iodide complex of $Me_7(NHMe)P_4N_3CH$ (see Section 4.1.3), which gives the linear
phosphazene oxide $HO(PMe_2N)_3PMe_2O$ (i.e. XXV, R=Me, X=OH).



XXIX

It is apparent that, in the azaphosphorin system, hydrolysis can
occur in two ways, (1) by loss of the exocyclic methylamino group, and (2)
initial cleavage of the endocyclic P=C bond, leading to ring opening.  A
similar situation has been reported for the hydrolysis of the di-imine
$PhN=P(Ph_2)CH_2P(Ph_2)=NPh$.  In basic solution, the expected diphosphine dioxide
is produced (Equation 15a), but under acidic conditions, hydrolysis results in
cleavage of a central P-C bond, and the formation of the simple oxides
$MePh_2PO$ and $(NHPh)Ph_2PO$ (Equation 15b)[243].  In the present case also, the
course of the hydrolysis reaction may be dependent on pH.  The sensitivity of
the amine-imine equilibrium to the nature of the solvent has already been
noted in the $^1H$ n.m.r. spectrum of $Me(NHMe)Ph_4P_3N_2CH$ (Section 4.2.1), and it
is likely that the influence of pH on the position of this equilibrium will
have profound effects on the chemical behaviour of the compounds.

$$O=P(Ph_2)CH_2P(Ph_2)=O \qquad \dots 15a$$

$$PhN=P(Ph_2)CH_2P(Ph_2)=NPh \quad \xrightarrow[\substack{H_2O \\ OH^-}]{} \quad$$

$$\xrightarrow[\substack{H_2O \\ H^+}]{} \quad (NHPh)Ph_2P=O \;+\; MePh_2P=O \qquad \dots 15b$$

### 4.4.2 Reaction of $Me_{2n-1}(NHMe)P_nN_{n-1}CH$ (n=3,4) with Methyl Iodide

As was mentioned in Chapter 1, the reaction of phosphorus ylids $R_3P=CHR$ with methyl iodide yields simple C-methylated phosphonium salts $[R_3PCHRMe]^+I^-$ [91-95]. Similarly, the azaphosphorin XXIX can be methylated (Equation 16) to give the expected phosphonium salt XXX. Deprotonation of this salt with ammonia then yields the neutral C-methyl phosphorin XXXI[216].



$$\dots 16$$

In the reaction of the azaphosphorins $Me_{2n-1}(NHMe)P_nN_{n-1}CH$ (n=3,4) with methyl iodide, simple methylation does occur, but the expected phosphonium salt XXXII is not isolated. It immediately undergoes a transylidation reaction (Equation 17) with a second mole of starting material to give the protonated salts XXXIV and XXXV, protonation taking place on carbon rather than on nitrogen. The occurrence of this transylidation reaction is unexpected, and indicates that, in this system, the normal order of acidities

XXXII

... 17

XXXIII

XXXIV

XXXV

(see Chapter 1) of C-methylated and C-protonated phosphonium salts is reversed. However, such behaviour is consistent with the acidities of aminophosphonium salts, e.g. the alkylation of simple phosphinimines is immediately followed by a proton transfer reaction with the starting material (Equation 18)[244,245]. This similarity between the protonated salts XXXIV and XXXV and simple aminophosphonium salts is interesting, and suggests that

although the protonation of the parent azaphosphorins occurs on carbon, the deprotonation of the resulting salts effects the removal of an NH proton rather than a CH proton.

$$R_3P{=}NH \ + \ RX \ \longrightarrow \ [R_3PNHR]^+X^-$$

$$[R_3PNHR]^+X^- \ + \ R_3P{=}NH \ \longrightarrow \ R_3P{=}NR \ + \ [R_3PNH_2]^+X^- \qquad \ldots \ 18$$

$$R_3P{=}NR \ + \ RX \ \longrightarrow \ [R_3PNR_2]^+X^-$$

The neutral products of the reaction of Equation 17 (XXXIII) have not been isolated. They also react with methyl iodide, and the phosphonium salts so formed then undergo a second transylidation reaction with the starting material. The observed stoichiometry of the overall reaction is as shown in Equation 19.

$$3Me_{2n-1}(NHMe)P_nN_{n-1}CH + 2MeI \longrightarrow 2Me_{2n-1}(NHMe)P_nN_{n-1}CH{\cdot}HI$$

$$\text{(n=3,4)} \qquad\qquad \text{+ unisolated neutral products} \qquad \ldots \ 19$$

### 4.4.3  Reaction of $Me_{2n-1}(NHMe)P_nN_{n-1}CH$ (n=3,4) with Benzoyl Chloride

In the reaction of the azaphosphorins $Me_{2n-1}(NHMe)P_nN_{n-1}CH$ (n=3,4) with methyl iodide, the reaction cannot be halted after the first stage (i.e. Equation 17), and the neutral C-methyl derivatives (XXXIII) have not been isolated. In order to confirm that that substitution does occur on carbon rather than nitrogen, a number of reactions have been carried out between $Me_{2n-1}(NHMe)P_nN_{n-1}CH$ (n=3,4) and benzoyl chloride, in the belief that the initially formed C-benzoylated derivatives would be less susceptible than their C-methylated analogues to further reaction.

In agreement with expectation, the reaction of benzoyl chloride and the tetrameric azaphosphorin, according to the stoichiometry shown in Equation 20, yields the C-benzoyl derivative $Me_7(NHMe)P_4N_3CCOPh$ (XXXVI). The reaction of the trimeric derivative with benzoyl chloride is more vigorous and, as with the reaction of the azaphosphorins with methyl iodide, cannot be halted at the first stage. Instead, the initially formed C-benzoyl derivative reacts with a second mole of benzoyl chloride (Equation 21), introducing a benzoyl group onto the exocyclic nitrogen, to give the N-benzoyl C-benzoyl azaphosphorin $Me_5(NMeCOPh)P_3N_2CCOPh$ (XXXVII).

$$2Me_7(NHMe)P_4N_3CH + PhCOCl \longrightarrow Me_7(NHMe)P_3N_2CCOPh \quad (XXXVI) \qquad \ldots 20$$
$$+ Me_7(NHMe)P_4N_3CH.HCl$$

$$3Me_5(NHMe)P_3N_2CH + 2PhCOCl \longrightarrow Me_5(NMeCOPh)P_3N_2CCOPh \quad (XXXVII) \qquad \ldots 21$$
$$+ 2Me_5(NHMe)P_3N_2CH.HCl$$
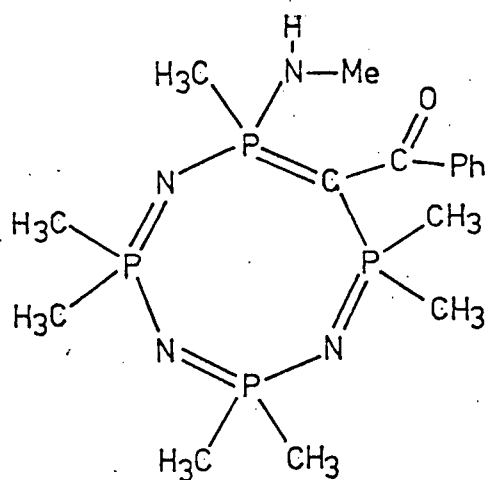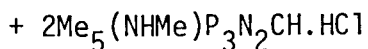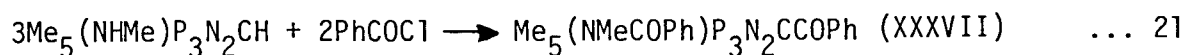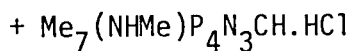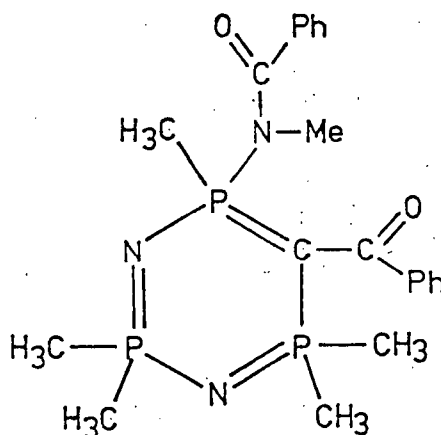


XXXVI



XXXVII

## 4.5 Spectra and Structure of Azaphosphorin Derivatives

### 4.5.1 $^1$H n.m.r. Spectra of Azaphosphorin Hydrohalides

The $^1$H n.m.r. spectra of the hydrohalides $Me_{2n-1}(NHMe)P_nN_{n-1}CH.HX$

(n=3,4; X=I,Cl) and $Me(NHMe)Ph_4P_3N_2CH.HI$ (Table 4.3) do not exhibit the effects

of proton exchange which are observed for the neutral azaphosphorins, and

are therefore more easily interpreted. Coupled with this simplification is

the advantage that, in the cations $[Me_{2n-1}(NHMe)P_nN_{n-1}CH_2]^+$ (n=3,4), the

cyclic charge distribution is less uniform than in the neutral compounds.

The differences in the magnetic environments of the formally distinct protons

are therefore greater, and allow the clear observation of individual resonances.

Although the absolute assignment of some of these resonances cannot be made

with complete certainty, their interpretation in terms of the proposed

structures is unambiguous.

The spectra of both the six- and eight-membered rings show the same

basic features (see Figure 4.5). The appearance of a complex multiplet at

$\delta \sim 2.8$ ppm, corresponding to the resonances of the methylene protons, is

important for two reasons; firstly because it indicates that protonation of

the neutral azaphosphorins occurs on the ring carbon atom, and secondly

because the AB coupling pattern (as revealed in the $^{31}$P decoupled spectra)

provides an absolute confirmation of the structure of the present

azaphosphorin system.

The magnetic inequivalence of seemingly identical nuclei has been

a subject of much interest[246], and is commonly observed in substituted

ethanes[247], but is also found in compounds of tri-[248] and penta-

coordinate[249,250] phosphorus. In the present case, the "intrinsic

Table 4.3 $^1$H n.m.r. parameters[a] of the azaphosphorin hydrohalides $Me_{2n-1}(NHMe)P_nN_{n-1}CH.HX$ and $Me(NHMe)Ph_4P_3N_2CH.HI$

| | $Me_5(NHMe)P_3N_2CH.HX$ | | $Me_7(NHMe)P_4N_3CH.HX$ | | $Me(NHMe)Ph_4P_3N_2CH.HI$ |
|---|---|---|---|---|---|
| X = | I | Cl | I | Cl | I[b] |
| $\delta$(MeN) | 2.65(13.5) | 2.63(13.5) | 2.62(13.0) | 2.57(13.5) | 2.19(14.5) |
| J(H-H) | 5.5 | 5.5 | 5.5 | 6.0 | 5.5 |
| $\delta$(HN) | 5.85 | 6.03 | 4.24 | 5.37 | 4.51 |
| $\delta$(MeP) | 1.99(13.0) | 1.99(13.5) | 1.96(13.5) | 2.04(13.5) | 1.83(14.5) |
| $\delta$(Me$_2$P)[c] | 1.86(13.5) | 1.79(14.0)[d] 1.73(14.0) | 1.79(13.5) | 1.78(13.5) | - |
| $\delta$(Me$_2$P')[c] | 1.58(14.0) | 1.53(14.0) | 1.53(13.5)[d] 1.49(13.5) | 1.58(15.0)[d] 1.51(15.0) | - |
| $\delta$(Me$_2$P")[c] | - | - | 1.49(13.5) | 1.51(15.0) | - |
| $\delta$(CH$_2$) H$_A$ | 3.74 (15.0,11.0) | 4.09 (14.0,11.0) | 3.75 (15.5,12.5) | 3.96 (15.0,12.0) | 3.77 (f) |
| H$_B$ | 2.78 (13.5,13.5) | 2.27 (14.0,13.5) | 3.05 (15.5,12.5) | 2.86 (15.0,13.0) | 3.55 (f) |
| $\delta$(H$_A$H$_B$) | 15.5 | 15.0 | 15.5 | 15.0 | 15.0 |

