SYNTHESIS, STRUCTURE AND REACTIVITY OF SOME CYCLIC PHOSPHORUS COMPOUNDS

A THESIS

SUBMITTED FOR THE DEGREE OF

Doctor of Philosophy

BY

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INDIA

DECEMBER 1998

Dedicated to my

Mother-in-law

(Late Smt. M. Maisamma)

and

Father-in-law

(Sri M. Narsimha Rao)

CONTENTS

DECLARATION

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in School of Chemistry, University of Hyderabad, Hyderabad under the supervision of Dr. K. C. Kumara Swamy.

In keeping with the general practice of reporting scientific observations, due acknowledgments have been made wherever the work described is based on the findings of other investigators. Any omission which might have occurred by oversight or error is regretted.

M. Vijjulatha

(M. Vijjulatha)

CERTIFICATE

This is to certify that the work described in this thesis entitled "Synthesis, Structure and Reactivity of Some Cyclic Phosphorus Compounds" has been carried out by M.Vijjulatha, under my supervision and the same has not been submitted elsewhere for any degree.

Hyderabad

December 1998

Kumara Swamy

K. C.Kumara Swamy

(THESIS SUPERVISOR)

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LIST OF PUBLICATIONS

1. The 1:1 Antimony Trichloride Adduct of Chloro bis (2,6-dimethylpiperidin-1-yl)-phosphine oxide.
   M. Vijjulatha, K. C. Kumara Swamy, V. Huch and M. Veith, *Acta Crystallogr* 1997, **C53**, 1789.
2. The Reaction of Chlorophosphates with Strong Bases: Synthesis and Characterization of the Phosphonate Salts.
   M.Vijjulatha, K. Praveen Kumar, K. C. Kumara Swamy and J. J. Vittal, *Tetrahedron Lett.* 1998, **39**, 1819.
3. Synthesis, reactivity and structures of spirocyclic products derived from octa chlorocyclotetraphosphazene- Comparison to spirocyclic cyclotriphosphazenes and linear phosphazenes.
   Sudha Kumaraswamy, M. Vijjulatha, C. Muthiah, K. C. Kumara Swamy and Udo Engelhardt [***J.Chem. Soc., Dalton Trans.*** (under revision)].
4. Synthesis and X-ray structural studies of new bridged diazadiphophetidines.
   M. Vijjulatha, K. C. Kumara Swamy and U. Engelhardt (to be submitted).
5. Synthesis and X-ray structure of 2-*cis*-4-bis(2,6-dimethylphenoxy)-1,3-di-*t*-butyldiazadiphosphetidines
   M.Vijjulatha, K.C.Kumara Swamy and L. L. Koh (to be submitted)

Papers presented in SYMPOSIUM

1. Rings and Cages Containing Phosphorus, Arsenic and Antimony- New Chemistry.
   Musa A. Said, M. Vijjulatha and K. C. Kumara Swamy, *Modern Trends in Inorganic Chemistry (MTIC)*, August 17-19, 1995, University of Hyderabad, India.

SYNOPSIS

The work embodied in this thesis is divided into three parts:

Part 1: Cyclic and linear phosphazenes-Reactions with difunctional reagents

Part 2: Reactions of cyclodiphosphazanes

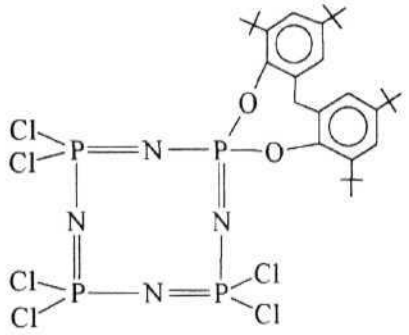
Part 3: Reactions of chlorophosphorus(III) and chlorophosphorus(V) compounds with Lewis acids and bases.

Each part is subdivided into four sections: X.1 Literature Survey, X.2 Results and Discussion, X.3 Experimental and X.4 References. Literature survey is done keeping in mind mostly the experimental work done in the present study and recent developments. The compounds obtained in the present study are in general characterized by m.p., IR and NMR techniques followed by elemental analysis. Wherever feasible, X-ray structure determination is undertaken. References are compiled at the end of each chapter.

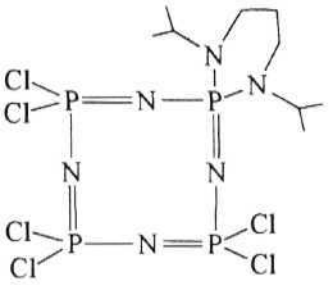
Part 1:

Although the reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (1.**1**) with difunctional reagents have been well-documented, studies on octachlorocyclotetraphosphazene, $N_4P_4Cl_8$ (1.**2**), are scanty mainly because of the instability of the products. Also the reaction of the linear phosphazene $Cl_3PNP(O)Cl_2$ (1.**3**) with difunctional reagents has not been studied so far. To fill in these lacunae we have used the difunctional reagents $CH_2[4,6\text{-}(t\text{-}Bu)_2C_6H_2OH]_2$ and $[HN(i\text{-}Pr)CH_2CH_2CH_2N(i\text{-}Pr)H]$ which provide steric protection at the reacting site. Spirocyclic derivatives $2,2\text{-}N_4P_4[\{O\text{-}C_6H_2\text{-}4,6\text{-}(t\text{-}Bu)_2\}_2CH_2]Cl_6$ (1.**99**), $2,2\text{-}N_4P_4[N(i\text{-}Pr)CH_2CH_2CH_2N(i\text{-}Pr)]Cl_6$ (1.**100**) and $2,2,6,6\text{-}N_4P_4[N(i\text{-}Pr)CH_2\,CH_2CH_2N(i\text{-}Pr)]_2Cl_4$ (1.**101**) have been synthesized as crystalline solids which are stable under nitrogen; these compounds to our knowledge, constitute the first examples of

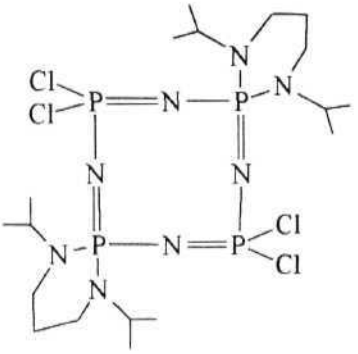
spirocyclic cyclotetraphosphazenes to be structurally characterized. We do not have evidence for the formation of *ansa* derivatives in these systems.



1.**99** (**X-ray**)

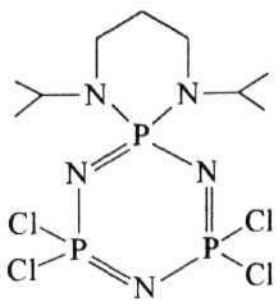


1.**100** (**X-ray**)

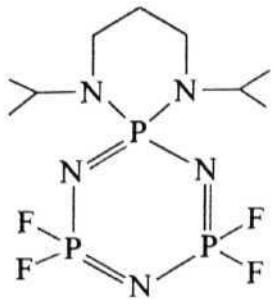


1.**101** (**X-ray**)

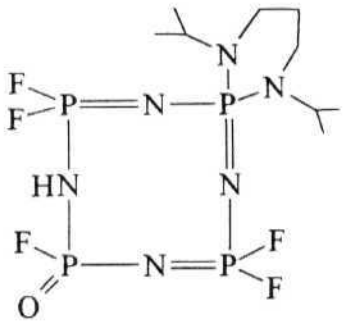
Interestingly in the synthesis of 1.**101** the other possible spirocyclic isomer, the 2,2,4,4-product, was not observed. The ease of isolation of 1.**100** makes it an excellent probe to study further reactions; thus when reacted with excess methylamine in chloroform, it gives the bicyclic phosphazene 1.**109** with a 2,2-spiro group. Also, in contrast to the easy fluorination of $N_3P_3[N(i\text{-Pr})CH_2CH_2CH_2N(i\text{-Pr})]Cl_4$ (1.**102**) to $N_3P_3[N(i\text{-Pr})CH_2CH_2CH_2N(i\text{-Pr})]F_4$ (1.**106**), (this study), compound 1.**100** undergoes partial hydrolysis while fluorinating to afford a product formulated as $N_4P_4F_5(OH)[N(i\text{-Pr})CH_2CH_2CH_2N(i\text{-Pr})]$ (1.**107**); the tautomeric form is shown in the diagram given below.



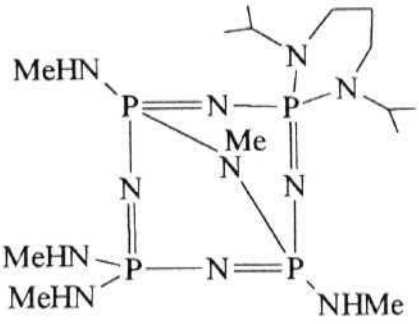
1.**102 (X-ray)**



1.**106**

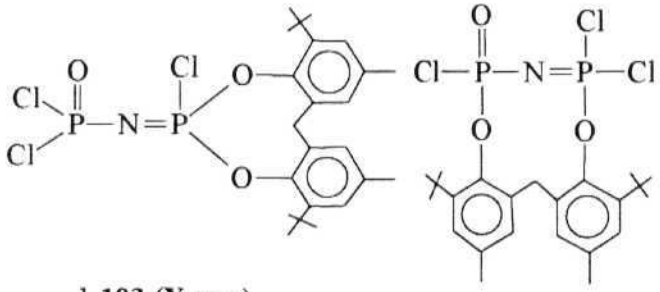


1.**107** (NMR, MS)



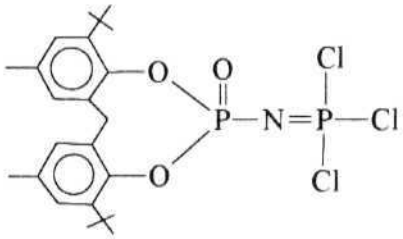
1.**109**

Reaction of the linear phosphazene $Cl_3P{=}NP(O)Cl_2$ (1.**3**) with CH_2[4-Me-6-*t*-Bu-$C_6H_2OH]_2$/ Et_3N afforded the cyclic compound 1.**103**. The other possible products (**R**) and (**S**) are not formed.



1.**103 (X-ray)**

(**R**)

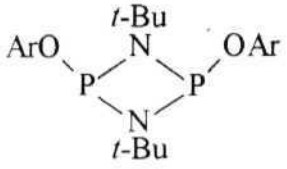


(S)

Part 2:

The first aspect of study in Part 2 deals with the reaction of (primarily) [ClPN-*t*-Bu]$_2$ (2.**1**) with phenols. In contrast to the isolation of *trans*-[(4-Me-C_6H_4O)PNPh]$_2$ (reported in the literature) by reacting $(ClPNPh)_2$ (2.**2**) with 4-Me-C_6H_4OH/ Et_3N, when

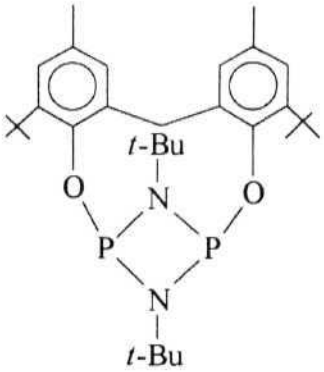
compound 2.**1** was treated with ArOH/ Et_3N, only *cis* [(ArO)PN-*t*-Bu]$_2$ (2.**38**-2.**43**) were isolated. The solid state structure of one of these compounds (2.**38**) has been determined by X-ray crystallography.



Ar =	2,6-Me_2-C_6H_3	[2.**38**, **X-ray**]
	2-Napthyl	[2.**39**]
	Oxinato	[2.**40**]
	4-MeO-C_6H_4	[2.**41**]
	4-*t*-Bu-C_6H_4	[2.**42**]
	4-Me-C_6H_4	[2.**43**]

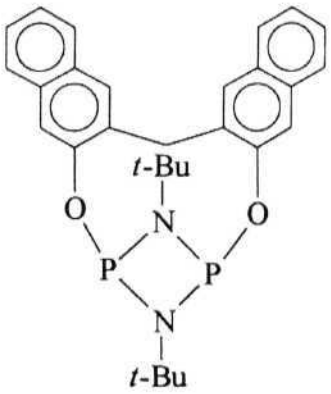
Use of the sodium salt of the phenol also led to the *cis*-isomer; however, when the lithium salt 2,6-$Me_2C_6H_3OLi$ was used, a *trans* isomer was indicated (but not isolated).

Since in the above reactions only *cis* isomers were obtained, it was thought prudent to utilize this result to prepare *ansa* type of compounds by treating 2.**1** with bifunctional reagents. Thus the novel compounds 2.**47**-2.**49** were isolated; in addition several others were identified by ^{31}P NMR spectroscopy. Interestingly in the reaction of 2.**1** with 2,2'-biphenol, the phosphazane ring cleaved end product 2.**55** was also isolated (^1H, ^{31}P, X-ray).