(a) $\delta$(ppm), in $CDCl_3$ solution, reference internal TMS. J(PH), in Hertz, in parenthesis. (b) Phenyl region omitted. (c) Absolute assignments of Me$_2$P, Me$_2$P' and Me$_2$P" protons are uncertain. (d) Methyl groups on the same phosphorus atom are magnetically inequivalent. (e) ABXY pattern, partially obscured by other signals; J(PH) values are approximate. (f) J(PH) values not assigned. In $CD_3CN$, H$_A$≡H$_B$, $\delta$ = 3.44 ppm, J(PH) = 13.0 Hz.
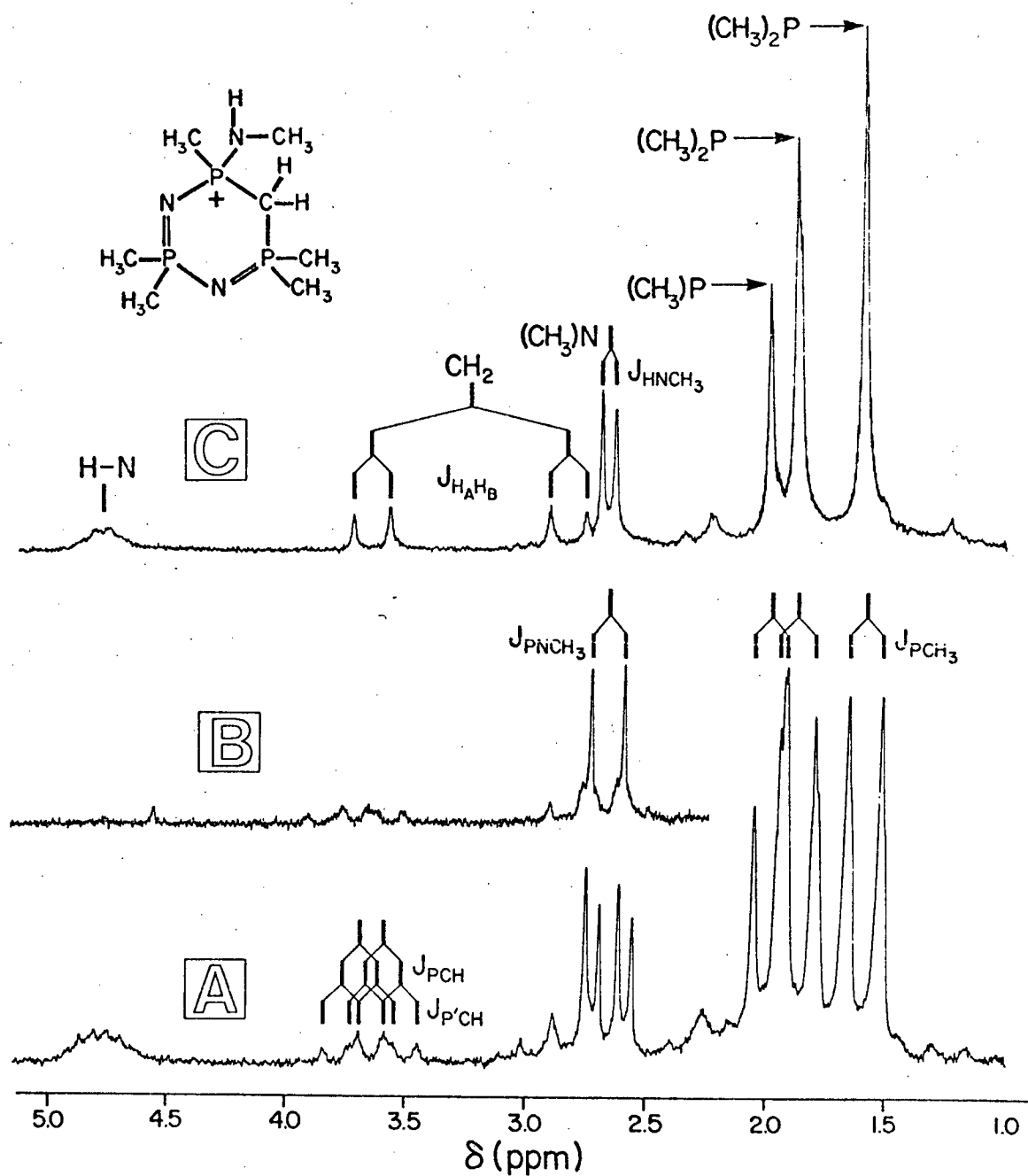
Figure 4.5. The 100 MHz $^1$H n.m.r. spectra of the azaphosphorin hydroiodide Me$_5$(NHMe)P$_3$N$_2$CH.HI, in CDCl$_3$ solution. (A) The ordinary high resolution spectrum, (B) the same spectrum with 1 drop of D$_2$O added, and (C) the $^{31}$P decoupled spectrum.

asymmetry"[251] of the methylene protons is caused by their interaction with

a phosphorus atom (the aminated atom) of low symmetry. As is demonstrated by

Figure 4.6, there are, theoretically, three rotational isomers for the

$-CH_2-P(NHMe)MeN=$ unit, but, because of the constraints of the cyclic

skeleton only two (A and C) are possible. It is readily apparent that, even

allowing for equal participation of both these structures, the average

environments of $H_a$ and $H_b$ are different.
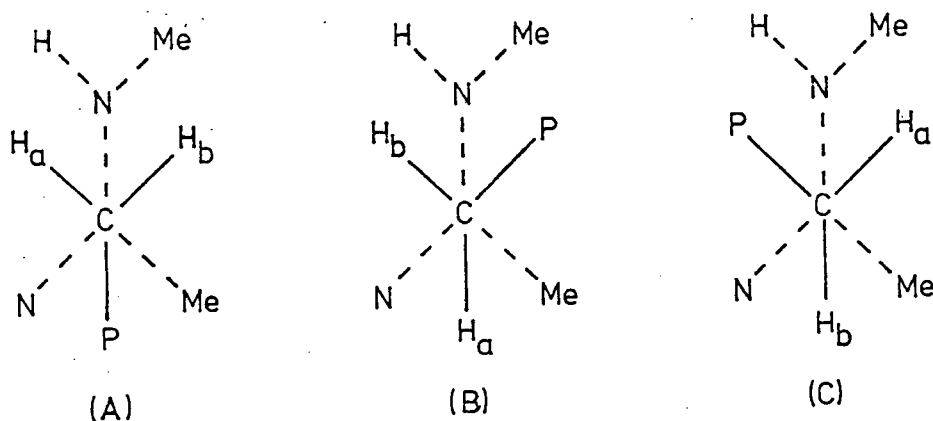


Figure 4.6.  Possible rotational isomers of the $CH_2-P(NHMe)MeN$ unit in the cations $[Me_{2n-1}(NHMe)P_nN_{n-1}CH_2]^+$ (n=3,4). In these structures, the methylene carbon atom is located above the aminated phosphorus atom (not shown).

The appearance and position of the resonance of the N-methyl protons

is similar to that found in simple phosphinimine salts (see Table 2.4),

exhibiting both $^{31}P-^1H$ and $^1H-^1H$ coupling. However, the addition of one

drop of $D_2O$ to a solution of $Me_5(NHMe)P_3N_2CH.HI$ in $CDCl_3$ brings about the

immediate collapse of $^1H-^1H$ coupling, and the loss of the NH resonance

(Figure 4.5B), indicating that proton exchange between the solvent and the

exocyclic nitrogen is rapid.

The methylene protons are expected to be less acidic, and their exchange with protic solvents is consequently slower, but the effect is nonetheless observable. For example, when $Me_5(NHMe)P_3N_2CH.HI$ is dissolved in $D_2O$, the methylene resonance appears as a simple triplet which, upon allowing the solution to stand, becomes less intense and finally vanishes (after about 2 hours).

4.5.2 $^1H$ n.m.r. Spectra of Phosphazene Oxides $Me_{2n-1}(O)P_nN_{n-1}CH_2$ (n=3,4)

As in the case of their parent azaphosphorins, the structures of the oxides $Me_{2n-1}(O)P_nN_{n-1}CH_2$ (n=3,4) can be represented by either of two tautomeric forms (XXXVIII or XXXIX). However, the appearance of characteristic methylene signals in their $^1H$ n.m.r. spectra (Table 4.4), and the absence of a $\nu(OH)$ band in their infrared spectra, clearly indicates that the equilibrium of Equation 22 favours the oxide structure (XXXIX).



XXXVIII          XXXIX          ... 22
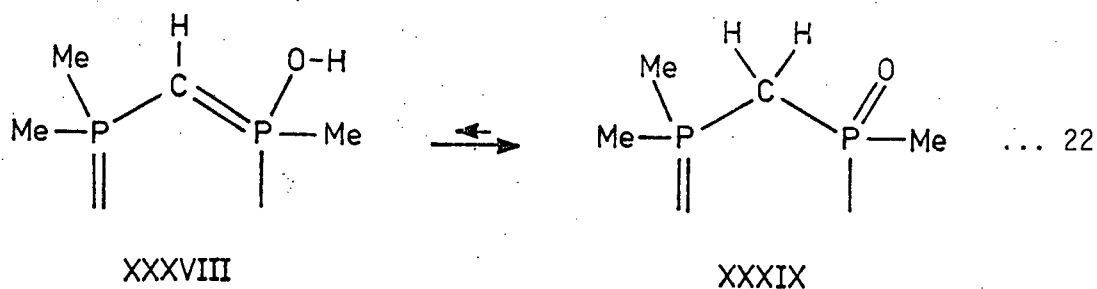
In the trimeric derivative, the methylene protons are magnetically inequivalent (as expected from structure XXXIX), and give rise to an AB coupling pattern. In the tetrameric oxide, some interaction of the methylene protons with oxygen is indicated, their equivalent resonances appearing (Figure 4.6) as a single triplet (due to $^{31}P$-$^1H$ coupling).

Table 4.4  $^{1}$H n.m.r. parameters$^{a}$ of phosphazene oxides $Me_{2n-1}(O)P_nN_{n-1}CH_2$ (n=3,4).

| | $\delta(CH_2)$ | $\delta(MeP)$ | $\delta(Me_2P)^b$ | $\delta(Me_2P')^b$ | $\delta(Me_2P'')^b$ |
|---|---|---|---|---|---|
| n = 3 | 1.95(13.5)$^c$ | 1.96(13.5) | 1.61(14.0) | 1.48(15.0)$^d$ | - |
| | 2.11(13.5) | | | 1.53(15.0) | |
| n = 4 | 2.31(12.5) | 1.94(13.0) | 1.63(14.0)$^e$ | 1.54(13.0)$^e$ | 1.47(14.0) |
| | | | 1.56(14.0) | 1.47(13.0) | |

(a) $\delta$(ppm) in CDCl$_3$ solution, reference internal TMS.  J(PH), in Hertz, in parenthesis.  (b) Absolute assignments of Me$_2$P, Me$_2$P' and Me$_2$P" protons are uncertain.  (c) ABXY pattern partially obscured by P-methyl resonances; J(PH) values are approximate; J(H$_A$H$_B$) = 13.5 Hz.  (d) Inequivalent geminal methyl groups displaying second order coupling.  (e) Inequivalent geminal methyl groups.

The position of the equilibrium of Equation 22 is in contrast to the imine-amine tautomerism of the azaphosphorin system, and indicates that the strength of the P=O bond in XXXXIX is sufficient to offset any increase in π-energy achieved by cyclic delocalization, as in XXXVIII$^{\ddagger}$.  Such is not the case in the phosphazenes $Ph_6(OH)_2P_4N_4$ (non-geminal) and $Ph_5(OH)P_3N_3$, for which the hydroxy (XL) rather than the oxide (XLI) structure has been proposed[160,253] (Equation 23).  For these latter compounds, the higher electronegativity of nitrogen (as compared to carbon), and its greater ability

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$\ddagger$ D(P=O) in Me$_3$P=O is 139.3 Kcal/mole, whereas D(P=N) in Me$_3$P=NEt is 97 Kcal/mole[252].
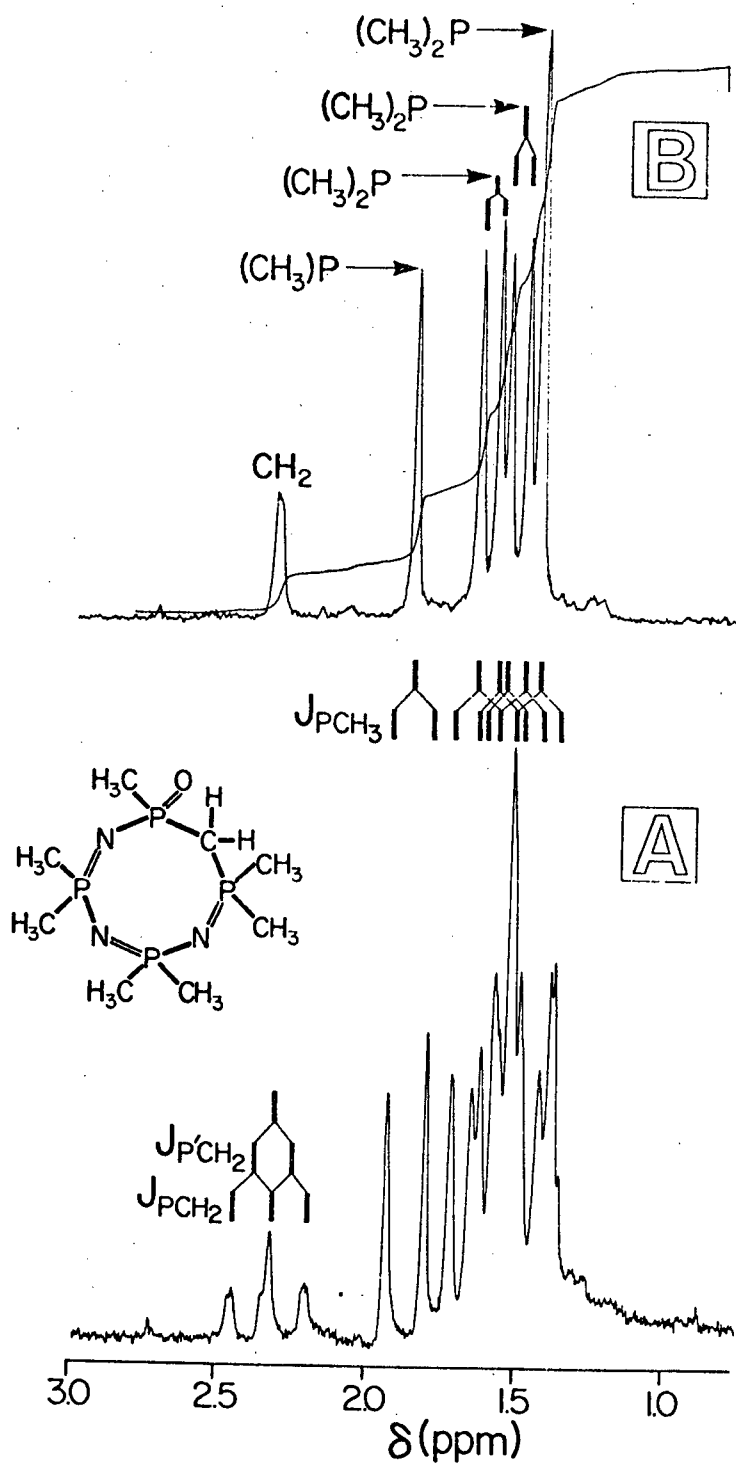
Figure 4.7. The 100 MHz $^1$H n.m.r. spectrum of the phosphazene oxide Me$_7$(O)P$_4$N$_3$CH$_2$, in CDCl$_3$ solution. (A) The ordinary high resolution spectrum, and (B) the $^{31}$P decoupled spectrum.

in forming $\pi$-bonds to phosphorus, is thought to account for the stability of the hydroxy form.

Ph—P(Ph)(=O)—N=P(O-H)(Ph)—Ph  $\rightleftharpoons$  Ph—P(Ph)(=O)—N(H)—P(=O)(Ph)—Ph  ... 23

XL                                         XLI
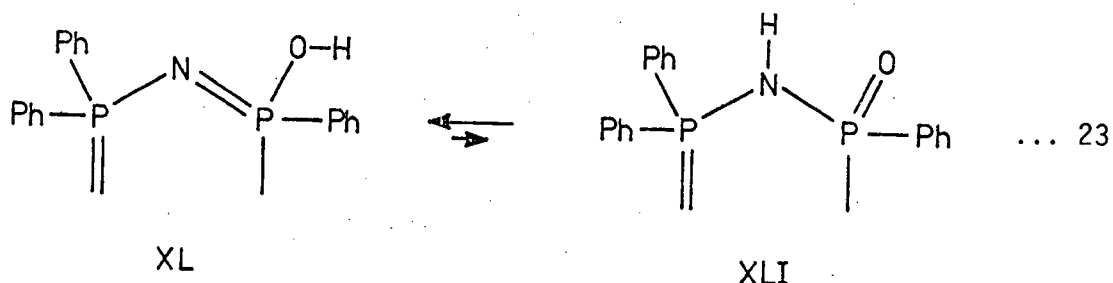
### 4.5.3 $^1$H n.m.r. Spectra of Benzoylated Azaphosphorins

As in the case of their parent azaphosphorins, the $^1$H n.m.r. spectra of the benzoylated derivatives $Me_5(NMeCOPh)P_3N_2CCOPh$ and $Me_7(NHMe)P_4N_3CCOPh$ (Table 4.5) reveal very little resolution of the P-methyl resonances, thereby indicating the uniformity of the charge distribution within the ring. For the tetrameric compound $^1$H-$^1$H coupling between the NH and N-methyl protons is observed (as it is in simple N-methyl amides); proton exchange between nitrogen and the benzoylated carbon is obviously suppressed by the low basicity of the latter. The shielding of the N-methyl protons in $Me_5(NMeCOPh)P_3N_2CCOPh$ ($\delta=2.50$ ppm) is greater than in N-methyl benzanilide ($\delta=3.40$ ppm[‡]), indicating that the diffusion of lone pair density from nitrogen to phosphorus is limited.

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[‡] On a sample in CDCl$_3$ solution. The compound was prepared by the benzoylation of N-methyl aniline[254].

Table 4.5  $^1$H n.m.r. parameters[a] and carbonyl stretching frequencies[b] of $Me_5(NMeCOPh)P_3N_2CCOPh$ and $Me_7(NHMe)P_4N_3CCOPh$.

|  | δ(MeN) | δ(MeP) | δ(Me$_2$P)[c] | ν(C=O) |
|---|---|---|---|---|
|  |  |  | 1.64(13.5) |  |
|  |  |  | 1.60(13.0) | 1502 |
| $Me_5(NMeCOPh)P_3N_2CCOPh$ | 2.50(9.0) | 1.70(15.0) | 1.55(13.5) | 1642 |
|  |  |  | 1.48(13.0) |  |
| $Me_7(NHMe)P_4N_3CCOPh$ | 2.46(14.0)[d] | e | e | 1530 |

(a) δ(ppm) in CDCl$_3$ solution, reference internal TMS.  J(PH), in Hertz, in parenthesis.  (b) ν(C=O) in cm$^{-1}$, from nujol mull spectra.  (c) Absolute assignments are uncertain.  (d) J(HH) = 5.5 Hz, δ(NH) = 2.70 ppm.  (e) All P-methyl resonances occur as an unresolved multiplet near δ = 1.55 ppm.

## 4.5.4  Infrared Spectra of Benzoylated Azaphosphorins

As with the other azaphosphorin derivatives, the infrared spectra of $Me_5(NMeCOPh)P_3N_2CCOPh$ and $Me_7(NHMe)P_4N_3CCOPh$ are too complex to allow a detailed interpretation.  However, their carbonyl stretching frequencies (Table 4.5) are well isolated and can be easily identified.  For both the trimeric and tetrameric derivatives, the betaine (XLII) carbonyl frequency is similar to that found in acylated ylids[84,255,256], and reflects the extent to which resonance structures such as XLIII (Equation 24) weaken the C=O bond.  The lower frequency found in the trimeric compound suggests that electron release onto the C-benzoyl group is greater for the six-membered ring.
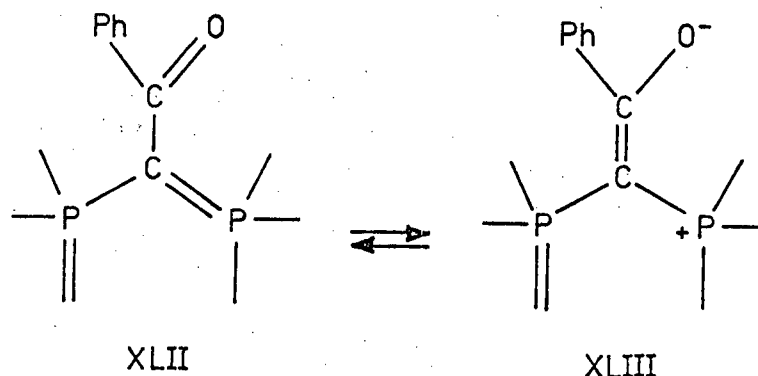
The amide carbonyl frequency of $Me_5(NMeCOPh)P_3N_2CCOPh$ (1642 $cm^{-1}$) is similar to that found in simple tertiary amides ($\nu(C=O)$ in $PhCONMe_2$ is 1640 $cm^{-1}$ [257], and, in PhCONMePh, is 1653 $cm^{-1}$ [‡]). In these latter compounds, the presence of an N-phenyl group produces an increase in $\nu(C=O)$, the competitive effect of the aromatic ring for the nitrogen lone pair reducing the influence of the ionic form $Ph-\overset{+}{N}=\overset{}{C}-O^-$ [259]. The relatively low value of the amide carbonyl frequency in $Me_5(NMeCOPh)P_3N_2CCOPh$ suggests that similar conjugative interactions, between phosphorus and nitrogen, are limited.

## 4.6 Experimental

Nearly all of the products and/or reactants in the following reactions were found to be sensitive to moisture and, in some cases, to oxygen. They were therefore manipulated in an oxygen-free dry box, and the reactions themselves were carried out under an atmosphere of dry nitrogen. The methylphosphazenium quaternary salts were prepared as described in Chapter II. Sodium metal, hexamethyldisilazane, methyl iodide and benzoyl chloride were commercial products, and were used without further purification.

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[‡] From the present work; the value quoted is from a sample in $CCl_4$ solution (in nujol mull, $\nu(C=O)$ is 1650 $cm^{-1}$). An earlier report[258] gave a lower value of 1641 $cm^{-1}$.

Potassium t-butoxide was also obtained commercially, but was purified by sublimation $\underline{\text{in}}$ $\underline{\text{vacuo}}$ before use[165]. The solvents hexane and octane were reagent grade and were not subjected to any drying procedures. Toluene, however, was dried by distillation from sodium, and diethyl ether by distillation from lithium aluminium hydride.

### 4.6.1   Reaction of $NaN(SiMe_3)_2$ with Methylphosphazenium Quaternary Salts

The following reactions all involve the same experimental procedure. Therefore, only one reaction (4.6.1.1) will be described in detail. The later experiments (4.6.1.1 to 4.6.1.5) were performed in an analogous fashion.

### 4.6.1.1  Reaction of $NaN(SiMe_3)_2$ with $(NPMe_2)_4.MeI$

Freshly cut sodium (0.200 g, 8.69 mmol) was added to a slurry of $(NPMe_2)_4.MeI$ (3.54 g, 8.01 mmol) in 200 ml of octane, and the mixture heated to the reflux temperature, whereupon $\sim \frac{1}{2}$ ml of $HN(SiMe_3)$ was injected, via a syringe and septum, into the reaction vessel. In practice, it was not necessary to add the correct stoichiometric amount of $HN(SiMe_3)_2$, since it was regenerated in the course of the reaction. However, to avoid possible evaporation losses (from boiling octane), further small additions ($\sim \frac{1}{2}$ ml) of $HN(SiMe_3)_2$ were made every 24 hours, in order to ensure an adequate supply. After 72 hours, the reaction mixture was cooled and filtered, and the solvent distilled from the filtrate to leave a white solid, which was purified by sublimation at $\sim 130°/0.01$ Torr and recrystallization from hot hexane to give colourless hygroscopic prisms of $Me_7(NHMe)P_4N_3CH$ (2.21 g, 7.04 mmol, 88%).

Anal. calcd. for $C_9H_{26}N_4P_4$: C, 34.29; H, 8.63; N, 17.77. Found: C, 34.44; H, 8.54; N, 17.57. M.pt. 104-105°C.

## 4.6.1.2 Reaction of $(NPMe_2)_3$.MeI with $NaN(SiMe_3)_2$

Powdered $(NPMe_2)_3$.MeI (5.107 g, 13.9 mmol) was allowed to react with sodium (0.352 g, 15.3 mmol) in 200 ml of octane. After 96 hours, the mixture was filtered (while still hot, to avoid recrystallization of the product) and the solvent distilled from the filtrate to leave a white solid, which was purified by sublimation at ∼130°C/0.01 Torr and recrystallization from hot hexane to give colourless hygroscopic plates of $Me_5(NHMe)P_3N_2CH$ (2.68 g, 11.2 mmol, 80%). Anal. calcd. for $C_7H_{20}N_3P_3$: C, 35.15; H, 8.43; N, 17.57. Found: C, 35.40; H, 8.50; N, 17.58. M.pt. 140-142°C.

## 4.6.1.3 Reaction of $Me_2Ph_4P_3N_3$.MeI with $NaN(SiMe_3)_2$

A sample of $Me_2Ph_4P_3N_3$.MeI (recrystallized from ethanol and powdered and dried at 100°C/760 Torr for 24 hours) (1.335 g, 2.17 mmol) and sodium (0.060 g, 2.61 mmol) were allowed to react together in 60 ml of boiling toluene. After 24 hours the mixture was filtered and the solvent distilled from the filtrate to leave a white solid which was purified by recrystallization from benzene/octane to give colourless prisms of $Me(NHMe)Ph_4P_3N_2CH$ (0.953 g, 2.01 mmol, 93%). Anal. calcd. for $C_{27}H_{28}N_4P_3$: C, 66.10; H, 5.33; N, 8.89. Found: C, 65.93; H, 5.55; N, 8.65. M.pt. 147-149°C.

## 4.6.1.4 Reaction of $(NPMe_2)_4$.2MeX with $NaN(SiMe_3)_2$

In two separate experiments $(NPMe_2)_4$.2MeSO$_3$F (a) and $(NPMe_2)_4$.2MeI (b) were allowed to react with 2 molar equivalents of sodium in boiling octane.

In experiment (a), after heating the mixture under reflux for 72 hours, a brown octane insoluble paste was left in the reaction flask, and no product was isolated upon removal of the solvent from the solution. In experiment (b), an octane soluble extract was isolated, but this consisted of an uncharacterizable oil.

### 4.6.1.5  Reaction of [(NPMe$_2$)$_{3,4}$.CH$_2$COOEt]$^+$I$^-$ with NaN(SiMe$_3$)$_2$

Equimolar quantities of [NPMe$_2$)$_{3,4}$.CH$_2$COOEt]$^+$I$^-$ and sodium were allowed to react in a slurry of boiling toluene. After 96 hours, the solution was separated from the residues, but evaporation of the solvent yielded only a small quantity of a brown tar.

### 4.6.2  Reaction of (NPMe$_2$)$_4$.MeI with KOtBu

Finely powdered (NPMe$_2$)$_4$.MeI (3.00 g, 6.80 mmol) was added to a slurry of KOtBu (0.839, 7.39 mmol) in 100 ml of hexane and the mixture heated under reflux for 24 hours. The mixture was filtered and the solvent distilled from the filtrate to leave a white solid (1.82 g) which was sublimed at $\sim$130°C/0.01 Torr onto a water cooled cold finger. The sublimate was recrystallized from hot hexane to give Me$_7$(NHMe)P$_4$N$_3$CH (1.71 g, 5.44 mmol, 80%), which was identified by comparison of its infrared spectrum with that of an authentic sample, and by its melting point, 104-105°C. The residual oil remaining in the sublimation vessel solidified into a white solid, which was purified by recrystallization from hot hexane to give colourless hygroscopic cubes of NHMe(PMe$_2$N)$_3$PMe$_2$O (0.11 g, 0.33 mmol, 5%). Anal. calcd. for C$_9$H$_{28}$N$_4$OP$_4$:  C, 32.50; H, 8.49; N, 16.86.  Found:  C, 32.62; H, 8.57; N, 16.89.  M.pt. 72-74°C.