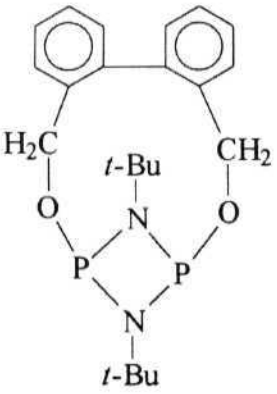
2.**47**

[δ(P): 143.9; **X-ray**]



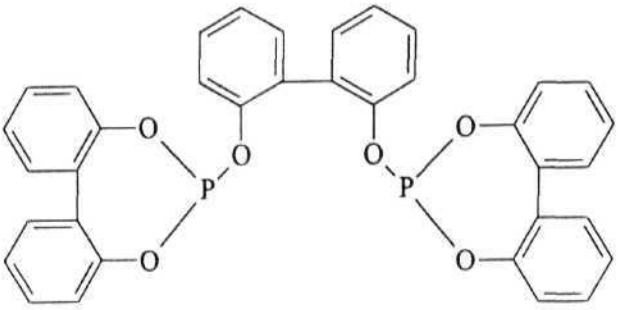
2.**48**

[δ(P): 181.4; **X-ray**]



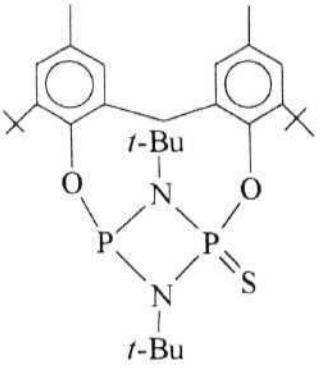
2.**49**

[δ(P): 125.6]

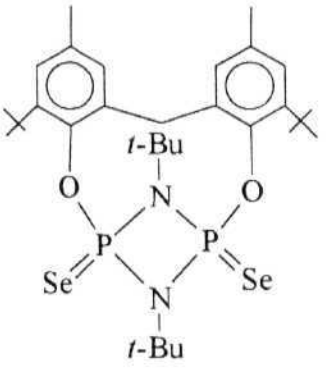


2.**55**

In contrast to the reaction of 2.**47** with excess of sulfur wherein the partially oxidized compound 2.**60** was isolated, the analogous reaction with selenium gave the fully oxidized product 2.**61**.



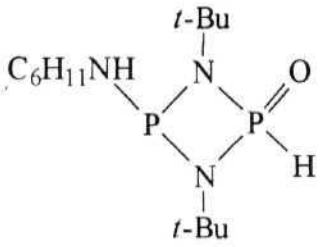
2.**60**



2.**61** [δ(P): 21.7; **X-ray**]

The last aspect on cyclodiphosphazanes concerns the attempted synthesis of partially substituted derivatives, [(ArO)P(N*t*-Bu)$_2$PCl]. We succeeded in isolating [(2,6-Me$_2$C$_6$H$_3$O)P(N*t*-Bu)$_2$PCl] (2.**56**) in a state of *ca* 90% purity by vacuum distillation, the other impurity being either the precursor (ClPN*t*-Bu)$_2$ (2.**1**) or the bis derivative [(2,6-Me$_2$C$_6$H$_3$O)$_2$PN*t*-Bu]$_2$ (2.**38**). Compound 2.**56** is quite reactive and in fact when an attempt was made to substitute the residual chlorine by a cyclohexylamino group, the only

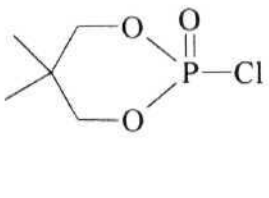
compound isolated was the hydrolyzed product 2.**59** in which the phosphoryl oxygen is *cis* to the cyclohexylamino group.



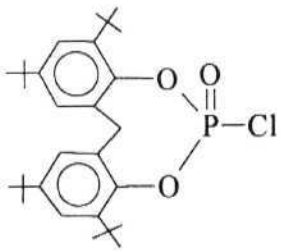
2.**59** (**X-ray**)

Part 3:

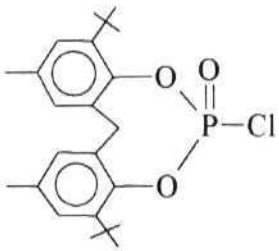
Here the first and the major theme is to study the reaction of cyclic chlorophosphate esters 3.**24**, 3.**25** and 3.**26** with strong bases [DBU, DBN, NMI, MI, DMAP] in an effort to isolate the reactive phosphate-base complexes such as **D**.



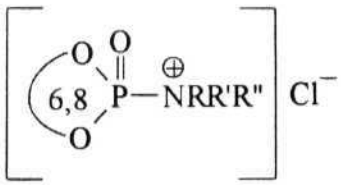
3.**24**



3.**25**

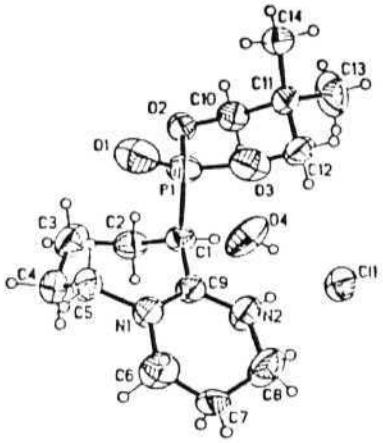


3.**26**

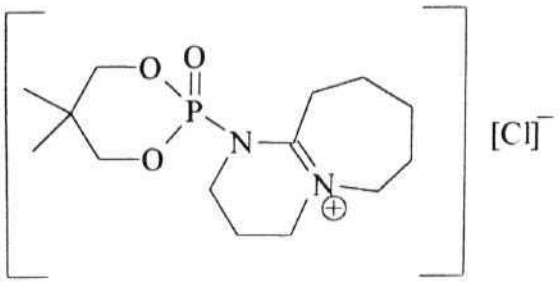


D

In an unusual reaction, 3.**24** reacted with DBU to give the phosphonate salt 3.**28** rather than the salt 3.**27** containing a P-N bond. A possible pathway involving the intial formation of 3.**27** was formulated.

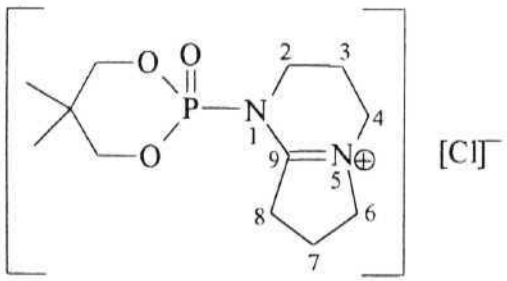


3.**28** [δ(P): 10.7]
ORTEP



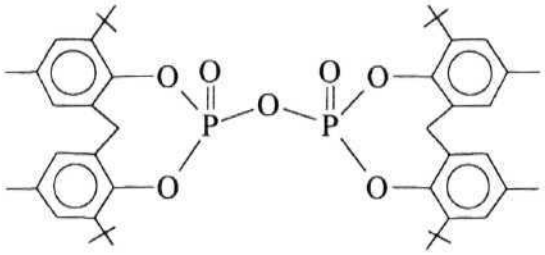
3.**27**

A compound analogous to 3.**28** has also been isolated from the reaction of the eight membered chloro compound 3.**26** with DBU. However the reaction of 3.**24** with DBN (which may be expected to give analogous products) took a different route and gave an air-sensitive product formulated as 3.**37** (NMR evidence).

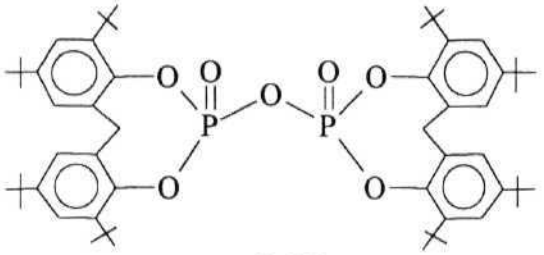


3.**37**

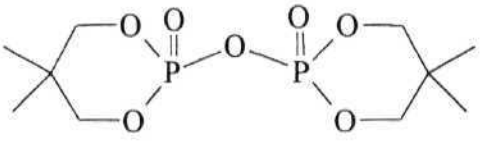
In many of these reactions the pyrophosphates, 3.**34,** 3.**35** and 3.**38** are also obtained presumably *via* the intermediacy of the salts; in solution the yields of these increase with time suggesting that they are formed by hydrolysis.



3.**34** (**X-ray**)

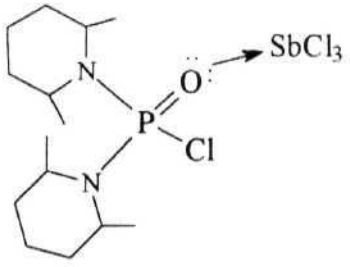


3.**35**

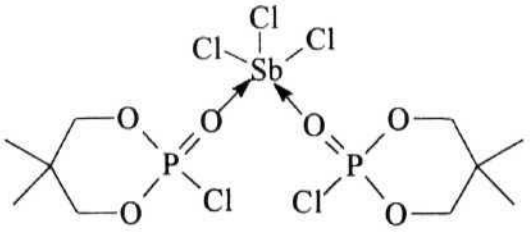


3.**38**

In the reaction of chlorophosphorus(III) compounds $[2,6\text{-}Me_2\text{-}C_5H_8N)]_2PCl$ (3.**45**), $(OCH_2CMe_2CH_2O)PCl$ (3.**39**) and $CH_2[4\text{-}Me\text{-}6\text{-}t\text{-}Bu\text{-}C_6H_2O]_2PCl$ (3.**40**) with bases we expected the salts $[2,6\text{-}Me_2(C_5H_8N)]_2P\text{-}Base]^+ Cl^-$, $[(OCH_2CMe_2CH_2O)P\text{-}Base]^+ Cl^-$ and $[CH_2(4\text{-}Me\text{-}6\text{-}t\text{-}Bu\text{-}C_6H_2O)_2P\text{-}Base]^+ Cl^-$; however, due to the extreme sensitivity of the products we could not isolate any well-defined product. The reaction of 3.**45** or 3.**39** with a Lewis acid such as $SbCl_5$ may be expected to lead to the phosphenium cations $[2,6\text{-}Me_2 (C_5H_8N)]_2P^+$ or $[OCH_2CMe_2CH_2O]P^+$ with the $[SbCl_6]^-$ counterion but the product that could be isolated was the phosphoryl adduct 3.**46,** probably *via* hydrolysis. Reaction of the Lewis acid $SbCl_3$ with $(OCH_2CMe_2CH_2O)P(O)Cl$ (3.**24**) also led to a crystalline acid-base adduct formulated as 3.**47** (evidence: analytical data).



3.**46** [δ(P): 23.3; **X-ray**]



3.**47** [δ(P): -3.4]

PART 1. PHOSPHAZENES

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1.1 *Introduction*

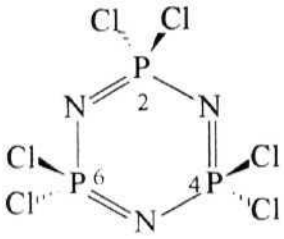
Phosphazenes are a class of compounds with a formal double bond between phosphorus and nitrogen. Among these, the chlorophosph(V)azenes with phosphorus(V) having a formal double bond to a two coordinated nitrogen atom and three additional σ-bonds (≡P=N-) are perhaps the most extensively studied; they can be short chain linear acyclic phosphazenes, cyclophosphazenes or long chain linear phosphazenes, more commonly known as poly(phosphazenes). The most straightforward synthetic route to these compounds involves ammonolysis of phosphorus pentachloride and subsequent thermolysis of the initial reaction product (eq 1.1).

$$PCl_5 + NH_4Cl \longrightarrow \underset{\text{Linear}}{P_XN_YCl_Z^{+}PCl_6^{-}} \xrightarrow{\Delta} \underset{\substack{\text{Cyclic}\\(n = 3, 4, 5, 6)}}{(NPCl_2)_n} \xrightarrow{\Delta} \underset{\substack{\text{Linear high}\\\text{polymer}}}{(NPCl_2)_n} \qquad (1.1)$$

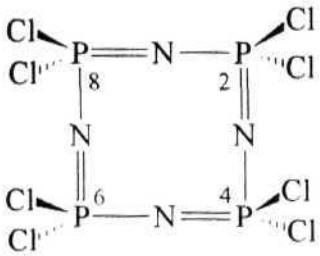
Because of the possibility of replacing the chlorines by various other functionalities which may be biologically or technologically useful, these phosphazenes have been attractive substrates for numerous researchers. Several of these derivatives are promising as a) thermally stable polymers[1-3] b) antitumour agents[4,5] c) anticoagulants[6] d) drug delivery systems[7,8] e) inhibitors in HIV-I (reverse transcriptase)[9] and other biochemical applications.[5]

There are several reviews available in the literature that deal with the chemistry of phosphazenes.[10-13] In this survey we largely confine ourselves to the (i) new developments during the past decade (1988 onwards) and (ii) reactions with di- and polyfunctional reagents. The substrates of interest are 2,2,4,4,6,6-hexachlorocyclotriphosphazene $N_3P_3Cl_6$ (1.**1**), 2,2,4,4,6,6,8,8-octachlorocyclotetra-

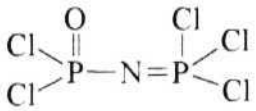
phosphazene $N_4P_4Cl_8$ (1.**2**) and the linear phosphazene $Cl_2P(O)=NPCl_3$ (1.**3**).* Whereas the first two can be conveniently prepared by the route shown in eq. 1.1,[14] compound 1.**3** can be obtained by treating phosphorus pentachloride with ammonium sulphate (eq 1.2).[15]



1.**1**



1.**2**



1.**3**

$$4PCl_5 + (NH_4)_2SO_4 \xrightarrow[1,1,2,2\text{-}C_2H_2Cl_4]{140^0C,\ 1h} \underset{\textbf{1.3}}{2Cl_2(O)P-N=PCl_3} + 8\,HCl + SO_2 + Cl_2 \qquad (1.2)$$

Phosphazene chemistry is predominantly the reactions (of these compounds) with nucleophilic reagents. Reactions of 1.**1**-1.**3** with monofunctional reagents could follow a geminal or a nongeminal replacement pattern or a combination of both. This point is elaborated in Scheme 1.1 which shows the possible isomeric compositions in the reaction using 1.**1**-1.**3** at the *bis* stage of substitution.