### 4.6.3   Reaction of (NPMe$_2$)$_3$.MeI with KOtBu

Similarly, (NPMe$_2$)$_3$.MeI (1.38 g, 3.76 mmol) was allowed to react with a slurry of KOtBu (0.50 g, 4.46 mmol) in 50 ml of hexane.  After 24 hours, the mixture was filtered and the solvent removed from the filtrate to leave a colourless oil.  Sublimation of this oil at ∿130°/0.01 Torr onto a cold finger at -78°C yielded a white hygroscopic solid, NHMe(PMe$_2$N)$_2$PMe$_2$O (0.886 g, 3,44 mmol. 92%), which was recrystallized as colourless plates by cooling a concentrated solution of it in pentane to -23°C.  Anal. calcd. for C$_7$H$_{22}$N$_3$OP$_3$: C, 32.69; H, 8.62; N, 16.34.  Found:  C, 32.58; H, 8.52; N, 16.0. M.pt.  35-37°C.

### 4.6.4   Reactions of (NPMe$_2$)$_4$.2MeSO$_3$F with KOtBu

In a similar experiment, (NPMe$_2$)$_4$.2MeSO$_3$F (2.70 g, 5.12 mmol) was allowed to react with a slurry of KOtBu (1.30 g, 11.6 mmol) in 60 ml of hexane.  After 24 hours, the solution was decanted from the pasty residue, and the solvent distilled from the solution to yield a white solid, which was recrystallized from hot hexane to give colourless feather-like crystals of NHMe(PMe$_2$N)PMe$_2$O (0.927 g, 5.02 mmol, 50%).  Anal. calcd. for C$_5$H$_{16}$N$_2$OP$_2$: C, 39.97; H, 8.85; N, 15.38.  Found:  C, 33.28; H, 8.94; N, 15.25. M.pt.  73-75°C.

### 4.6.5   Reaction of (NPMe$_2$)$_4$.MeI with Methyllithium

A solution of methyllithium in diethyl ether (8.3 ml, 5.5 mmol of MeLi) was added to a slurry of (NPMe$_2$)$_4$.MeI (2.225 g, 5.03 mmol) in 125 ml of ether.  After a few moments, effervescence was observed in the reaction

mixture. The mixture was heated under reflux for 2 hours, and then quenched by the addition of 20 ml of water. Potassium fluoride (250 mg) was added to the aqueous layer, and after filtration of the solution from the precipitated lithium fluoride, the filtrate was evaporated to dryness (<u>in vacuo</u>). The residual solid was extracted with benzene to yield as the benzene soluble part a colourless, hygroscopic crystalline solid, which was recrystallized from benzene/octane as $HO(PMe_2N)_3PMe_2O$ (0.50 g, 1.5 mmol, 30%). Anal. calcd. for $C_8H_{25}N_3O_2P_4$: C, 30.10; H, 7.89; N, 13.16. Found: C, 29.87; H, 7.94; N, 13.08. M.pt. 96-100°C.

### 4.6.6 Reaction of $Me_2Ph_4P_3N_3$.MeI with Methyllithium

A solution of methyllithium in ether (4.4 ml, 1.54 mmol) was added to a slurry of $Me_2Ph_4P_3N_3$.MeI (0.784 g, 1.40 mmol) in 50 ml of ether. After 24 hours, the mixture was quenched with 50 ml of water, producing a white solid which was insoluble in both solvents. This solid was washed with benzene to leave, as a benzene insoluble part, $Me(NHMe)Ph_4P_3N_2CH$.HI (0.319 g, 0.52 mmol, 34%), which was recrystallized from acetonitrile/toluene as colourless blocks. Anal. calcd. for $C_{27}H_{30}IN_3P_3$: C, 52.70; H, 4.75; I, 20.62; N, 6.83. Found: C, 52.57; H, 4.80; I, 20.45; N, 6.67. Dec. 248-252°C.

### 4.6.7 Hydrolysis of $Me_{2n-1}(NHMe)P_nN_{n-1}CH$ (n=3,4)

A sample (300-400 mg) of $Me_{2n-1}(NHMe)P_nN_{n-1}CH$ (n=3,4) was dissolved in 25 ml of a 50/50 ethanol-water mixture and the solution left to stir overnight. The following day, the solvent was removed at room temperature

in vacuo to leave a white solid. For n=3, recrystallization of this solid from benzene gave colourless hygroscopic blocks of $Me_5(O)P_3N_2CH_2$. Anal. calcd. for $C_6H_{17}N_2OP_3$: C, 31.87; H, 7.58; N, 12.39. Found: C, 32.20; H, 7.59; N, 12.28. M. pt. 184-186°C. For n = 4, recrystallization of the solid from hot hexane gave colourless feather-like crystals of $Me_7(O)P_4N_3CH_2$. Anal. calcd. for $C_8H_{23}N_3OP_4$: C, 31.90; H, 7.70; N, 13.95. Found: C, 32.12; H, 7.91; N, 13.98. M.pt. 140-143°C.

### 4.6.8 Reaction of $Me_{2n-1}(NHMe)P_nN_{n-1}CH$ (n=3,4) with Methyl Iodide

The addition of an excess of methyl iodide to a solution of $Me_{2n-1}(NHMe)P_nN_{n-1}CH$ (n=3,4) in ether resulted in the precipitation of the hydroiodide salts $Me_{2n-1}(NHMe)P_nN_{n-1}CH.HI$ (n=3,4). For n = 3, 4.33 mmol (1.04 g) of the azaphosphorin was converted into 2.70 mmol (0.990 g) of the hydroiodide. Similarly for n = 4, 1.39 mmol (0.438 g) of the azaphosphorin yielded 0.973 mmol (0.430 g) of the hydroiodide. Attempts to isolate that part of reacted azaphosphorin (approximately ⅓ of the quantity of starting material) (see Text, Section 4.4.2) which remained in solution were unsuccessful. Both hydroiodides are air-stable crystalline solids which can be recrystallized from acetonitrile/toluene. For n = 3, anal. calcd. for $C_7H_{21}IN_3P_3$: C, 22.90; H, 5.77; I, 34.57; N, 11.45. Found: C, 22.96; H, 5.88; I, 34.20; N, 11.30. M.pt. 194-195°C. For n = 4, anal. calcd. for $C_9H_{27}IN_4P_4$: C, 24.45; H, 6.15; I, 28.70; N, 12.67. Found: C, 24.52; H, 6.30; I, 28.55; N, 12.57. M.pt. 155-156°C.

## 4.6.9  Reaction of Me$_7$(NHMe)P$_4$N$_3$CH with Benzoyl Chloride

A solution of benzoyl chloride (0.124 g, 0.88 mmol) in 10 ml of ether was added dropwise to a stirred solution of Me$_7$(NHMe)P$_4$N$_3$CH (0.555 g, 1.77 mmol) in 50 ml of ether. A fine white precipitate was immediately formed. After 3 hours the mixture was filtered to yield a white hygroscopic solid, which was recrystallized from acetonitrile/benzene to give small colourless cubes of Me$_7$(NHMe)P$_4$N$_3$CH.HCl (0.256 g, 0.73 mmol). Anal. calcd. for C$_9$H$_{27}$ClN$_4$P$_4$: C, 30.82; H, 7.76; N, 15.98. Found: C, 30.86; H, 7.66; N, 15.87. M. pt. 193-195°C. The solvent was distilled from the filtrate to leave a yellow oil which, on drying in vacuo, solidified into a yellow, air stable powder. Recrystallization of this solid from hot hexane yielded yellow mica-like plates of Me$_7$(NHMe)P$_4$N$_3$CCOPh. Anal. calcd. for C$_{16}$H$_{30}$N$_4$OP$_4$: C, 45.98; H, 7.23; N, 13.39. Found: C, 45.73; H, 7.30; N, 13.10. M.pt. 133-134°C.

## 4.6.10  Reaction of Me$_5$(NHMe)P$_3$N$_2$CH with Benzoyl Chloride

## 4.6.10.1  Ratio of PhCOCl:Me$_5$(NHMe)P$_3$N$_2$CH = 1:2

A solution of PhCOCl (0.178 g, 1.26 mmol) in 20 ml of ether was added dropwise to a stirred solution of Me$_5$(NHMe)P$_3$N$_2$CH (0.609 g, 2.55 mmol) in 100 ml of ether. A white precipitate was immediately produced. After three hours the mixture was filtered, and residue recrystallized from acetonitrile/benzene to give colourless hygroscopic cubes of Me$_5$(NHMe)P$_3$N$_2$CH . HCl (0.569 g, 2.07 mmol; expected yield = 1.26 mmol). Anal. calcd. for C$_7$H$_{21}$ClN$_3$P$_3$: C, 30.50; H, 7.68; Cl, 12.86; N, 15.24. Found: C, 30.20; H, 7.80; Cl, 12.55; N, 15.00. M.pt. 194-197°C. The

solvent was distilled from the filtrate to leave a yellow paste (0.26 g) from which a small quantity (0.041 g) of a white air-stable solid was obtained by the addition of hexane. This solid was recrystallized from hot benzene/ octane to give colourless blocks of $Me_5(NMeCOPh)P_3N_2CCOPh$. Anal. calcd. for $C_{21}H_{28}N_3O_2P_3$: C, 56.38; H, 6.32; N, 9.39. Found: C, 56.13; H, 6.20; N, 9.60. Dec. 181-184°C.

### 4.6.10.2  Ratio of $PhCOCl:Me_5(NHMe)P_3N_2CH$ = 2:3

A solution of benzoyl chloride (0.211 g, 1.49 mmol) in 20 ml of ether was added dropwise to a stirred solution of $Me_5(NHMe)P_3N_2CH$ (0.540, 2.25 mmol) in 100 ml of ether. After three hours the mixture was filtered to leave, as above, $Me_5(NHMe)P_3N_2CH \cdot HCl$ (0.452 g, 1.64 mmol, expected yield = 1.49 mmol). Distillation of the solvent from the filtrate left crude $Me_5(NMeCOPh)P_3N_2CCOPh$ (0.261 g, 0.59 mmol, expected yield = 0.75 mmol), which was purified as described above (Section 4.6.10.1).

CHAPTER V

MOLECULAR STRUCTURES OF METHYLPHOSPHAZENES

AND METHYLAZAPHOSPHORINS

The physical and chemical properties referred to in earlier chapters provide substantial evidence for the existence of a delocalized π-system in phosphazenes. More detailed information concerning the extent and nature of π-bonding comes from the study of their molecular structures, and towards this end the crystal and molecular structures of a number of the compounds prepared in this work have recently been determined. The purpose of the present chapter is to describe and discuss the salient features of these structures, and relate them, where possible, to the current theories on bonding in phosphazene derivatives.

## 5.1 Conformations of Methylphosphazenes

The relatively high melting points of the methylphosphazenes are in contrast to the properties of many other phosphazenes $(NPX_2)_n$ (e.g. F, Cl), and to the isoelectronic series of siloxanes $(OSiMe_2)_n$[260], which are noted for their extreme flexibility[261,262]. This difference in behaviour, which can be attributed to the high polarity of the P=N bond in methylphosphazenes[‡], is

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[‡] Although σ-polarity is expected to be greater in siloxanes, the added effect of π-polarity in phosphazenes makes the P=N bond more polar (e.g. the bond moment of dimethylsiloxanes has been estimated at 2.2D[263], whereas the P=N bond moment in phosphinimines is greater than 4D[264,265].

particularly useful from a structural point of view, since it allows a detailed comparison of the molecular structures of different ring sizes, and an estimate of the nature of the forces which control their conformations.