Shaw has elegantly summarized the earlier studies on 1.**1** and 1.**2** and these are given pointwise below;[16] more details from recent literature are added wherever appropriate.

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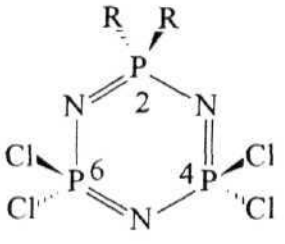
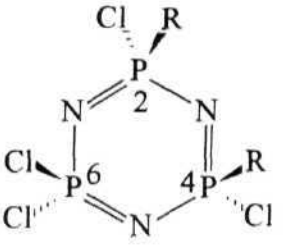
*Note: Numbering of the compounds is done in the following way: Part number followed by the actual compound number in that part. Predicted compounds or possible isomers are designated by letters A, B, etc. or Roman numerals.

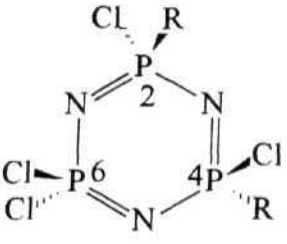
Scheme 1.1



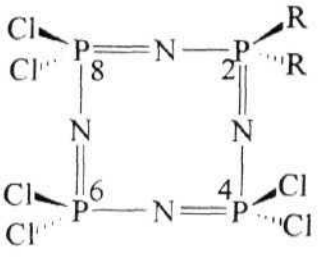
(2,2) (**A**)



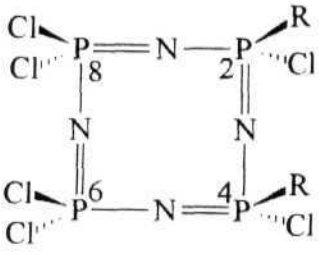
(2,4-*cis*) (**B**)



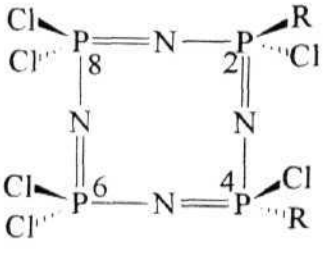
(2,4-*trans*) (**C**)



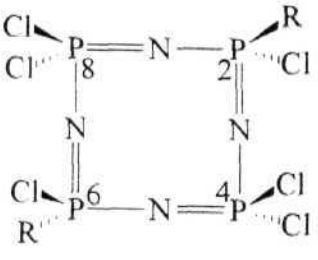
(2,2) (**D**)



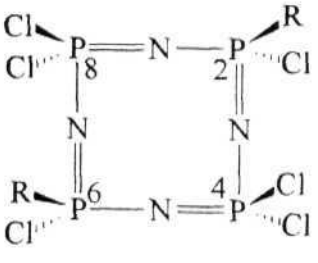
(2,4-*cis*) (**E**)



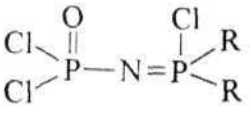
(2,4-*trans*) (**F**)



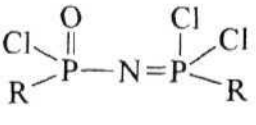
(2,6- *trans*) (**G**)



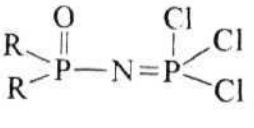
(2,6-*cis*) (**H**)



(**I**)



(**J**)



(**K**)

1.11 *Reactions with monofunctional nucleophiles*

(A) Reactions of $N_3P_3Cl_6$ (1.1)

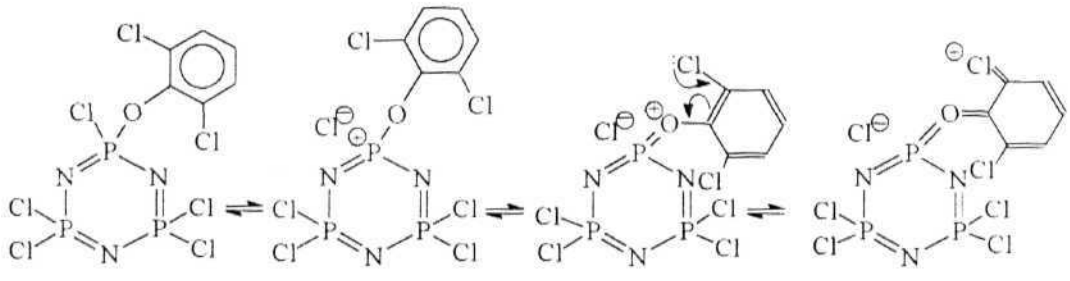
(i) Ammonia gives exclusively the geminal product, $N_3P_3(NH_2)_2Cl_4$ at the *bis* stage.[17]

(ii) Primary amines, RNH_2, depending on their reactivity and the reaction mechanism they follow, give at the *bis* stage, i.e. $N_3P_3(NHR)_2Cl_4$, either nongeminal (e.g: $EtNH_2$)[18] or geminal products (e.g: *t*-$BuNH_2$).[19] Bulky amines (e.g: 1-adamantylamine) may prefer a geminal pathway.[20] Geminal structures 2,2,4,4-$N_3P_3(NHR)_4Cl_2$ are overwhelmingly preferred at the *tetrakis* stage.

(iii) Secondary amines, R_2NH follow in general a nongeminal pathway, though at the *tris* stage $N_3P_3(NR_2)_3Cl_3$, solvent effects become important.[21]

(iv) Both alcohols (ROH) and phenols (ArOH) react almost exclusively by the nongeminal pathway. However recent work by Allcock and coworkers show that sterically hindered phenols (2,6-dichloro and 2,6-dimethyl phenol) prefer to attack by a geminal pathway at the *bis* stage of substitution.[22] A possible explanation involving some resonance stabilization in which structure (**O**) is claimed to have a stabilizing effect on the cation, is offered (Scheme 1.2). The leaving group departs with its bonding electron pair, followed rapidly by the attack of the organic nucleophile on the positively charged substrate.

Scheme 1.2



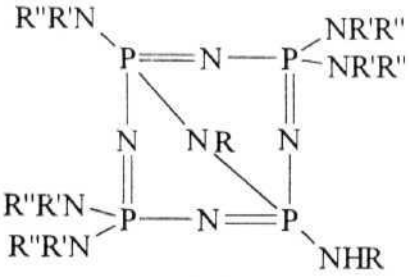
(**L**) (**M**) (**N**) (**O**)

The reaction with β-diketonates, (e.g. acetylacetonate or 1,3-cyclohexanedionate anion) produces both nongeminal and geminal products with the former predominating.[23]

(v) Mercaptans (RSH) prefer a geminal pathway throughout; in fact with thiophenol, only the *bis* 2,2-$N_3P_3(SPh)_2Cl_4$ and the *hexakis* $N_3P_3(SPh)_6$ derivatives are the major products.[24]

(B) Reactions of $N_4P_4Cl_8$ (1.2)

Here the potential number of products is much greater at each stage of substitution and hence structure determination is more difficult; thus studies on 1.**2** are rather limited.[25] Ammonia reacts with 1.**2** to give both geminal and nongeminal 2,6-derivatives at the *bis* replacement stage, $N_4P_4(NH_2)_2Cl_6$.[26] Primary amines tend to give a lot of resinous material due to cross-linkage reactions, thus making the amine difunctional. Thus exhaustive ammonolysis of 1.**2** leads to the "bicyclic" phosphazenes 1.**4** as one of the products.[27-30]



1.**4**

In partial aminolysis, those which give non-geminal *bis* derivatives (e.g. NH_2Et) with the trimer 1.**1** give only 2,6-*bis* derivatives, $N_4P_4(NHR)_2Cl_6$ with the tetramer 1.**2**,[31] whilst those which give geminal *bis* derivatives with 1.**1** tend to give both 2,4- and 2,6-derivatives $N_4P_4(NHR)_2Cl_6$ [R = *t*-Bu] with 1.**2**, (*cf* Scheme 1.2), with no geminal products.[32] Alcoholysis[33] and phenolysis[34] of 1.**2** follow predominantly a non-geminal pathway. However, in the reaction of 1.**2** with 2,6-dichlorophenol the major product at

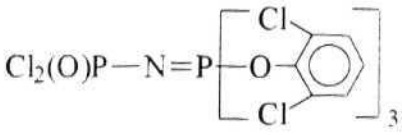
the *tetrakis* stage is 2,2,6,6-N_4P_4(O-2,6-$Cl_2C_6H_3$)$_4Cl_4$ (1.**5**).[22] Mercaptolysis follows a geminal pathway and at the *tetrakis* stage 2,2,6,6-$N_4P_4(SR)_4Cl_4$ has been isolated.[35]

(C) Reactions of $Cl_2P(O)$-N=PCl_3 (1.3)

Treatment of 1.**3** with an excess of methylamine affords two products 1.**6** and 1.7 (eq 1.3); the latter product probably arises due to partial hydrolysis.[36,37] The fully substituted amino derivatives, $(Me_2N)_2P(O)N=P(NMe_2)_3$ and $(PhNH)_2P(O)$-N=$P(NHPh)_3$ have also been synthesized.[38] Aryloxy derivatives are in general synthesized by the sodium salt route (eq. 1.4).[39-41] Only in the case of 2,6-dichlorophenol, a partially substituted derivative 1.**9** has been synthesized.[22]

$$Cl_2(O)P{-}N{=}PCl_3 + 10\ MeNH_2 \xrightarrow{5\ MeNH_3Cl} \underset{\mathbf{1.6}}{(MeNH)_2(O)P{-}N{=}P(NHMe)_3} + \underset{\mathbf{1.7}}{(MeNH)_2P(O){-}NH{-}P(O)(NHMe)_2} \qquad (1.3)$$

$$Cl_2(O)P{-}N{=}PCl_3 \xrightarrow[-NaCl]{6NaOAr} \underset{\mathbf{1.8}}{(ArO)_2(O)P{-}N{=}P(OAr)_3} \qquad (1.4)$$



1.9

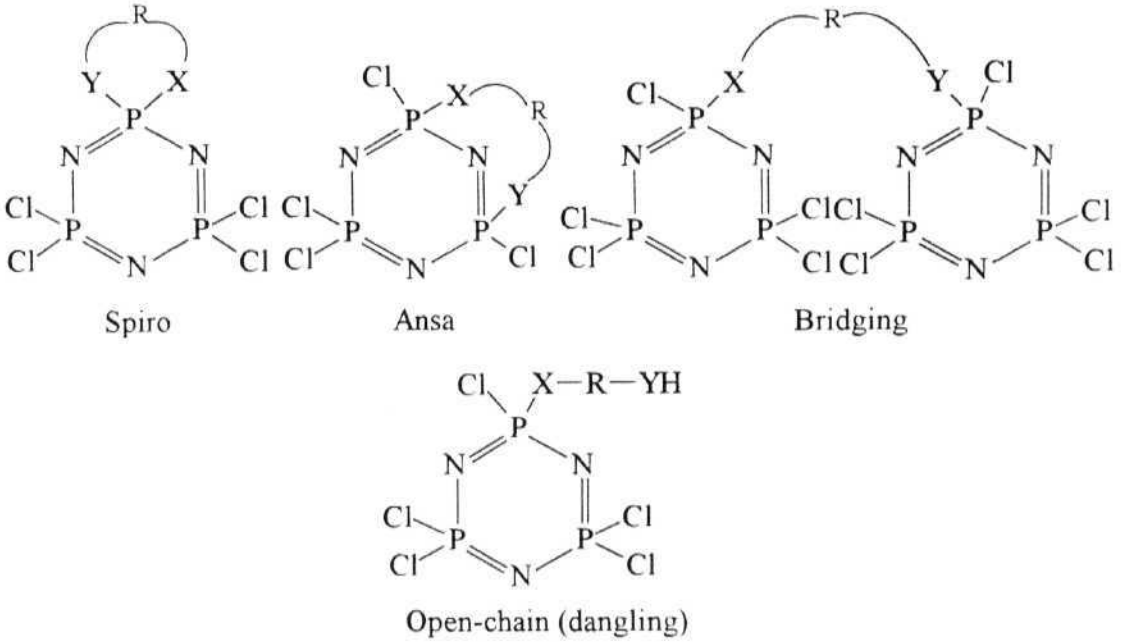
1.12 *Reactions with difunctional nucleophiles*

(A) Reactions of $N_3P_3Cl_6$ (1.1)

Difunctional reagents can react with 1.**1** to give, in principle, four types of products: (i) spiro (ii) ansa (two ends of the reagent attached to different P atoms in the same molecule), (iii) bridging (two ends bonded to P atoms from different phosphazene

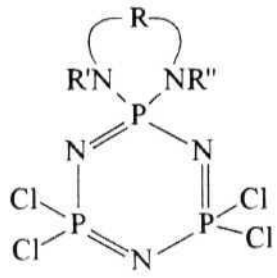
units) and (iv) dangling (only one end of the difunctional reagent attached to P) (Scheme 1.3). Some of the known monospirocyclic derivatives along with their ^{31}P NMR data are shown in Chart 1.1.

Scheme 1.3

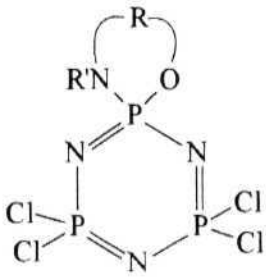


The following dispirocycles have been synthesized by analogous routes: $N_3P_3[MeNCH_2CH_2NMe]_2Cl_2$ (1.**29**),[56] $N_3P_3[HN(CH_2)_3NH]_2Cl_2$ (1.**30**),[57] $N_3P_3[MeN(CH_2)_3NH]_2Cl_2$ (1.**31**),[45] $N_3P_3[HN(CH_2)_2NH][HN(CH_2)_3NH]Cl_2$ (1.**32**),[58] $N_3P_3[HN(CH_2)_4NH]_2Cl_2$ (1.**33**),[57] $N_3P_3[HNCH_2CH_2NH][HN(CH_2)_4NH]Cl_2$ (1.**34**),[58] $N_3P_3[HN(CH_2)_3NH][HN(CH_2)_4NH]Cl_2$ (1.**35**),[58] $N_3P_3[HN(CH_2)_2O]_2Cl_2$ (*cis* + *trans*) (1.**36**),[42] $N_3P_3[MeN(CH_2)_2O]_2Cl_2$ (*cis*) (1.**37**),[49] $N_3P_3[HN(CH_2)_3O]_2Cl_2$ (*cis* + *trans*) (1.**38**),[50] $N_3P_3[MeN(CH_2)_2O]_2Cl_2$ (*cis*) (1.**39**),[50] $N_3P_3[HN(CH_2)_3O]_2Cl_2$ (*cis* + *trans*) (1.**40**),[50] $N_3P_3[O(CH_2)_nO]_2Cl_2$ [n = 2 (1.**41**), 3 (1.**42**), 4 (1.**43**)][16], $N_3P_3[2,2'\text{-}O_2\text{-}(C_6H_4)_2]_2Cl_2$ (1.**44**),[59] $N_3P_3[1,2\text{-}(NH)_2\text{-}(C_6H_4)]_2Cl_2$ (1.**45**)[60] and $N_3P_3[1,2\text{-}O_2C_6H_4]_2Cl_2$ (1.**46**).[61]

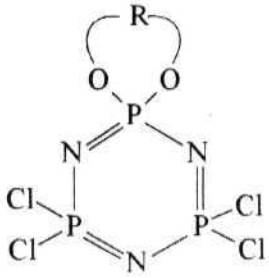
Chart 1.1. Selected spirocyclic cyclotriphosphazenes with their ^{31}P NMR data



(I)



(II)



(III)

Structure **I**

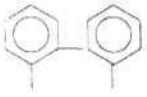
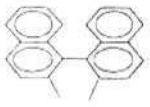
Compd. No.	R	R'	R''	$\delta(PCl_2)$	$\delta(P)$ (spiro)	J(P-P) (Hz)	Ref.
1.**10**	$-CH_2-CH_2-$	H	H	23.5	22.8	45.7	42
1.**11**	$-CH_2-CH_2-$	Me	Me	20.4	23.8	41.8	38
1.**12**	$-(CH_2)_3-$	H	H	21.5	7.5	45.5	43
1.**13**	$-(CH_2)_3-$	Me	Me	16.5	19.6	-	44
1.**14**	$-(CH_2)_3-$	H	Me	20.3	9.8	39.1	45
1.**15**	$-(CH_2)_4-$	H	H	21.2	12.8	46.0	46
1.**16**		H	H	21.3	13.6	70	47
1.**17**		H	H	20.6	15.0	55	47
1.**18**		H	H	18.9	13.5	63	47

contd..

Structure **II**

Compd. No.	R	R'	$\delta(PCl_2)$	δ(P) (spiro)	J(P-P) (Hz)	Ref.
1.**19**	$-CH_2-CH_2-$	H	24.9	24.3	53.9	48
1.**20**	$-CH_2-CH_2-$	Me	25.1	22.4	53.9	49
1.**21**	$-(CH_2)_3-$	H	22.4	7.20	53.9	50

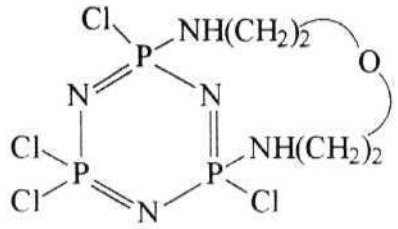
Structure **III**

Compd. No.	R	$\delta(PCl_2)$	δ(P) (spiro)	J(P-P) (Hz)	Ref.
1.**22**	$-CH_2-CH_2-$	22.5	23.8	67	51
1.**23**	$-(CH_2)_3-$	23.0	2.4, 2.2	70.8	52
1.**24**	$-HCMeCH_2CH_2-$	22.10, 25.59	2.74	[a]	53
1.**25**	$-(CH_2)_4-$	23.0	9.3	74.3	52
1.**26**		22.03	20.56	88	54
1.**27**		25.44	13.54	71	59
1.**28**		23.48	14.98	70.96	55

[a] J(A-B) = 57.9, J(A-X) = 61.7, J(B-X) = 78.6 Hz.

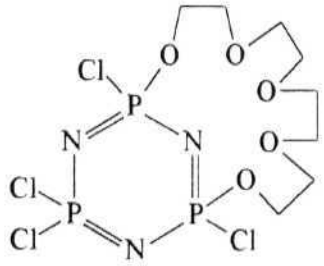
Examples of *tris* spiro derivatives include $N_3P_3[MeNCH_2CH_2NMe]_3$ (1.**47**),[56] $N_3P_3[HN(CH_2)_3NH]_3$ (1.**48**),[57] $N_3P_3[MeN(CH_2)_3NH]_3$ (1.**49**),[45] $N_3P_3[1,2\text{-}(NH)_2C_6H_4]_3$ (1.**50**),[47] $N_3P_3[HNCH_2CH_2O]_3$ (1.**51**),[42] $N_3P_3[MeNCH_2CH_2O]_3$ (1.**52**),[49] $N_3P_3[O_2C_6H_4]_3$ (1.**53**),[63] $N_3P_3[1,8\text{-}O_2C_{10}H_6]_3$ (1.**54**),[62] $N_3P_3[2,2'\text{-}O_2C_{12}H_8]_3$ (1.**55**)[63] and $N_3P_3[1,2\text{-}S_2C_6H_4]_3$ (1.**56**).[47]

Ansa compounds have not been so commonly encountered. The derivative 1.**57** with a chain of seven atoms between the two phosphorus atoms is prepared by treating 1.**1** with 1,5-diaminodiethylether, $H_2N(CH_2)_2O(CH_2)_2NH_2$.[64] Reaction of 1.**1** with

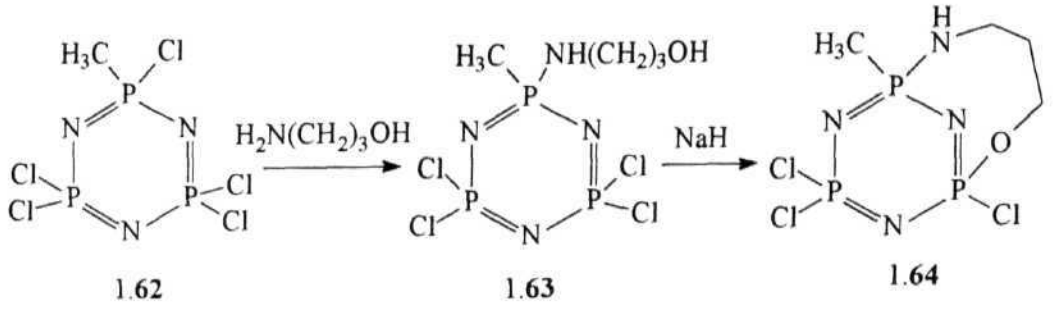


1.**57**

$HO(CH_2)_2O(CH_2)_2OH$ is reported to yield three products: *spiro*-2,2 $N_3P_3[O(CH_2)_2O(CH_2)_2O]Cl_4$ (1.**58**), *ansa*-2,4-$N_3P_3[O(CH_2)_2O(CH_2)_2O]Cl_4$ (1.**59**) and the bridged derivative $(N_3P_3Cl_5)_2[O(CH_2)_2O(CH_2)_2O]$ (1.**60**). The diphosphaza crown 1.**61** is another interesting *ansa* compound and has been reported by Brandt and co-workers.[65,66] However the first *ansa* compound (1.**64**) was prepared by Harris and Williams by an indirect route (eq. 1.5).[67] Subsequently, the *ansa* compounds 1.**65** and 1.**66** have also been synthesized.[16] An elegant approach has been devised by Allcock and coworkers to obtain *ansa* derivatives (Scheme 1.4).[54] Bis ansa compounds 1.**74** and 1.**75** are also reported recently.[68]

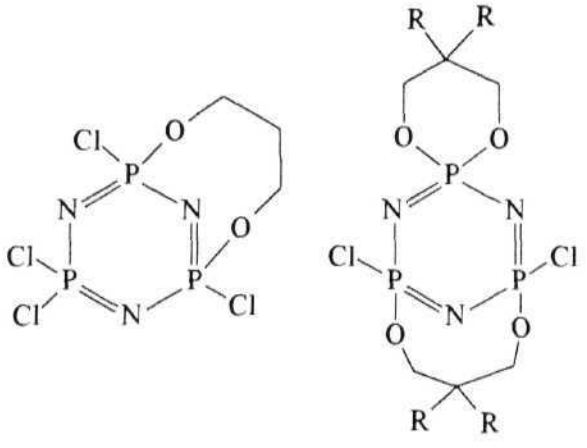


1.**61**



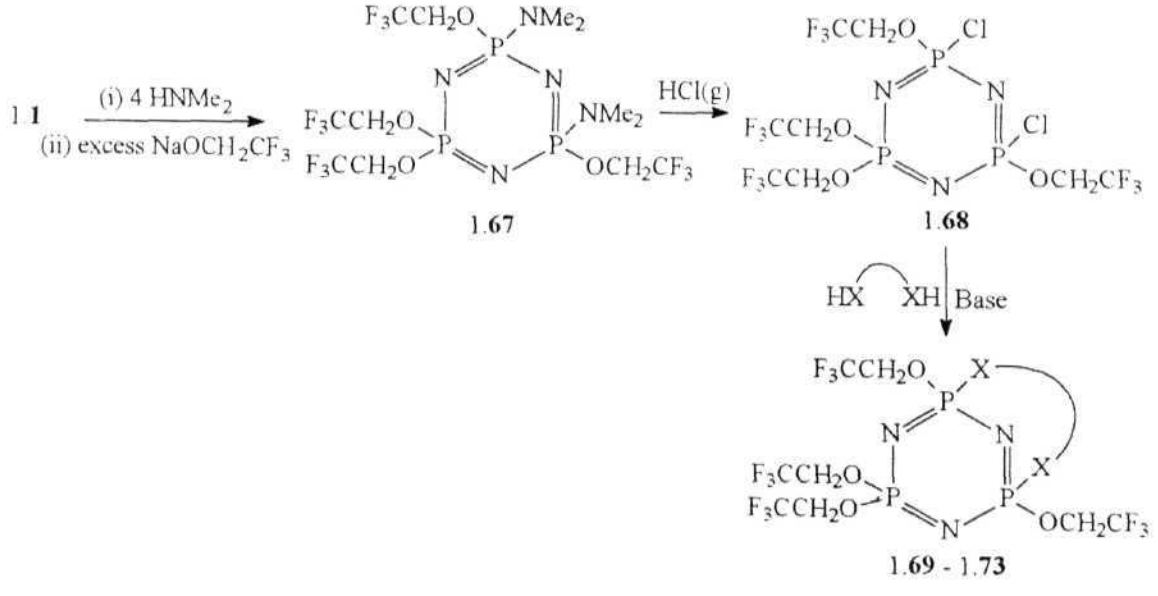
(1.5)