To the present date, the molecular structures of four methylphosphazenes are known[125-127]; their geometries are illustrated in Figures 5.1 and 5.2. As in other phosphazenes, the basic structural parameters within each ring vary little from their mean values (Table 5.1) (e.g. all the bond lengths are nearly equal, even though they are not required to be so by symmetry), and

Table 5.1.  Mean values of principal structural parameters in methylphosphazenes

|  | L(P=N) (Å) | L(P-C) (Å) | $\widehat{PNP}$ (deg) | $\widehat{NPN}$ (deg) | $\widehat{CPC}$ (deg) |
|---|---|---|---|---|---|
| $(NPMe_2)_4$ [a] | 1.596 | 1.805 | 132.0 | 119.8 | 104.1 |
| $(NPMe_2)_5$ [b] | 1.586 | 1.804 | 133.0 | 118.6 | 104.3 |
| $(NPMe_2)_7$ [c] | 1.593 | 1.805 | 134.1 | 117.3 | 103.8 |
| $(NPMe_2)_8$ [c] | 1.578 | 1.797 | 139.9 | 117.2 | 103.5 |

(a) M.W. Dougill, J. Chem. Soc., 5471 (1961).  (b) M.W. Dougill and N.L. Paddock, unpublished results.  (c) S. Rettig, unpublished results.

those fluctuations which are observed can be attributed to changes in σ-hybridization at phosphorus and nitrogen (as in $(NPCl_2)_5$[4,265]) rather than to π-effects.  The absence of any structural parameter which is dependent on the shape of the molecules is important, and suggests that the relative orientation of successive $-N=PMe_2-$ units does not affect the extent of π-bonding.
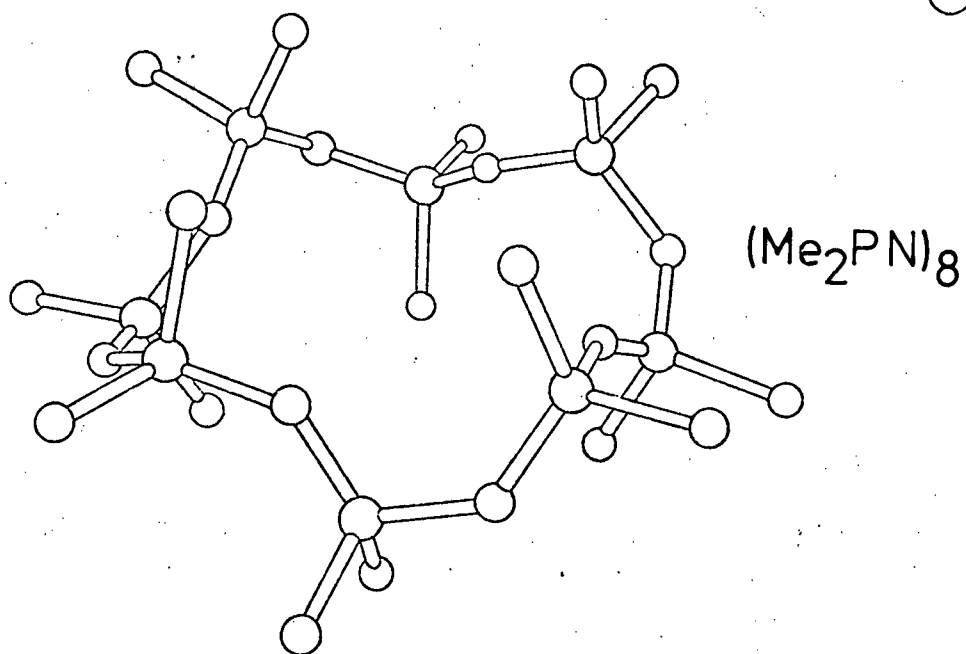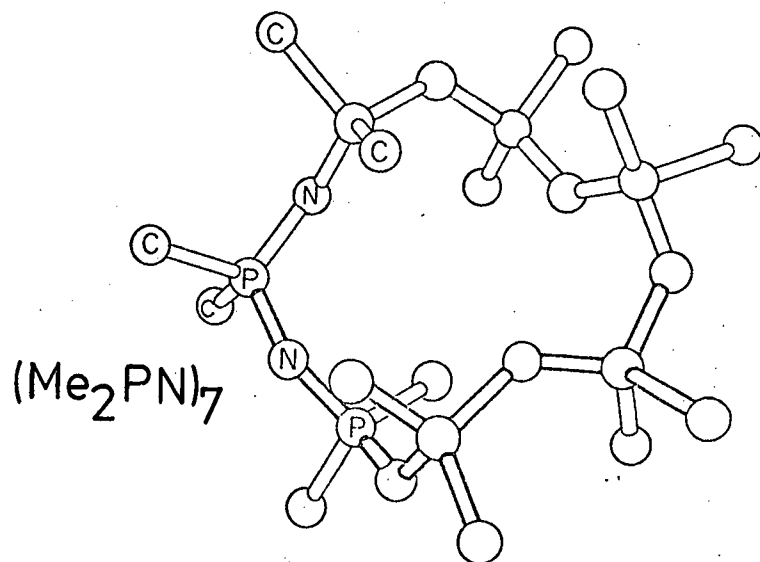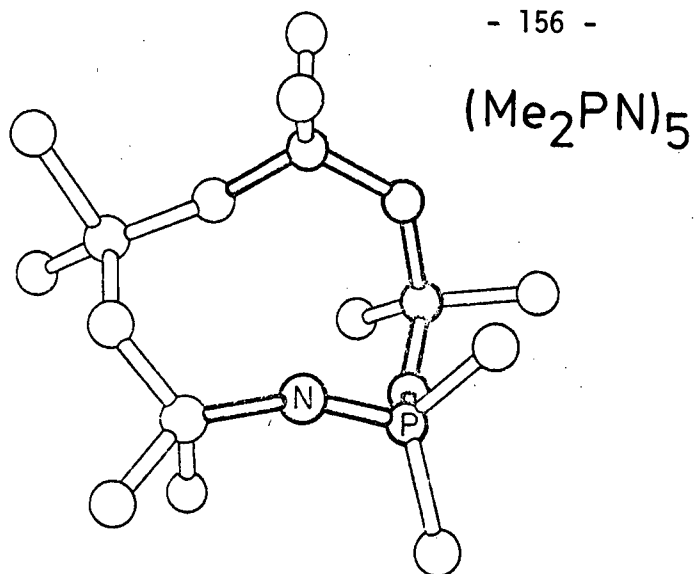
Figure 5.1. Overall views of some methylphosphazene structures [(Me₂PN)₅, M.W. Dougill and N.L. Paddock, unpublished results; (Me₂PN)₇,₈, S. Rettig, unpublished results].
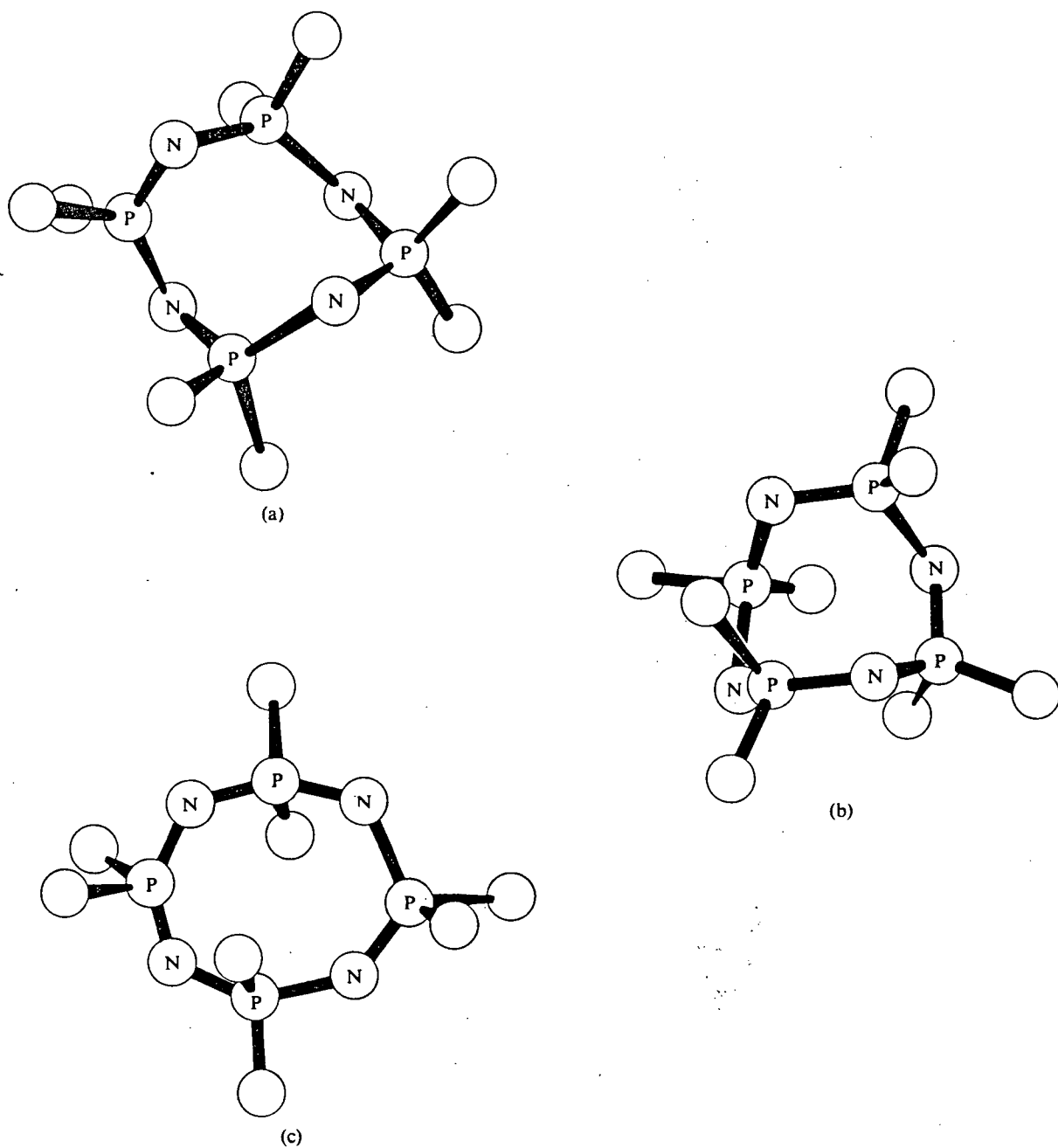
Figure 5.2. Three possible conformations for 8-memberd phosphazene rings $(NPX_2)_4$: (a) $D_{2d}$ (saddle), (b) $S_4$ (tub), (c) $C_{2h}$ (crown). The actual structure of $(Me_2PN)_4$ lies between $S_4$ and $D_{2d}$ (M.W. Dougill, J. Chem. Soc., 5471 (1961).

In order to understand more clearly the meaning of this conclusion,
it is useful, at this point, to describe the way in which $\pi$-bonds can be
formed in phosphazene derivatives. If it is assumed that the $\sigma$-skeleton of
phosphazenes is composed of two $sp^3$ hybrid orbitals on each phosphorus and two
$sp^2$ hybrid orbitals on each nitrogen, then $\pi$-bonds between the ring atoms can
be formed in two ways, overlap occurring between (i) the $2p_z$ orbital on
nitrogen and a 3d orbital on phosphorus, and (ii) the remaining $sp^2$ hybrid
orbital on nitrogen and a 3d orbital on phosphorus. In planar molecules, the
two types of overlap give rise to two different $\pi$-systems, the former being
termed the out-of-plane $\pi_a$ system and the latter the in-plane $\pi_s$ system. In
non-planar molecules, the classification into $\pi_a$ and $\pi_s$ retains only its local
significance and, for example, a nitrogen orbital with $\pi_a$ properties will
overlap with orbitals of $\pi_s$ symmetry on phosphorus, and vice versa.

Although the contributions to bonding of the two $\pi$-systems are not
required to be equal[14,52], their equality is indicated by the apparent lack of
conformational preferences of many phosphazene rings. For example, for
tetrameric derivatives, several different conformations are found, all of which
are shown (in idealized form) in Figure 5.1. The pure $D_{2d}$ "saddle" structure,
in which the phosphorus atoms are coplanar, has been observed so far only in one
molecule, $N_4P_4Me_4F_4$ (the trans-geminal isomer)[267]. The "saddle" can be
transformed progressively into the $S_4$ "tub" form, and the molecules
$N_4P_4(OMe)_8$ (close to "saddle")[60], $N_4P_4(NMe_2)_8$[65], $N_4P_4Me_8$[126], and
$N_4P_4Cl_8(K)$[129a] (close to "tub") fall in this conformational series. The $C_{2v}$
"chair" conformation is represented by another polymorphic form of
$N_4P_4Cl_8(T)$[129b], and by two non-geminally substituted derivatives $N_4P_4Ph_4Cl_4$

and $N_4P_4Ph_4(NHMe)_4$[268].

On the basis of the above evidence, the two components of the double $\pi$-system in phosphazenes do not differ greatly in strength, so that between them they provide little resistance to torsional motion about the ring bonds. It is therefore expected that nonbonded interactions will play an important role in determining the preferred conformations of phosphazene structures. Their influence on the structures of methoxyphosphazenes has already been examined[61,62], but attempts to relate the observed shapes to sterically acceptable conformations in a quantitative manner were hampered by the asymmetric nature of the ligands.

In the case of the methylphosphazene structures described here, the approximately spherical shape of the methyl ligands simplifies the conformational analysis. Even so, the minimization of all nonbonded interactions is possible only for the 8-membered ring[269]; for the larger ring sizes, numerical estimates must be restricted to calculations on parts of the molecules. Therefore, in order to study the $(NPMe_2)_n$ series as a whole, an examination has been made of the fragment $(PN)_2PMe_2$ (Figure 5.3). Similar models have been used in the analysis of methoxyphosphazene structures[61,62], and, in the present case, the conformational energy of the $(PN)_2PMe_2$ unit, as a function of the two angular variables $\psi_1$ and $\psi_2$, provides an insight into the preferred local conformations at successive phosphorus atoms in an $(NPMe_2)_n$ ring. The justification for this treatment of the molecules as a set of such fragments is its success in accounting for the main qualitative features of the observed structures.
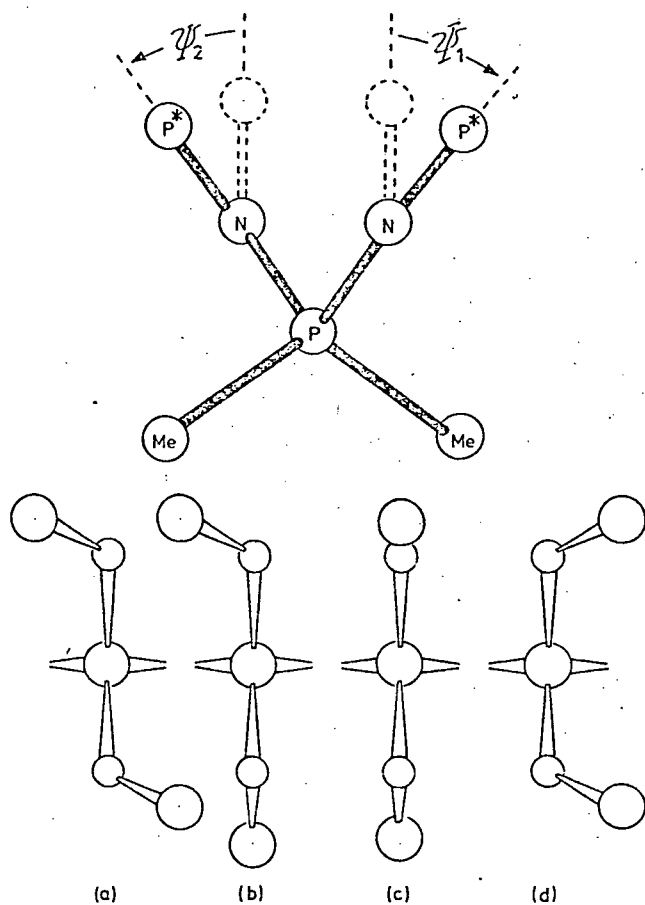
Figure 5.3. Angular conventions for the measurement of torsion angles in a $(PN)_2PMe_2$ unit. The angles $\psi_{1,2}$ have the same sign when the terminal phosphorus atoms $(P^*)$ lie on opposite sides of the NPN plane. A number of idealized conformations are also illustrated: (a) GG ($\psi_1=\psi_2=60°$), (b) GT ($\psi_1=60°$, $\psi_2=180°$), (c) CT ($\psi_1=0°$, $\psi_2=180°$), (d) GG' ($\psi_1=-60°$, $\psi_2=60°$).