1.62 1.63 1.64

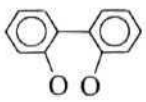
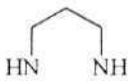


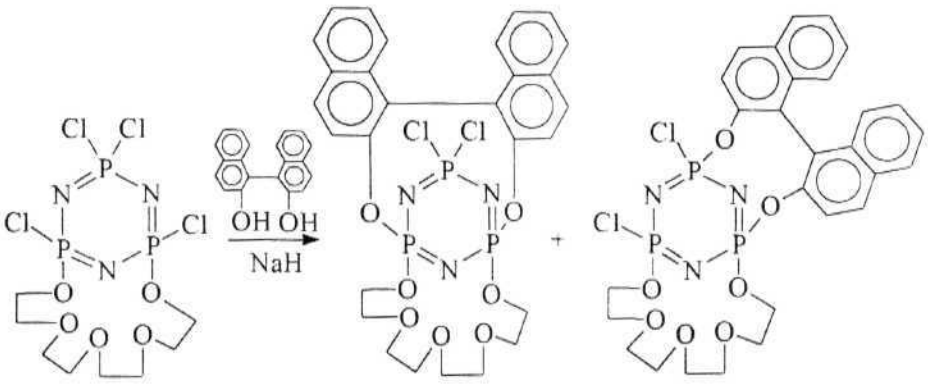
1.65 1.66 (**a**: R = H; **b**: R = Me)

Scheme 1.4



1.67 1.68 1.69 - 1.73

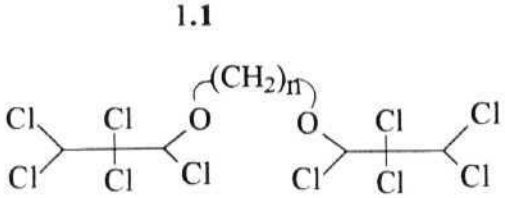
Compd. No	X---X	^{31}P NMR			
		δ(A)	δ(B)	δ(C)	J(PNP) (Hz)
1.69		22.03	20.56	--	88
1.70		26.96	25.61	22.0	79, 88, 91
1.71		22.77	21.22	--	87
1.72		26.14	21.14	--	70
1.73		26.96	20.66	--	73



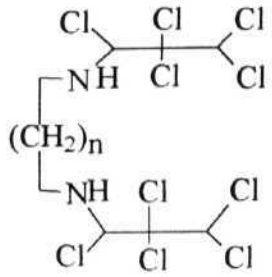
1.61 **1.74** **1.75**

In the case of diols $HO(CH_2)_nOH$ (n = 3 or 4) and diamines $H_2N(CH_2)_nNH_2$ (n = 5-10) singly bridged derivatives $N_3P_3Cl_5[O(CH_2)_nO]N_3P_3Cl_5$ (**1.76**) and $N_3P_3Cl_5[NH(CH_2)_nNH]N_3P_3Cl_5$ (**1.77**), respectively, have been isolated.[69] For the diamines where n = 6 or 8 the doubly bridged $N_3P_3Cl_4[NH(CH_2)_nN_3P_3Cl_4]$ (**1.78**) and the triply bridged $N_3P_3Cl_3[NH(CH_2)_nN_3P_3Cl_3]$ (**1.79**) are also formed.[70]

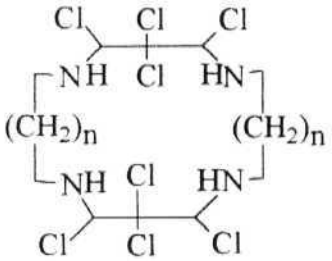
1.1



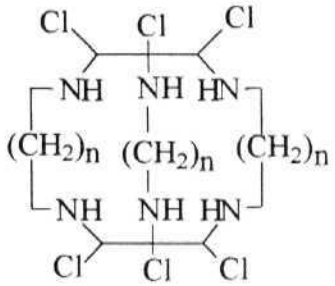
1.76 (n = 3,4)



1.77 (n = 5, 8)

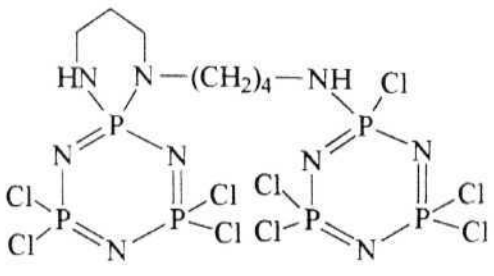


1.78 (n = 6, 8)

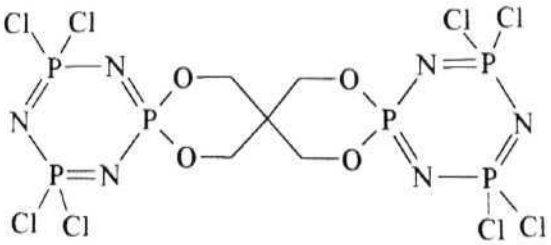


1.79 (n = 6, 8)

Bridged compounds are also common if tri- and tetrafunctional reagents are used. Two examples are compounds **1.80** and **1.81**.[71]



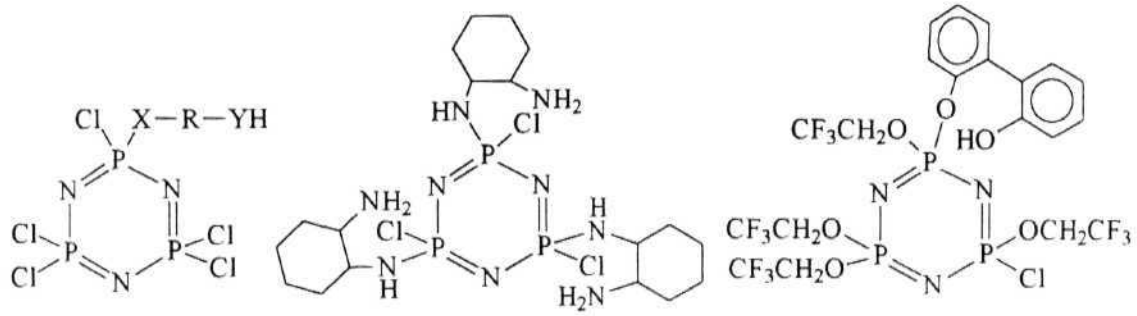
1.80



1.81

Lastly, one of the ends of the di/ polyfunctional reagents may remain unreacted. Examples of this type, other than 1.**63**, are shown in Chart 1.2.

Chart 1.2



1.**82** X = Y = O; R = $(CH_2)_3$ (ref. 60) 1.**85** (ref. 45)
1.**83** X = Y = O; R = $(CH_2)_4$ (ref. 16)
1.**84** X = Y = O; R = $(CH_2)_n$ (not isolated; ref. 16)

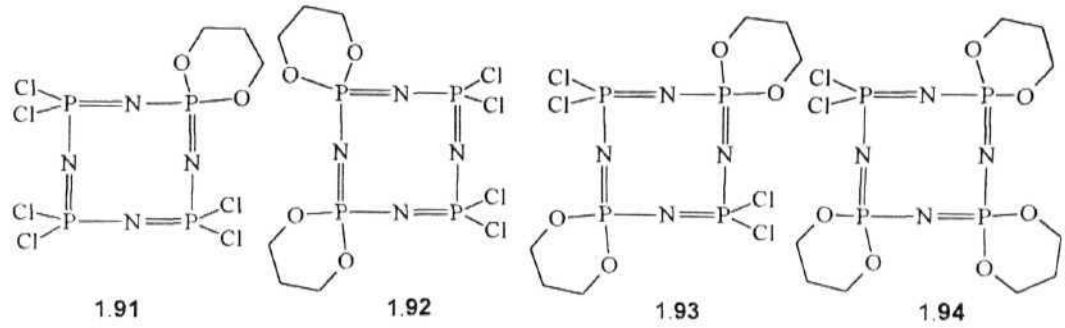
1.**86** (ref. 52)

(B) Reactions of $N_4P_4Cl_8$ (1.2)

The tetramer 1.**2** is more reactive than the trimer and gives rise to a much larger number of products. Even after isolation most of the characterization is done by NMR (^1H and ^{31}P). The spirocyclic derivatives $N_4P_4[MeN(CH_2)_2NMe]_2Cl_4$ (1.**87**)[72] and $N_4P_4[NH(CH_2)_3NH]Cl_6$ (1.**88**)[72] have been isolated prior to the year 1984. The compounds $N_4P_4(NMe_2)_6[O(CH_2)_2NMe]$ (1.**89**)[73] and $N_4P_4(OMe)_6[O(CH_2)_3O]$ (1.**90**)[73] were characterized after derivatization.[72] The product from the reaction of 1.**2** with ethylene glycol was too unstable to be isolated.[72] Later work was done mainly by Shaw and coworkers though much of it, to our knowledge, remains unpublished in full form. These results are summarized below.[16]

From the reaction of 1,3-propanediol, one mono derivative $N_4P_4[O(CH_2)_3O]Cl_6$ (1.**91**), two isomeric *bis* derivatives $[N_4P_4O(CH_2)_3O]_2Cl_4$ (1.**92**, 1.**93**) and one *tris* derivative $N_4P_4[O(CH_2)_3O]_3Cl_2$ (1.**94**) have been isolated.[16] Compounds analogous to 1.**91** and 1.**93** have also been isolated using 1,4-butanediol; the third compound $N_4P_4[O(CH_2)_4O]_2Cl_4$ showed a single line ^{31}P NMR signal and is assigned a structure similar to 1.**92**. Analysis is done mainly by NMR; as an illustration, the ^{31}P NMR spectra

of 1.**91**(A_2MX) and 1.**93** (AA'XX') are shown in Fig 1.1. It is noted that the instability of the product with a given diol is considerably greater for the tetrameric system than for the trimeric system. Other known spirocyclic derivatives of the tetrameric system are 1.**95**-1.**97**.[16,61]



1.**91** 1.**92** 1.**93** 1.**94**

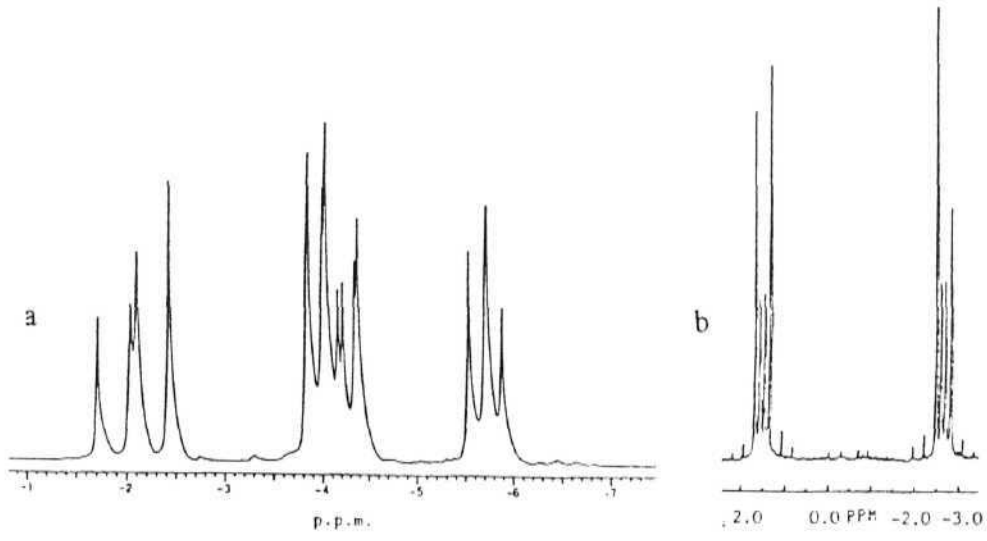
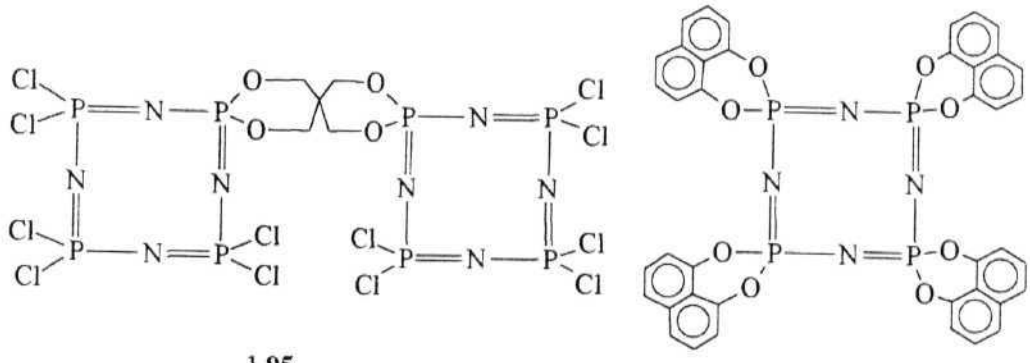
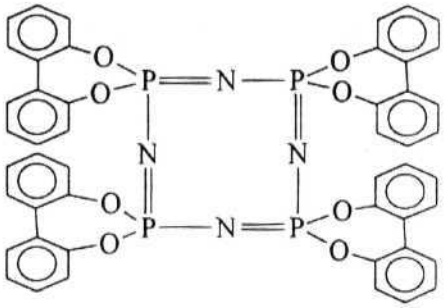


Fig 1.1 ^{31}P NMR spectra of (a) compound 1.**91** and (b) compound 1.**93**.



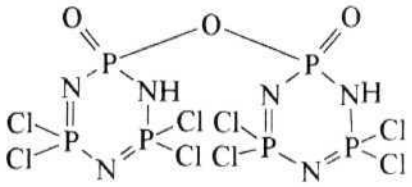
1.**95** 1.**96**



1.97

1.13 *Other aspects of cyclophosphazene chemistry*

Hydrolysis products of cyclophosphazenes undergo tautomerism; for example, in the controlled hydrolysis of $N_3P_3Cl_6$ (1.**1**) compound 1.**98** is isolated.[71] Even the alkoxy



1.98

phosphazenes undergo thermal rearrangement.[74] For example *cis*-N_3P_3(O-C_6H_4-Me-p)$_2$(OMe)$_4$ undergoes thermal rearrangement to *cis*-$N_3Me_3P_3O_3$(OMe)(OC_6H_4-Me-p)$_2$.[75] Since aminophosphazenes provide basic nitrogen sites, complexation is also possible; several papers have appeared in the literature on this aspect.[76-80] Polyphosphazenes with various side groups have several potential applications and this aspect has been a subject of study for the past several years.[18,81-90]

1.14 *Structural aspects*

^{31}P NMR spectroscopy is the most valuable tool for structural characterization of cyclophosphazenes in solution. Selected data that may be useful in analysing the spectra in the present work are listed in Table 1.1 (see also Chart 1.1). X-ray crystallography,

obviously, has been the tool of choice in the solid state. Aspects of bond lengths and bond angles will be brought forth in the Results and Discussion section to avoid duplication. Apart from the structural proof, the interests in these studies include mainly (i) P-N bond lengths and angles and (ii) Phosphazene ring conformations.[12]

Table 1.1 ^{31}P NMR spectroscopic data for selected cyclophosphazenes

Compound	Struct.	$\delta(PCl_2)$	$\delta(PClR)$	$\delta(PR_2)$	J(Hz)	Ref.
$N_3P_3Cl_6$		19.3				91
$N_3P_3(NH_2)_2Cl_4$	2,2	18.3	----	9.0	48.5	92
$N_3P_3(HN\text{-}i\text{-}Pr)_2Cl_4$	2,2	19.8	----	9.4	49.5	93
$N_3P_3(HN\text{-}t\text{-}Bu)_2Cl_4$	2,2	17.5	----	0.7	44.7	91
$N_3P_3(HN\text{-}1\text{-}ad)_2Cl_4$[a]	2,2	18.2(d)	----	1.1(t)		20
$N_3P_3(O\text{-}2,6\text{-}Cl_2C_6H_4)_2Cl_4$	2,2	22.8	----	-1.3	70	22
$N_3P_3[O\text{-}CMe{=}CH\text{-}C(O)Me]_2Cl_4$	2,4	25.3	13.5	----	66.3	23
$N_3P_3[O\text{-}CMe{=}CH\text{-}C(O)Me]_2Cl_4$	2,2	24.6	----	-5.62	64.3	23
$N_3P_3[HN(CH_2)_2NH]F_4$	----	10.2	----	30.1	990[b]	50
$N_3P_3(HN(CH_2)_3NH)F_4$		10.6		16.3	910[b]	50
$N_3P_3(O(CH_2)_3O)F_4$		9.00		15.2	910[b]	50
$N_3P_3[O(CH_2CH_2O)_4]Cl_4$[c]	2,2	15.9(t)		23.2(d)	-62.6	94
$N_3P_3[O(CH_2CH_2O)_4]Cl_4$(*ansa*)[d]	2,4	----	18.7(d)	25.0(t)	67.4	94
$N_3P_3[HN(CH_2)_4NH]_3$	----	21.2,	----	12.8,	46.0	46
		20.8		13.1		
$N_4P_4Cl_8$		-6.5				95
$N_4P_4(NH_2)_2Cl_6$	2,6	-5.8			69.0	96
$N_4P_4(NH_2)_4Cl_4$	2,2,6,6	-13.1		0.0		96

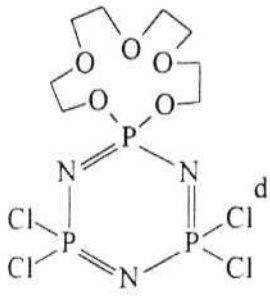
contd..

Table 1.1 contd..

$N_4P_4(NC_2H_4)_2Cl_6$	2,2	-6.5, -5.9	18.8	11.6,26.1	97
$N_4P_4(NMePh)_4Cl_4$	2,2,6,6	-11.5	-5.4	37.1	98
$N_4P_4(NMeCH_2CH_2NMe)Cl_6$		-8.3 (A)	6.1(spiro)	42.1 (AB),	72
		-6.2 (B)	(X)	27.1 (AX)	
				-1.1 (BX)	
$N_4P_4(NMe_2)_6[NH(CH_2)_3NH]$			1.6, 7.2,	42.2 (AB)	72
			8.9	36.8 (AX)	
				-1.1 (BX)	
$N_4P_4(O\text{-}2,6\text{-}Cl_2C_6H_3)_4Cl_4$		-	29.6(2B)	83.0	22
		18.5(2A)			
$Cl_2P(O)N{=}PCl_3$		-12.7(d)		19.5	99
		-1.1 (d)			
$Cl_2P(O)N{=}P(O\text{-}2,6\text{-}Cl_2C_6H_4)_3$		-22.0	-16.0	58	22
$N_4P_4(NHMe)_6(NMe)$[e]		18.5	21.5	39.0	100
$N_4P_4(NHMe)_6(NMe).HCl$		15.6	18.0	37.0	100
$N_4P_4(NMe_2)_5[NEt(NHEt)]$[e]		19.7	22.5	42.7, 42.7	101
		18.9		33.0	

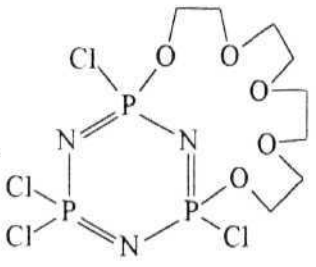
[a] 1-ad = 1-adamantyl [b] $^1J(PF)$; $^2J(P\text{-}P)$ could not be determined.

c =



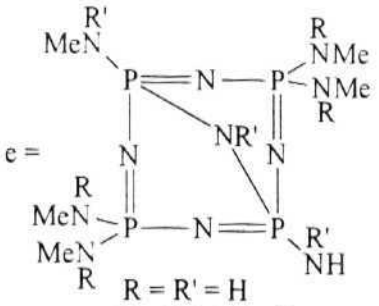
Spiro

d =



Ansa

e =



R = R' = H
R = Me, R' = Et

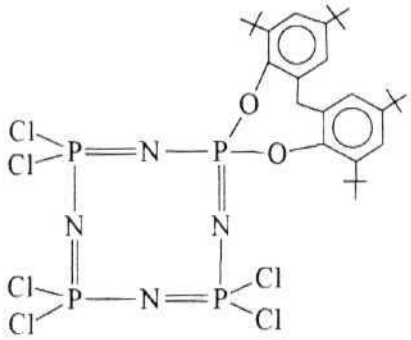
1.15 *OBJECTIVES OF THE PRESENT WORK*

The main objective of this part of the work is to study the reactions of octachlorocyclotetraphosphazene ($N_4P_4Cl_8$) with difunctional reagents in an effort to isolate structurally (X-ray) characterizable products and to compare the structural features with those obtained by using hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) and the linear phosphazene $Cl_2P(O)N{=}PCl_3$.

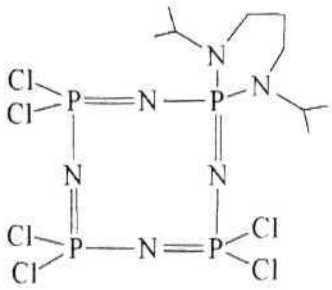
1.2 *Results and Discussion*

The reaction of $N_4P_4Cl_8$ (1.**2**) with the difunctional reagents 2,2'-methylenebis(4,6-di-*t*-butyl phenol) [as its sodium salt] and N,N'-diisopropyl-1,3-propanediamine gives the spirocyclic products 2,2-N_4P_4\{[O-C_6H_2-4,6-(*t*-Bu)$_2$]$_2$$CH_2$\}$Cl_6$ (1.**99**) and 2,2-N_4P_4[N(*i*-Pr)-$CH_2CH_2CH_2$N(*i*-Pr)]Cl_6 (1.**100**). Further reaction of **1.100** with two mole equivalents of N,N'-diisopropyl-1,3-propanediamine affords the novel dispiro derivative 2,2,6,6-N_4P_4[N(*i*-Pr)$CH_2CH_2CH_2$N(*i*-Pr)]$_2Cl_4$ (1.**101**). Analogous reaction of $N_3P_3Cl_6$ (1.**1**) with the above diamine gives the monospiro derivative N_3P_3[N(*i*-Pr)$CH_2CH_2CH_2$N(*i*-Pr)]Cl_4 (1.**102**) readily. The linear phosphazene, $Cl_2P(O)N{=}PCl_3$ (1.**3**) reacts with CH_2[4- Me-6-*t*-Bu-$C_6H_2OH]_2$ and Et_3N to give the cyclic product $Cl_2P(O)N{=}P$[(O-4-Me-6-*t*-Bu-$C_6H_2)_2CH_2$]Cl (1.**103**). The structures of 1.**99**-1.**103** are shown in Chart 1.3. The yields in all these reactions are moderate (60-

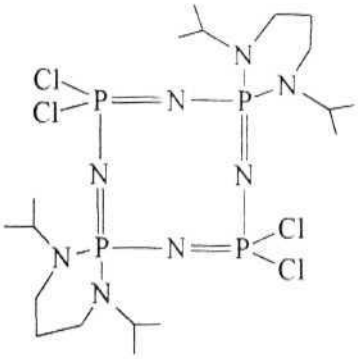
Chart 1.3



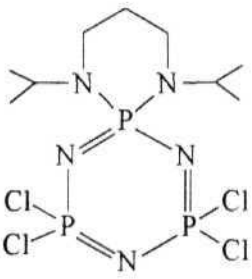
1.**99** (X-ray)



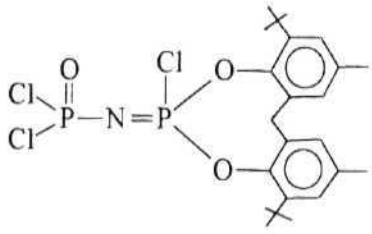
1.**100** (X-ray)



1.**101** (X-ray)

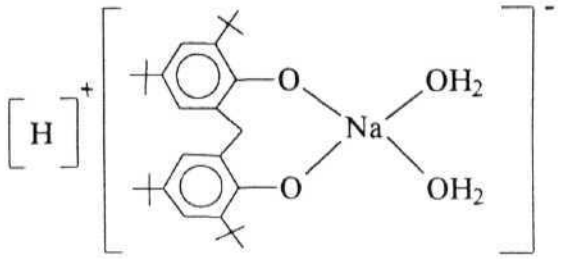


1.**102** (X-ray)