The potential functions used to simulate van der Waals' interactions were of the Lennard-Jones and Devonshire (6-12) type, and were minimized not at the normal van der Waals' distance[270], but at a slightly greater distance $R_o$ (see footnote, Table 5.2 for details). This larger value $R_o$ was used for two reasons, firstly to take into account the bulky nature of the P* "atoms" (Figure 5.2), which are in fact $PMe_2N$ groups, and secondly to allow for the

Table 5.2.   Interatomic potential constants[a] used for the calculation of
            van der Waals interactions in a $(PN)_2PMe_2$ unit.

| Interaction | $R_o$ | A | B |
|---|---|---|---|
| P...P | 4.8 | 3.8473 | 3.4613 |
| Me...P | 4.4 | 3.6712 | 3.4382 |
| N...P | 3.9 | 3.3647 | 3.2584 |

(a) Potential $V = (A/r)^{12} - (B/r)^6$, kcal mol$^{-1}$ for r in Å.  Constants by
method of R.A. Scott and H.A. Scheraga (J. Chem. Phys., 42, 2209 (1965));
B from Slater-Kirkwood expression and A by minimization of V at $R_o$ (Å).  $R_o$
equal to sum of van der Waals radii of interacting atoms; for Me and N,
normal values (A. Bondi, J. Phys. Chem., 68, 441 (1964)) were used, but for
phosphorus the value was increased by 0.5 Å (see Text).

difference between the equilibrium distances of a pair of atoms when isolated

and when in a condensed phase[271]. The potential energy diagram for the

$(PN)_2PMe_2$ unit based on the use of these functions is shown in Figure 5.4(a).

As expected intuitively, the conformational energy is minimized when all the

bonds are mutually staggered.  There are two minima, corresponding

approximately to the GG and CT conformations[‡] shown in Figure 5.3.  Using the

parameters indicated, the GG structure is favoured over the CT by about 1½

kcal/mole, and even when the model and functions are varied, GG maintains the

lower energy.

However, this order can be reversed or equalized (depending on the

particular numerical choice) by the inclusion of Coulombic interactions (as

[‡] Terminology from Mizushima[272]; the terms GT, CT, etc. refer to the approximate
orientation of NP* bonds (Gauche-Trans, Cis-Trans, etc.); see Figure 5.3.

(a)



(b)
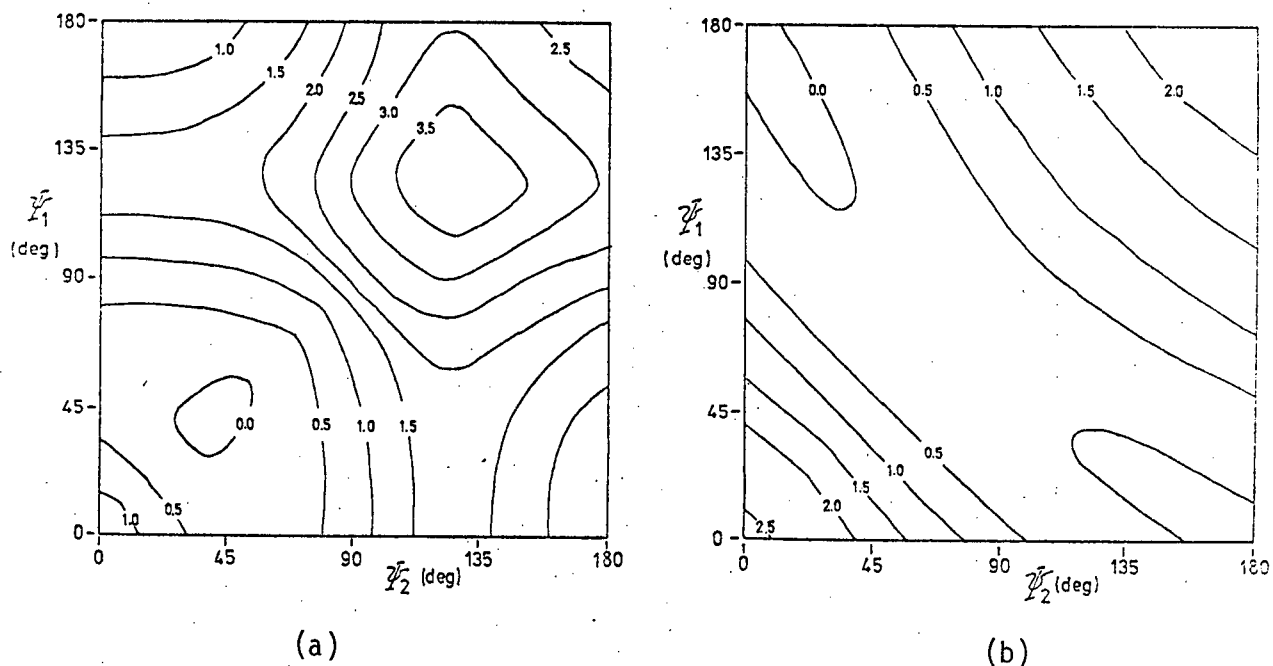
Figure 5.4. Potential energy (a) and electrostatic energy (b) contours
(kcal mol$^{-1}$) of $(PN)_2PMe_2$ unit as a function of $\psi_1$ and $\psi_2$
(energies quoted are relative). Electrostatic energy (E)
calculated using q(P) = $+\frac{1}{2}$, q(N) = $-\frac{1}{2}$, E = $K\Sigma(q(P).q(N))/r_{PN}$
(K = $3.3207 \times 10^2$ kcal.Å.mol$^{-1}$). The $(PN)_2PMe_2$ model used has
L(P=N) = 1.59Å, L(P-C) = 1.80Å, $P\widehat{N}P$ = 135°, $N\widehat{P}N$ = 120°,
$C\widehat{P}C$ = 105°.

point charges q(P)(+) and q(N)(-) on phosphorus and nitrogen). Such a

consideration has been found necessary to rationalize the structures of

polypeptides[273,274], and in view of the substantial polarity of the P=N bond

in $(NPMe_2)_n$, is probably equally important in the present system. Because of

ignorance of the total charge distribution, the extent of Coulombic interactions

cannot be estimated as accurately as van der Waals potentials; the combined

effect of the two types of interaction is therefore unknown. Nonetheless, the

effect of electrostatic forces (Figure 5.4(b)) is such as to stabilize the

structures in the region of GT and CT with respect to the energy of the GG

conformation.

Table 5.3. Observed torsion angles[a] and local conformations in methylphos-
phazenes.

| Molecule (symmetry) | Atom | $\psi_1$ (deg) | $\psi_2$ (deg) | Conformation |
|---|---|---|---|---|
| $(NPMe_2)_4(S_4)$ | $P_{1,2,3,4}$ | 31.5 | 54.7 | GG |
| $(NPMe_2)_5(C_1)$ | $P_1$ | 32.0 | 64.1 | GG |
| | $P_2$ | -128.2 | 11.0 | ∿CT |
| | $P_3$ | 67.9 | 16.4 | ∿GG |
| | $P_4$ | - 79.3 | 39.1 | GG |
| | $P_5$ | 119.1 | -73.0 | GG'∿GT |
| $(NPMe_2)_7(C_2)$ | $P_1$ | 36.1 | 68.7 | GG |
| | $P_{2,2'}$ | ±156.4 | ∓46.3 | GT |
| | $P_{3,3'}$ | ± 57.4 | ±72.7 | GG |
| | $P_{4,4'}$ | ±166.8 | ∓36.1 | GT |
| $(NPMe_2)_8(C_{4v})$ | $P_{1,3,5,7}$ | 61.3 | 27.8 | GG |
| | $P_{2,4,6,8}$ | 156.5 | 76.8 | GT |

(a) The signs of $\psi_{1,2}$ (see Fig. 5.3) are such that a clockwise rotation has a
positive sign. In the case of $(NPMe_2)_7$, the atoms $P_{n,n'}$ (n=2-4) are related
by a two-fold axis through $P_1$; the values of $\psi_{1,2}$ are identical, but their
signs are reversed.

The effectiveness of the $(PN)_2PMe_2$ model in predicting the preferred local conformations is confirmed by the actual torsion angles (defined in terms of $\psi_1$ and $\psi_2$) observed in the methylphosphazenes. Their values (Table 5.3) show that the majority of local conformations can be classified as approximately GG or GT. Only in the case of $(NPMe_2)_5$, which has a low overall molecular symmetry, are significant deviations observed. The predominance of GG in the tetramer can be attributed to cyclic constraints, i.e. it is impossible to close an 8-membered ring containing a CT conformation at one phosphorus atom. However, on progressing to larger rings, such restrictions are removed, and an increasing abundance of GT conformations is found.

It is suggested that further work (already in progress) on the structures of even larger methylphosphazene rings (e.g. $(NPMe_2)_{9,10}$) will show an increasing proportion of GT and CT conformations. This belief is supported by the known structures of the high polymers $(NPF_2)_\infty$ (conformer B)[275] and $(NPCl_2)_\infty$[276], both of which exist as planar (or nearly so) CT chains.

## 5.2 Structures of Azaphosphorin Derivatives

The fact that the conformational trends observed in phosphazene structures can be adequately interpreted in terms of nonbonded interactions supports the belief that the two $\pi$-systems ($\pi_a$ and $\pi_s$) within the cyclic PN framework are energetically equivalent. More quantitative evidence concerning their relative importance has been obtained from the recently determined molecular structures[277] of a number of the azaphosphorin derivatives described in the previous chapter.
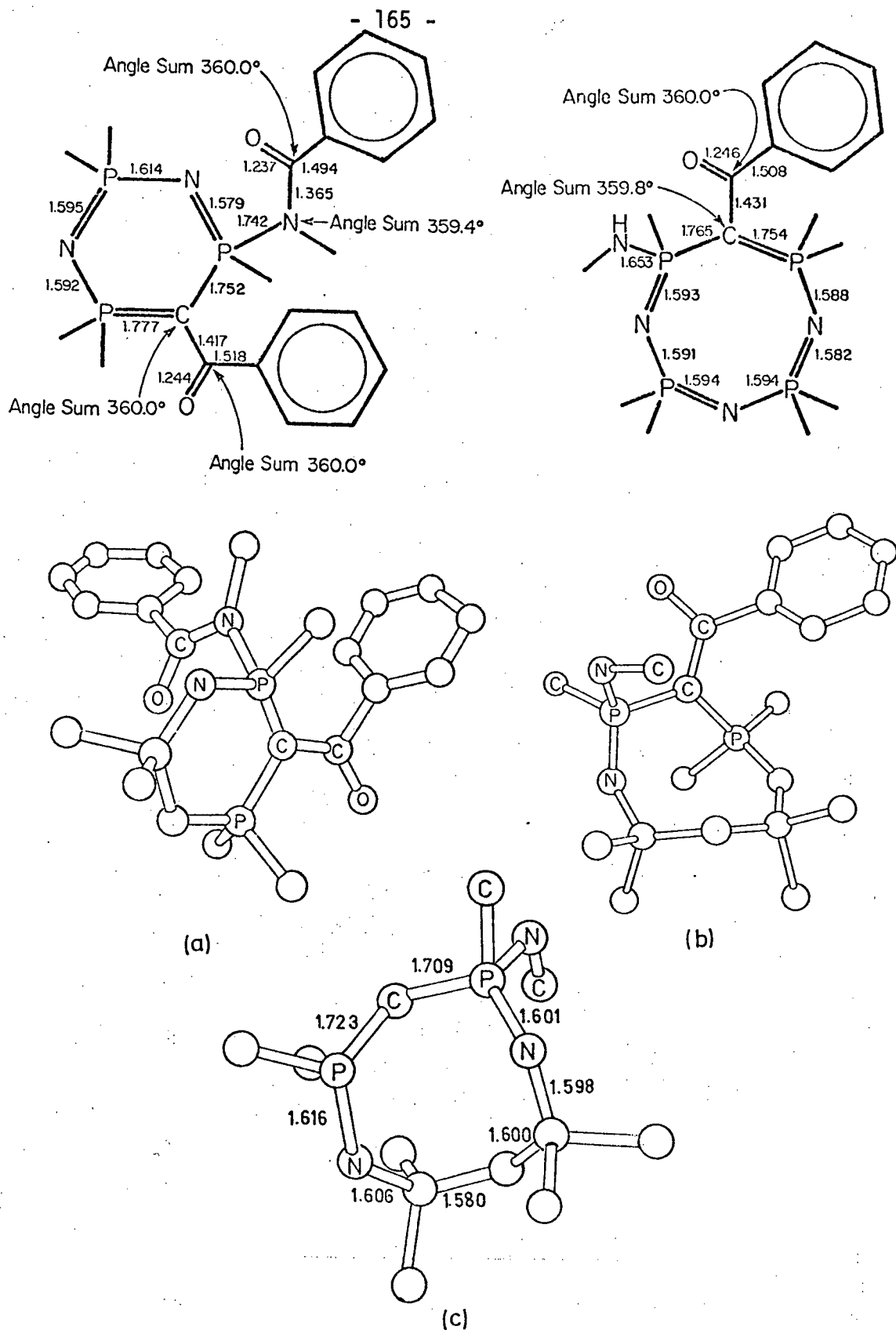
Figure 5.5.  Overall geometries and principal structural parameters of methylazaphosphorins.  (a) Me₅(NMeCOPh)P₃N₂CCOPh.
(b) Me₇(NHMe)P₄N₃CCOPh.  (c) Me₇(NHMe)P₄N₃CH.  [S. Rettig and H.P. Calhoun, unpublished results].