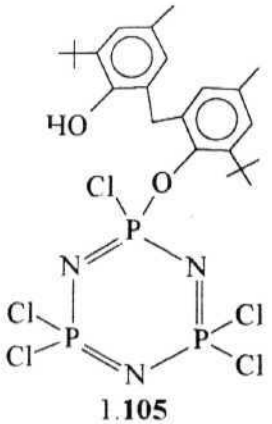
1.**103** (X-ray)

90%) except in the case of 1.**99** (~ 23%); the lower yield of the latter may be due to incomplete formation of the disodium salt of the diol. In fact the compound $[Na]^+[H]^+\{(O\text{-}4,6\text{-}(t\text{-}Bu)_2C_6H_4)_2\text{-}CH_2\}^{2-}.2H_20$ (1.**104**), obtained by reacting the diol with an excess of sodium followed by crystallization in air, has been structurally characterized



1.**104**

in our laboratory.[102] We did not succeed in isolating a compound analogous to 1.**99** in a pure state using $N_3P_3Cl_6$ (1.**1**). However when the sodium salt of the closely related diol, 2,2'-methylenebis-(4-methyl-6-*t*-butyl-phenol) was used, the major product (~30%) showed a doublet at 21.8 ppm (2P, $^2(J(P\text{-}P) = 61.0$ Hz) and a triplet at 8.2 ppm (1P) in the ^{31}P NMR [Fig 1.2]; the monosubstituted structure $N_3P_3(O\text{-}4\text{-}Me\text{-}6\text{-}t\text{-}Bu\text{-}C_6H_2\text{-}CH_2\text{-}4\text{-}Me\text{-}6\text{-}t\text{-}Bu\text{-}C_6H_2OH)Cl_5$ (1.**105**) is assigned for this on the basis of mass spectrum and available data on the trends in ^{31}P NMR [For a spiro derivative we expect a triplet upfield to 8.2 ppm; for an ansa derivative, an upfield *doublet* and a down field *triplet* is expected[11a]]. In addition, in the ^1H NMR spectrum two peaks each for the methyl and *t*-butyl protons are observed, as expected for an unsymmetrically linked diol residue.



1.**105**

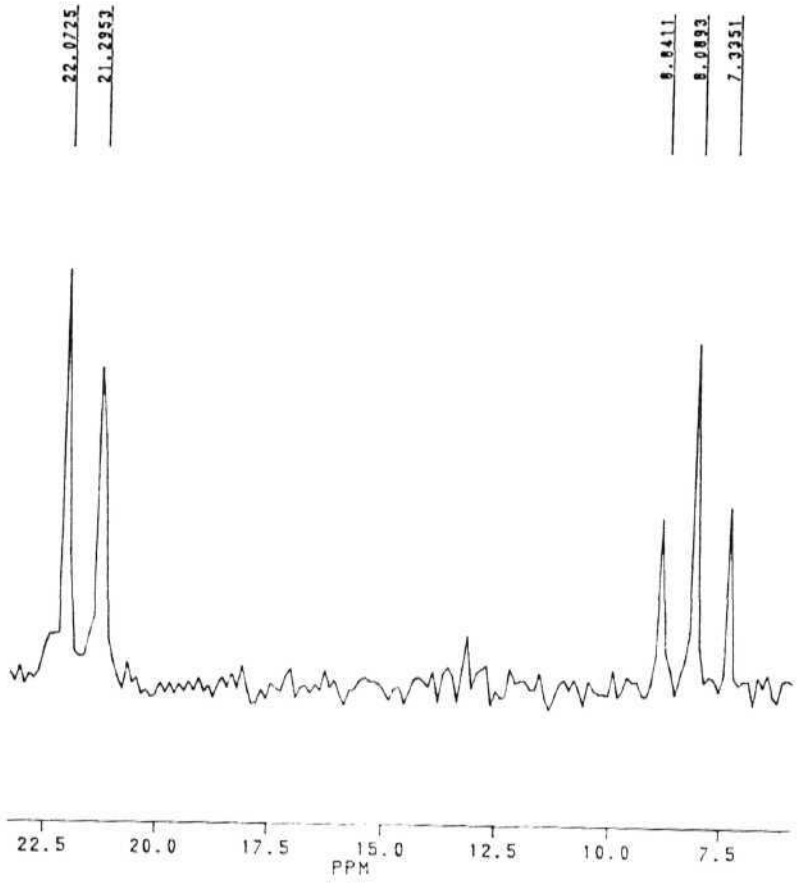
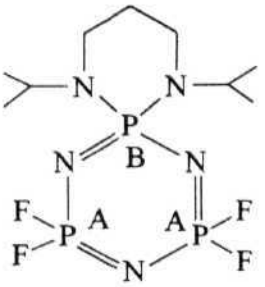


Fig. 1.2 ^{31}P NMR spectrum of compound 1.**105**

Compounds 1.**99**-1.**103** are stable under dry nitrogen in the solid state at room temperature; however the monospiro derivatives 1.**99** and 1.**100** are very unstable to moisture. The difference in stability between the tetrameric compound 1.**100** and the trimeric compound 1.**102** is also reflected, to some degree, in the fluorination reactions. While 1.**102** can be readily fluorinated by KF/ CH_3CN[50] to give the new fluorospirocycle $N_3P_3[N(i\text{-}Pr)\text{-}CH_2CH_2CH_2\text{-}N(i\text{-}Pr)]F_4$ (1.**106**; Fig 1.3(a) shows the ^{31}P NMR) the hygroscopic product obtained by fluorinating the tetrameric compound 1.**100**, had only



δ (P_A): 11.4 [^1J(P-F) ~ 965 Hz]
δ (P_B): 15.4 [^2J(P-P) ~ 90 Hz]

1.**106**

one discernible PF_2 triplet [δ: -13.6, $^1J(P\text{-}F)$ ~850 Hz) in the ^{31}P NMR (Fig 1.3(b)] instead of the expected two; this suggests a partial hydrolysis in the latter case. There are also peaks in the region -2.1 to 2.0 ppm and -10.0 to -12.8 ppm which are attributable to the PF(O)-NH group but the spectrum is too complicated to analyse further. The ^1H NMR also showed a complex spectrum. A peak corresponding to $[N_4P_4F_5(H)\ (OH)]^+$ is observed in the mass spectrum suggesting that it is probably $N_4P_4F_5(OH)[N(i\text{-}Pr)\text{-}CH_2CH_2CH_2N(i\text{-}Pr)]$ (1.**107**);[50,72] such a feature has been observed for several spirocyclic

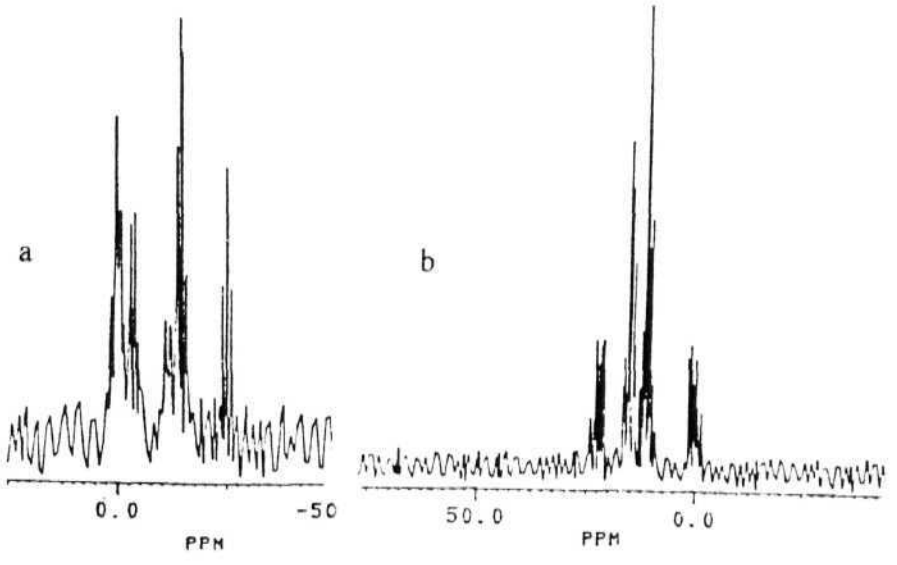
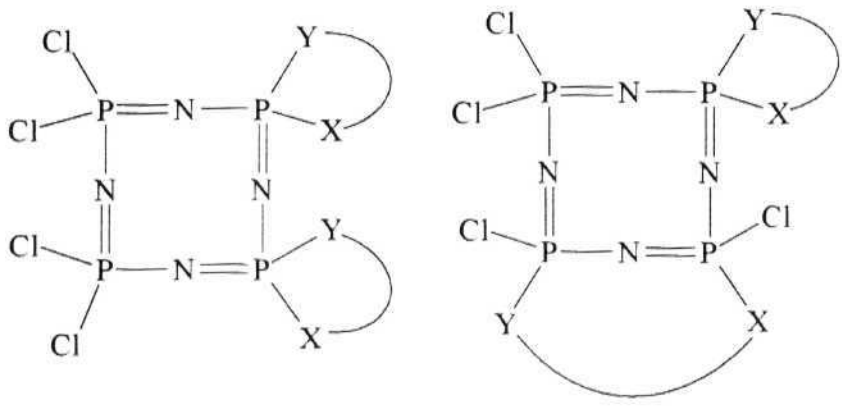


Fig 1.3 ^{31}P NMR spectra of a) 1.**106** and b) the product 1.**107** obtained by fluorinating 1.**100**.

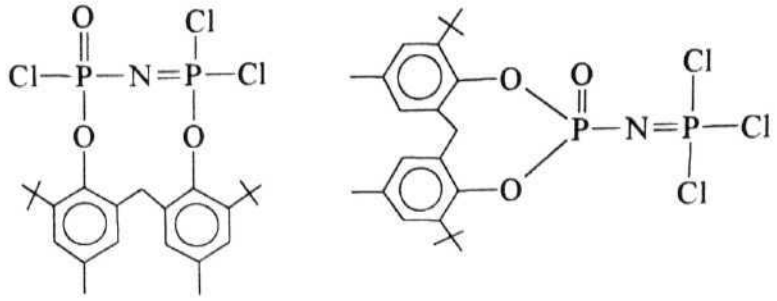
cyclotriphosphazenes $N_3P_3(X\text{--}Y)F_4$ where a peak at $[N_3P_3F_4(H)(OH)]^+$ is always observed.[50] Previously also hydrolyzed products were obtained in the attempted dimethylaminolysis of the product from the reaction of 1.**1** with 1,2-diaminoethane.[72]

Isolation of the spirocyclic products 1.**99**-1.**101** clearly shows that this pathway is favoured in the reaction of 1.**1** with difunctional reagents under the conditions employed. Formation of 2,2,6,6-$N_4P_4[N(i\text{-Pr})\text{-}CH_2CH_2CH_2N(i\text{-Pr})]_2Cl_4$ (1.**101**) at the second stage in high yields in preference to the 2,2,4,4- [structure **P**] or a 2,2,4,6- [structure **Q**] product is also a point to be noted; one factor responsible for this observation is the hindrance of the bulky first spirocycle to an incoming reagent at the 4-position.



(2,2,4,4-) (**P**) (2,2,4,6-) (**Q**)

For the reaction of the linear phosphazene $Cl_2P(O)N{=}PCl_3$ (1.**3**) with diol/ Et_3N, two products (**R, S**) other than 1.**103** are possible, in principle. Isolation of 1.**103** as the only product suggests that the $=PCl_3$ end is more reactive; this observation is similar to that noted by Allcock *et al.*[22]



(R) **(S)**

In contrast to other 2,2-disubstituted derivatives that usually show an AB_2C or AB_2X pattern [72, 11a, 97] in the ^{31}P NMR, compound 1.**99** exhibits an AM_2X spectrum [Fig. 1.4(a)] from which the coupling constants can be readily obtained. This is probably a result of the extreme upfield shift caused by the presence of the eight-membered phosphocin ring containing aryloxy substituents. Even in 1.**103**, which contains a similar ring, the =P(O-Ar-O)Cl [δ: ~-14 ppm] is upfield by *ca* 10 ppm compared to $=PCl_3$ in 1.**3** [δ(P): -4.1].[103] Other points of interest are as follows:

(i) The δ[P(spiro)] value in 1.**99**-1.**101** [Fig. 1.4] is much upfield to δ[PCl_2], in contrast to the five membered ring containing spirocycle $N_4P_4[N(Me)CH_2CH_2N(Me)]Cl_6$ {δ[P(spiro)]: 6.1; δ[PCl_2]: -8.3, -6.2}, where P(spiro) appears downfield to PCl_2. This is on expected lines[72] and is similar to the trends observed in penta- and hexa-coordinated phosphoranes.[104]

(ii) The signal for P(spiro) moves upfield upon introduction of a second spiro ring into 1.**100** (from -14.6 for 1.**100** to -19.4 for 1.**101**; Fig. 1.4) which is a reverse of that observed for the set $N_3P_3[(Me)N(CH_2)_3NH]Cl_4$ {δ[P(spiro)] 9.8} and $N_3P_3[(Me)N(CH_2)_3NH]_2Cl_2$ {δ[P(spiro)] 21.6}.[45] However, upon methylamination (see below) the chemical shift range narrows down significantly [Fig.1.4(d)].