Table 5.4. Values of P=C and P-C (mean) bond lengths in a selection of phosphorus ylids.

| Compound | L(P=C) (Å) | L(P-C) (Å) | Ref. |
|---|---|---|---|
| $Ph_3P=C=PPh_3$ | 1.629 | 1.832 | a |
|  | 1.633 | 1.837 |  |
| $Ph_3P=C=C=O$ | 1.648 | 1.805 | b |
| $Ph_3P=CH_2$ | 1.661 | 1.823 | c |
| $Ph_3P=C=C=S$ | 1.677 | 1.795 | d |
| $Ph_3P=C=C(OEt)$ | 1.682 | 1.832 | e |
| $Ph_3P=\overline{C-CF_2-CF_2-CF_2}$ | 1.713 | 1.799 | f |
| $Ph_3P=\overline{C-CH=CH-CH=CH}$ | 1.718 | 1.806 | g |
| $Ph_3P=ClCOPh$ | 1.71 | 1.786 | h |
| $Ph_3P=CClCOPh$ | 1.736 | 1.806 | h |
| $Ph(C_3H_7)_2P=C(CN)_2$ | 1.743 | 1.799 | i |

(a) A.T. Vincent and P.J. Wheatley, J. Chem. Soc., Dalton, 617 (1972).

(b) J.J. Daly and P.J. Wheatley, J. Chem. Soc., A, 1703 (1966).

(c) J.C.J. Bart, J. Chem. Soc., B, 350 (1969).

(d) J.J. Daly, J. Chem. Soc., A, 1913 (1967).

(e) H. Burzlaff, U. Voll and H.J. Bestmann, Chem. Ber., 107, 1949 (1974).

(f) M.A. Howells, R.D. Howells, N.C. Baenziger and D.J. Burton, J. Amer. Chem. Soc., 95, 5366 (1973).

(g) H.L. Ammon, G.L. Wheeler and P.H. Watts Jr., J. Amer. Chem. Soc., 95, 6158 (1973).

(h) F.S. Stephens, J. Chem. Soc., 5640, 5658 (1965).

(i) W. Dreissig, H.J. Hecht and K. Plieth, Z. Kristallogr., 137, 132 (1973).

The overall geometries and principal structural parameters of the compounds to be discussed are given in Figure 5.5. As in the structures of phosphorus ylids containing electron withdrawing substituents on carbon (Table 5.4), the P=C bond lengths found in the azaphosphorin $Me_7(NHMe)P_4N_3CH$ (mean value 1.716 Å) are longer than the value of 1.66 Å predicted for a P=C double bond[278], and indicate the extent to which electron density is delocalized from carbon into the phosphazene ring. As expected, charge delocalization is enhanced, and the P=C bond lengthened, by the substitution of a benzoyl group onto the endocyclic carbon (Table 5.5). Conjugation with the C-benzoyl group is also indicated by the long C=O bond (a normal C=O double bond is 1.23 Å[278]) and the short central C-C bond ($L((sp^2)C-C(sp^2))$ = 1.46 Å[279], 1.48-1.49 Å[280]), but, because of the competing influence of the phosphazene ring, its extent is less than that found in simple C-benzoylated ylids[281] (Table 5.5).

Table 5.5. Bond lengths and torsion angles ($\tau$) in C-benzoylated ylids

| Compound | L(P=C) (Å) | L(C-C) (Å) | L(C=O) (Å) | $\tau$(C-C) (deg) | $\tau$(C-Ph) (deg) |
|---|---|---|---|---|---|
| $Me_5(NMeCOPh)P_3N_2CCOPh$[a] | 1.765[c] | 1.431 | 1.244 | 7.8 | 33.5 |
| $Me_7(NHMe)P_4N_3CCOPh$[a] | 1.760[c] | 1.417 | 1.246 | 29.4 | 41.6 |
| $Ph_3P=CClCOPh$[b] | 1.71 | 1.36 | 1.28 | 11 | 51 |
| $Ph_3P=CClCOPh$[b] | 1.736 | 1.35 | 1.301 | 4.7 | 57.6 |

(a) S. Rettig, unpublished results. (b) Mean value. (c) F.S. Stephens, J. Chem. Soc., 5640, 5658 (1965).

Probably for steric reasons, the P=C-C(O)Ph unit is not planar; torsion about the central C-C bond is small enough to allow conjugation between the P=C and C=O bonds, but, as the C(O)-Ph distances reflect, conjugation with the phenyl group is prohibited by a large torsion angle, as in simple C-benzoylated ylids[281] (Table 5.5).

Conjugation between the ring and the exocyclic methylamino group is indicated by the shortness of the exocyclic P-N bond, which, at 1.653 Å, is shorter than the average value found for the exocyclic bond in dimethylamino-phosphazenes[65-67]. Substitution of a benzoyl group onto the nitrogen lengthens the P-N bond dramatically (L(P-N) in $Me_5(NMeCOPh)P_3N_2CCOPh$ is 1.742 Å), indicating the effectiveness of the N-benzoyl group in competing with the phosphazene ring for electron density from nitrogen. The extent of conjugation in the benzamide moiety was also noted in the increased shielding of the N-methyl protons and the low $\nu(C=O)$ frequency of the amide carbonyl group (see Chapter IV, Sections 4.5.3 and 4.5.4).

The above features are localized, and do not depend on a unique property of the phosphazene ring, nor do they provide any direct information on the nature of cyclic $\pi$-bonding. In the latter regard, the P=N bond lengths in the azaphosphorin rings are more useful (Table 5.6).

The discussion of these distances is best approached by assuming that the azaphosphorin rings are homogeneously substituted on all the phosphorus atoms. Strictly speaking this assumption is incorrect, but the inhomogeneity caused by the presence of the amine (or amide) ligand does not appear to offset significantly the twofold symmetry of the $P_n N_{n-1} C$ rings.

Table 5.6.  Mean bond lengths[a] in azaphosphorin and protonated phosphazene structures.

| Compound | $X-P_1$ | $P_1-N_1$ | $N_1-P_2$ | $P_2-N_2$ |
|---|---|---|---|---|
| $Me_7(NHMe)P_4N_3CH$[b] | 1.716 | 1.608 (0.008) | 1.602 (0.002) | 1.590 (-0.010) |
| $Me_7(NHMe)P_4N_3CCOPh$[c] | 1.760 | 1.591 (0.000) | 1.587 (-0.004) | 1.594 (0.003) |
| $Me_8P_4N_4H^+$ [d] | 1.695 | 1.538 (-0.040) | 1.614 (0.036) | 1.582 (0.004) |
| $Me_5(NMeCOPh)P_3N_2CCOPh$[c] | 1.765 | 1.586 (-0.009) | 1.605 (0.010) | - |
| $(Me_2N)_6P_3N_3H^+$ [e] | 1.669 | 1.561 (-0.018) | 1.598 (0.018) | - |

(a) In Angstroms, values averaged from two bonds.  Deviation from mean PN bond length in parenthesis.  See Figure 5.6 for nomenclature of bonds.
(b) H.P. Calhoun, unpublished results.   (c) S. Rettig, unpublished results.
(d) J. Trotter, S.H. Whitlow and N.L. Paddock, Chem. Commun., 695 (1969).
(e) H.R. Allcock, E.C. Bissell and E.T. Shawl, Inorg. Chem., 12, 2963 (1973).
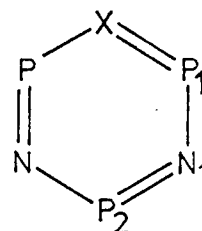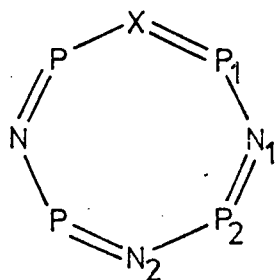


X = CR or NH+

Figure 5.6.  Nomenclature system for ring bonds in azaphosphorin and protonated phosphazene structures.

Using this model, the most noticeable feature of the azaphosphorin structures is the near equality of all the PN ring bonds (Table 5.6), which behaviour is in contrast to the alternation in bond lengths observed in protonated phosphazenes[282,283]. Formally, the two types of molecule are isoelectronic; in both cases only one orbital (the $p_z$) is available on the X atom (Figure 5.6) for $\pi$-bonding to phosphorus. On the other ring nitrogen atoms, the $sp^2$ hybrids, as well as the $p_z$ orbitals, are capable of $\pi$-bond formation.

In protonated phosphazenes, the localization of two electrons in one $sp^2$ orbital on nitrogen perturbs the in-plane $\pi_s$ system, and the variation in the calculated bond orders expected by such a perturbation is in excellent agreement with the observed alternation in bond lengths (Figure 5.7). Moreover, the lengths of the ring bonds to the protonated nitrogen now corresponds to the use of a single $\pi$-component (the $\pi_a$), the deficit in length from the 1.77 Å characteristic of a single P-N bond[54] being approximately halved.

In the calculation of expected bond orders in azaphosphorin structures (using simple Huckel M.O. Theory) a second factor, quite apart from the loss of one orbital in the $\pi_s$ system, must be taken into account. It is connected with the perturbation of the out-of-plane $\pi_a$ system which results from the replacement of a nitrogen atom with a carbon atom, and affects $\pi$-bond formation in two ways. (i) Because of the difference in nuclear charge of carbon and nitrogen, the $2p_z$ orbital on carbon will be of higher energy than its counterpart on nitrogen. (ii) Because of the lower electronegativity of carbon, the d-orbitals on the phosphorus atoms adjacent to the endocyclic carbon will be less effectively stabilized, and their Coulomb parameters will therefore
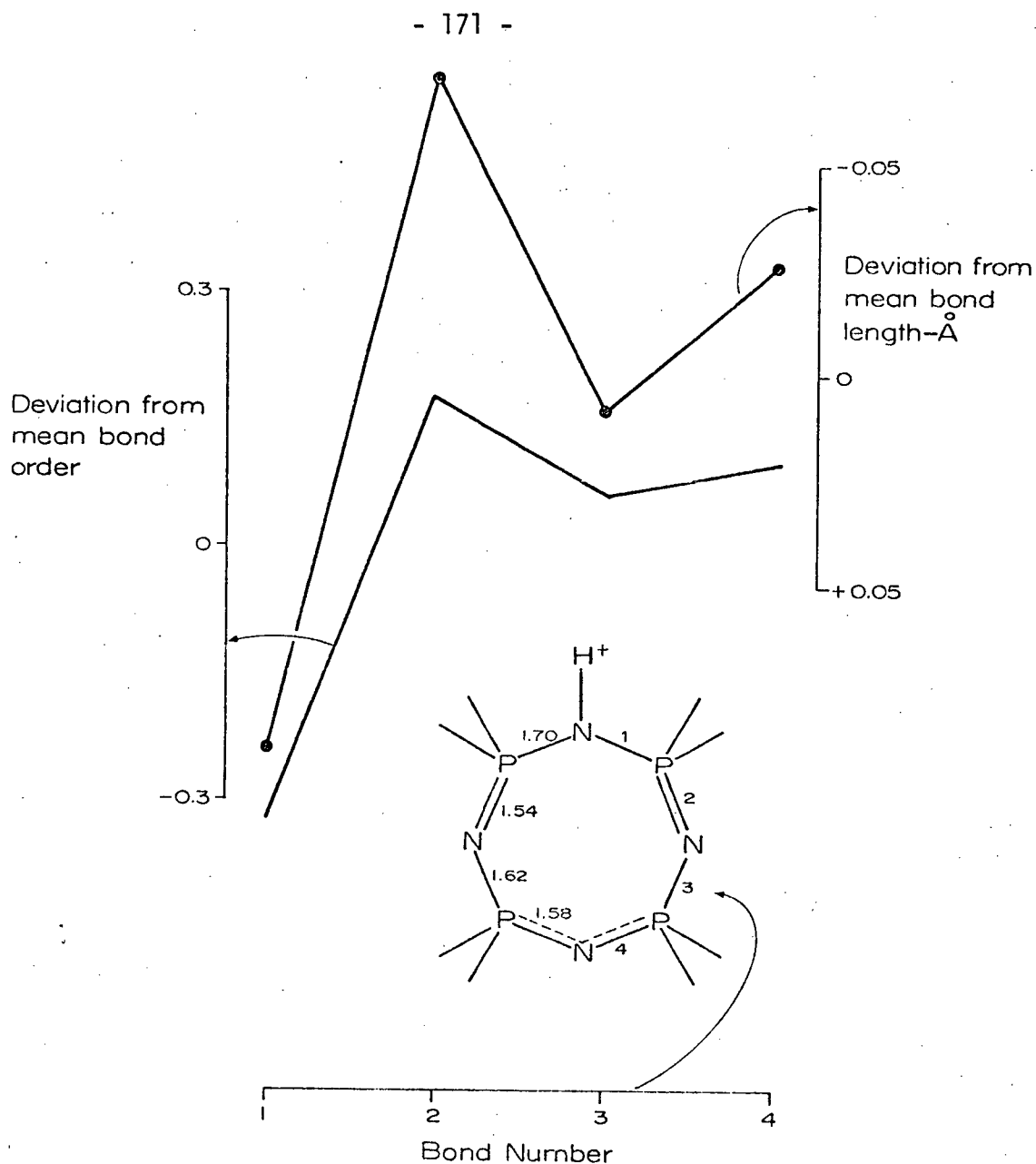
Figure 5.7. Calculated bond orders and observed bond length inequalities in a protonated tetrameric phosphazene ring (J. Trotter and S.H. Whitlow, J. Chem. Soc., A, 455 (1970)).

be algebraically greater than those on the phosphorus atoms bound to two nitrogens. Of the two effects the first is more important (vide infra).

Figure 5.8 illustrates the calculated bond orders in the $\pi_a$ and $\pi_s$ systems of a $P_4N_3C$ ring. As in the case of protonated phosphazenes, the removal

of one orbital from the $\pi_s$ system strengthens the $P_1N_1$ and $P_2N_2$ bonds at the expense of the $P_2N_1$ bond. By contrast, the reverse order is found in the $\pi_a$ system. The values shown for this latter case were calculated for a model in which the Coulomb parameters of all phosphorus 3d orbitals ($\alpha_p$) were identical, as were those of the nitrogen 2p orbitals ($\alpha_N$). The Coulomb parameter of the carbon 2p orbital ($\alpha_C$) was then set (arbitrarily) equal to the average of $\alpha_N$ and $\alpha_p$. All the resonance integrals $\beta$ were assumed to be equal, and were related to the Coulomb parameters by the expression $\beta = (\alpha_N - \alpha_p)/2$. Refinements of the model, using different values of $\alpha_p$ for the phosphorus orbitals adjacent to carbon, changed the magnitude of the variation shown in Figure 5.8, but not the trend in bond orders.

Hence, if the $\pi_a$ and $\pi_s$ system are assumed to be equally important, the combination of the two separate trends in bond order is such as to minimize the variation in total bond order, thereby providing an explanation for the near equality of the observed lengths of the $P_1N_1$, $P_2N_1$ and $P_2N_2$ bonds. The agreement between theory and experiment is substantial, and establishes that the same theoretical model which predicts the bond length inequalities in protonated phosphazenes can be used to rationalize the equivalence of bonds in azaphosphorin structures. The necessary link which must be used to connect the two systems is the dual nature of the $\pi$-bonding in the PN skeleton.

The same model used above to describe the bond lengths in the azaphosphorin structure $P_4N_3C$ also provides a rationale for its formation from the deprotonation of the N-methyl quaternary salt $(NPMe_2)_4.MeI$ (see Chapter IV). Figure 5.9(a) shows the typical energy levels found for the $\pi_a$ or $\pi_s$ system in a tetrameric phosphazene. Figure 5.9(b) then corresponds to the
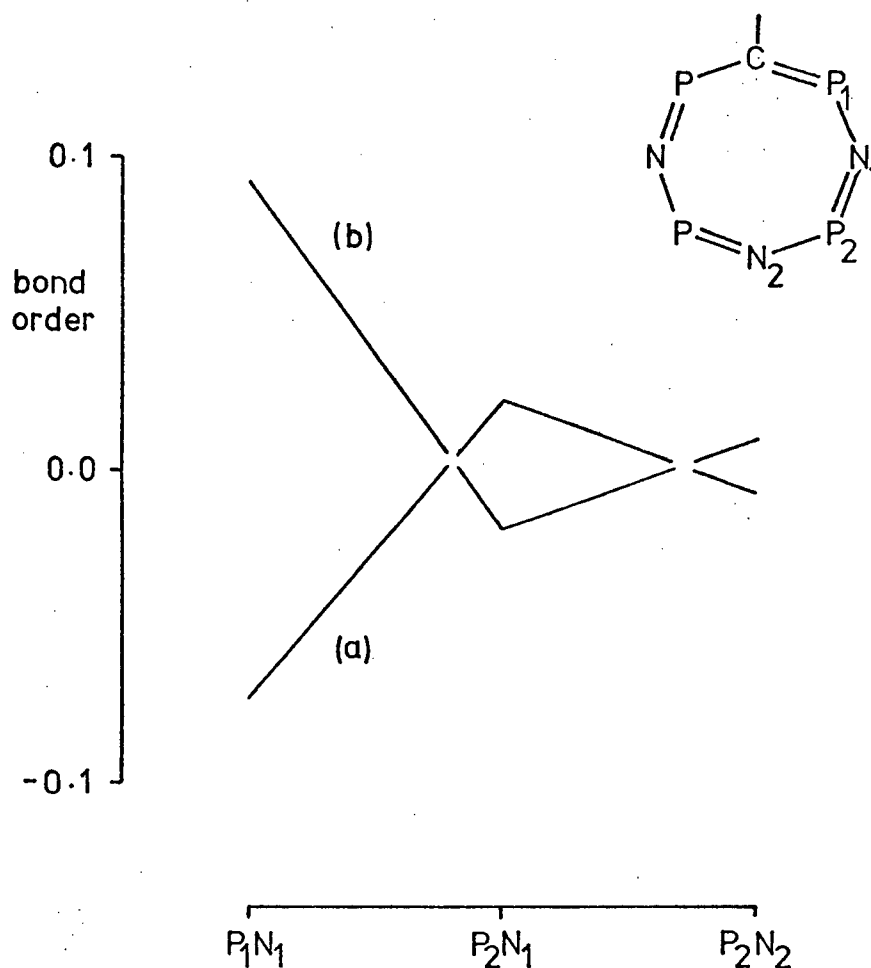
Figure 5.8. Calculated (HMO) bond orders (relative to a $P_4N_4$ ring) in the out-of-plane $\pi_a$ (a) and in-plane $\pi_s$ (b) components of the $\pi$-system in a $P_4N_3C$ azaphosphorin ring. Coulomb parameters ($\alpha$) related to the resonance integral ($\beta$) such that $\alpha_N = \alpha_P + 2\beta$, $\alpha_C = (\alpha_N + \alpha_P)/2$.

energy levels found in the $\pi_a$ system of the exocyclic ylid which is formed (presumably) as the initial product of the deprotonation of a methylphosphazene quaternary salt. As expected, the $\pi$-electron energy/electron of the system is lowered by the addition of the exocyclic ylid, but can be increased by the phosphazene-azaphosphorin rearrangement (Figure 5.9(c)). A $\pi_s$ system (Figure 5.9(d)) is present in both the ylid and azaphosphorin structures, and is not affected by the rearrangement.
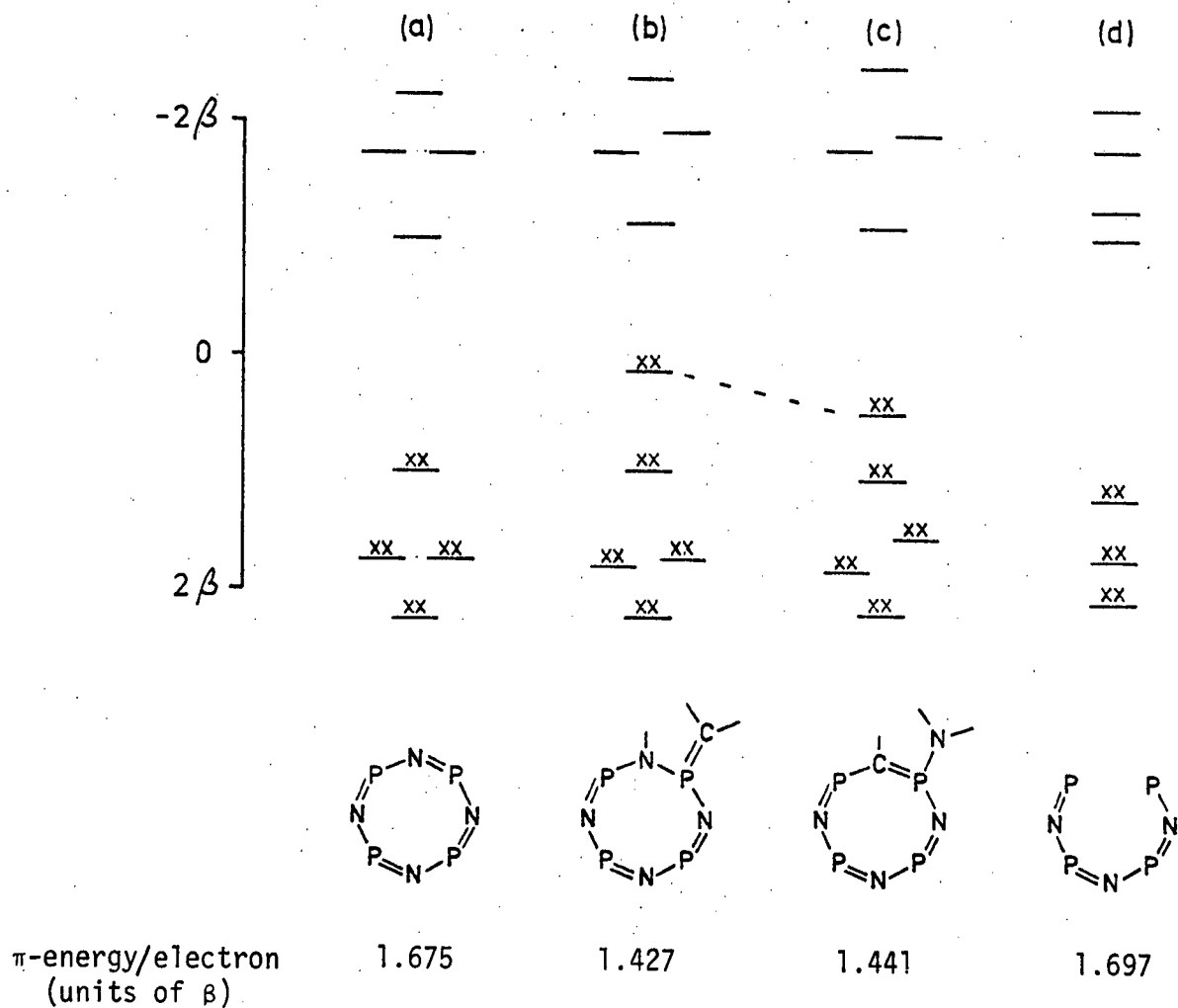
Figure 5.9. Energy level diagrams and $\pi$-electron energies for a number of phosphazene and azaphosphorin structures. [$\alpha_N = \alpha_P + 2\beta$, $\alpha_C = (\alpha_N + \alpha_P)/2$].

## 5.3 Summary

The classical model of bonding in phosphazenes[3], using 3d orbitals on phosphorus and 2p orbitals in nitrogen to form a delocalized $\pi$-system, forms a useful basis for the study of their physical and chemical properties. The acidic behaviour of methylphosphazenes, as described in earlier chapters, provides chemical evidence that charge density on the ligands can be diffused

into the cyclic π-system, and the formation of azaphosphorin derivatives by
the deprotonation of their quaternary salts illustrates the extent to which
the molecular skeleton will rearrange to optimize such delocalization.  The
structural work described in the present chapter has refined the simple
concept of bonding, and stresses the presence of two components to the π-system.
The equivalence of these two components is illustrated by the flexibility of
the PN framework, and the conformations of methylphosphazenes appear to be
controlled largely by non-bonded forces.  The duality of the π-system also has
an influence on the bonds themselves, and provides a basis for the under-
standing of the bond length behaviour found in the structures of azaphosphorins.

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APPENDIX

Details of the instruments used for recording the various types of spectra were not discussed in the main text of the thesis. A summary of pertinent details is given below.

i) <u>Infrared Spectra</u>: These were all recorded on a Perkin-Elmer 457 grating spectrophotometer, and calibrated against a standard polystyrene spectrum. Unless otherwise indicated, all spectra were recorded on samples in nujol (and hexachlorobutadiene) mulls, using cesuim iodide plates. Solution spectra were taken using cells with potassium bromide windows.

ii) <u>Raman spectra</u>: These were recorded on a Cary 81 Laser Raman spectrophotometer. No depolarization measurements were taken.

iii) <u>Mass Spectra</u>: These were all recorded at 70 e.v. on an A.E.I. type M.S. 9 mass spectrometer, samples being admitted through conventional inlet systems.

iv) <u>N.m.r. Spectra</u>: $^1$H n.m.r. spectra were run at 60 MHz on a Varian T-60 n.m.r. spectrometer and at 100 MHz on a Varian HA-100 n.m.r. spectrometer. 220 MHz spectra were obtained by courtesy of the 220 MHz n.m.r. facility at the University of Toronto. $^{31}$P n.m.r. spectra were recorded at 40.1 MHz on a Varian XL100 n.m.r. spectrometer. $^{31}$P-$^1$H decoupling experiments were carried out using a recently described double resonance technique[†].

[†]see L.D. Hall and R. Burton; Can. J. Chem., <u>48</u>, 59 (1970).

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