(iii) The $^2J(P\text{-}N\text{-}P)$ values for the tetrameric compounds 1.**100** and 1.**101** are lower than that for the trimeric compound 1.**102**. It appears that this is a general trend

for (amino)cyclophosphazenes,[72, 11a] and may reflect a weaker π-contribution to bonding in these cyclotetraphosphazenes relative to cyclotriphosphazenes.

The ease of isolation, stability and ready identification of P(spiro) groups by NMR make 1.**100** and 1.**101** excellent probes for studying further reactions on tetrameric cyclophosphazenes. For example, treatment of 1.**100** with methylamine in chloroform leads to both the *normal* (1.**108**) and *trans-annular fused (bicyclic)*[27-30] (1.**109**) products; compound 1.**109** is obtained in a pure state as shown by ^{31}P NMR [Fig. 1.5(b)] and

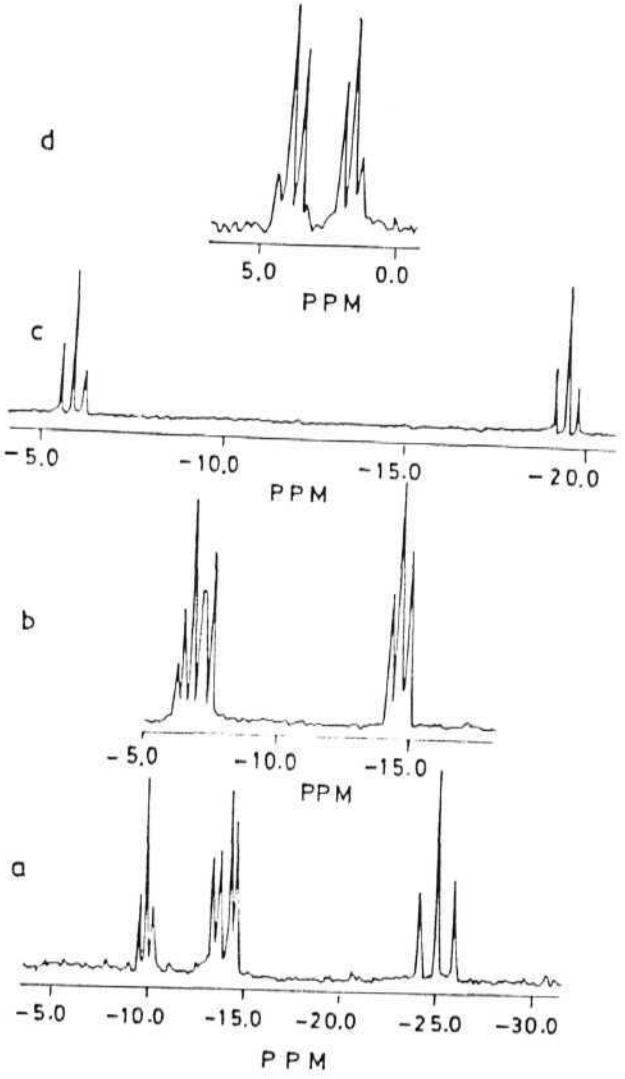


Fig 1.4 ^{31}P NMR spectra of a) 1.**99** b) 1.**100** c) 1.**101** and d) $N_4P_4[N(i\text{-}Pr)CH_2CH_2CH_2N(i\text{-}Pr)]_2(NHMe)_4$ (1.**110**).

elemental analysis. The chemical shift range is clearly in the *bicyclic* region[11a] and as expected, an AB_2C spectrum is obtained. The ^1H NMR (Fig. 1.6) is also consistent with the assigned structure; the two sets of methyls on the 1,3,2-diazaphosphorinane ring show two separate doublets centered at 1.08 and 1.15 ppm since one is facing the bridgehead nitrogen and the other is opposite to it. In the reaction of the dispirocycle 1.**101** with methylamine, the fully substituted product $N_4P_4(NHMe)_4[N(i\text{-}Pr)\text{-}CH_2CH_2CH_2N(i\text{-}Pr)]_2$ (1.**110**) is obtained as a crystalline solid; the residue obtained by evaporation of the mother liquor showed a singlet at 18.7 (probably the bicyclic product) and a broad multiplet centred at 3.4 ppm (unassigned) in the ^{31}P NMR.

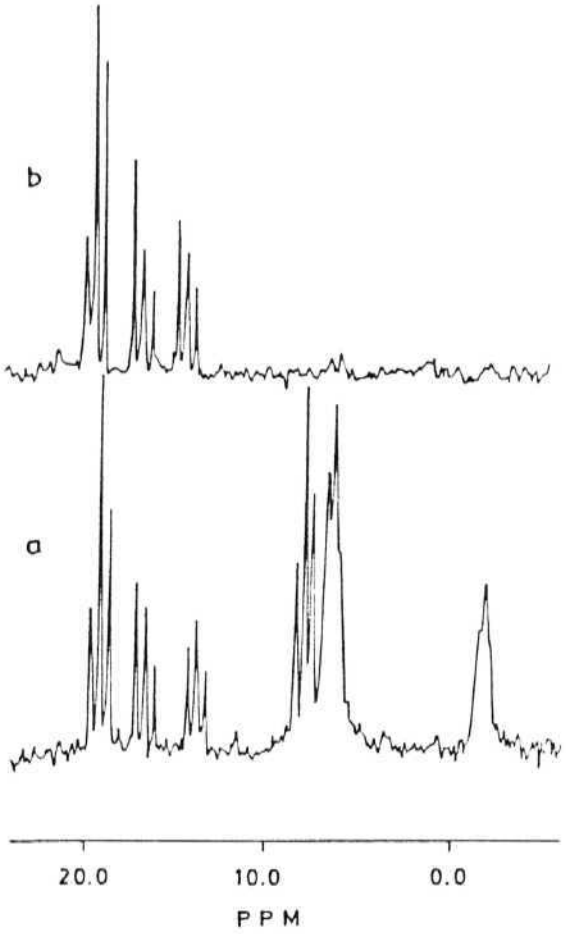
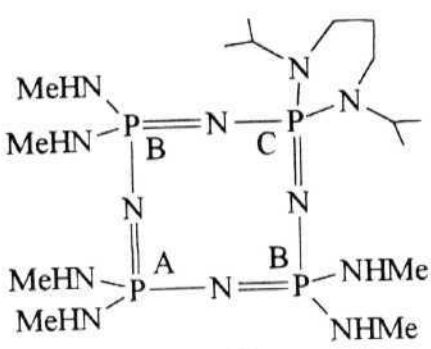
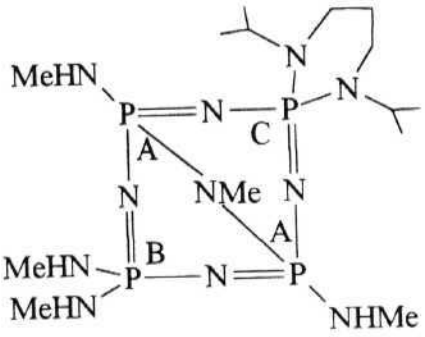


Fig 1.5 ^{31}P NMR spectra of a) mixture of $N_4P_4[N(i\text{-}Pr)CH_2CH_2CH_2N(i\text{-}Pr)](NHMe)_6$ (1.**108**) and $N_4P_4[N(i\text{-}Pr)CH_2CH_2CH_2N(i\text{-}Pr)](NHMe)_4(NMe)$ (1.**109**) and b) 1.**109**.



1.**108**



1.**109**

^{31}P NMR: 8.0 [t, P(A), ^{2}J(P-P) = 32 Hz]
6.5 [br, P(B)]
-1.8 [br, P(C)]

19.2 [t, or dd, P(A)]
16.6 [t, P(B)]
13.8 [t, P(C)]
2J(P-P) ~ 40 Hz

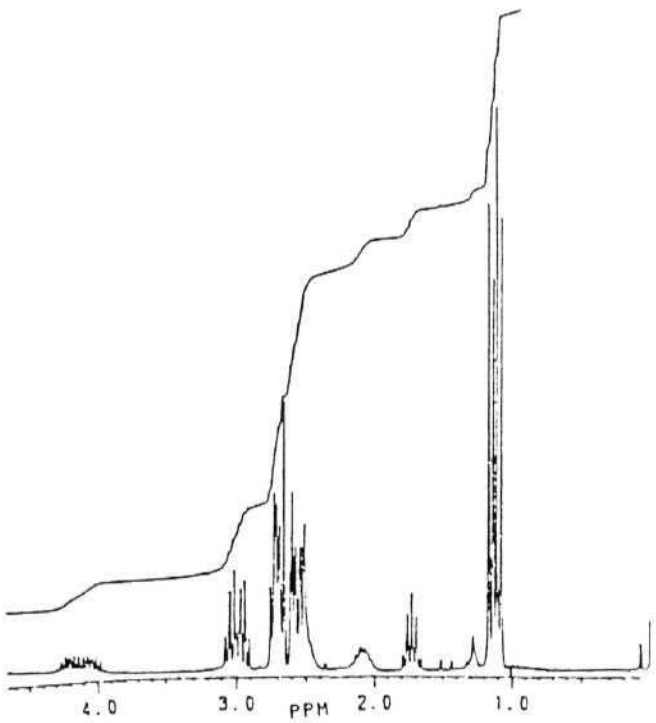


Fig 1.6 ^{1}H NMR spectrum of 1.**109**

1.22 *Structures*

The molecular structures of compounds 1.**99**·1/2$C_4H_8Cl_2$ and 1.**100**-1.**103** are shown in Figs. 1.7-1.11. Selected bond parameters are given in Tables 1.2-1.6 and atomic coordinates are available in the Appendix.

Compound 1.**99**.1/2$C_4H_8Cl_2$ (Fig. 1.7, Table 1.2) crystallizes in the space group $P\bar{1}$ with the solvent molecule positioned around the centre of symmetry of the unit cell so that only half of it belongs to the asymmetric unit. There is disorder in the solvent

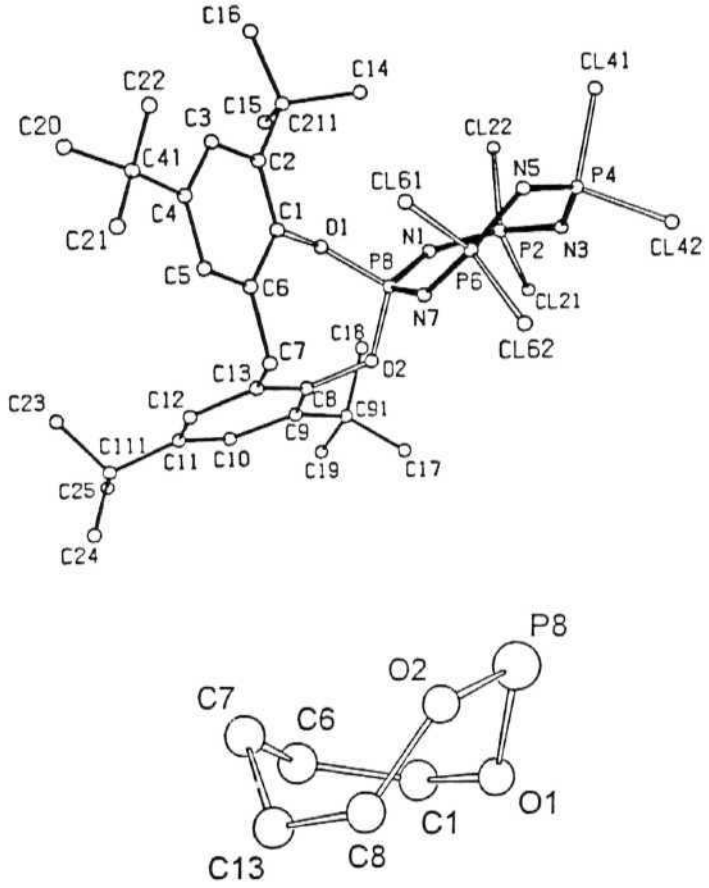


Fig 1.7 Molecular Structure of 1.**99**·1/2$C_4H_8Cl_2$. The solvent as well as the hydrogen atoms are omitted for clarity. Also shown at the bottom is the conformation of the eight membered 1,3,2-dioxaphosphocin ring.

Table 1.2. Selected bond lengths (Å) and bond angles (deg) for 1.**99**.1/2$C_4H_8Cl_2$ with esd's in parentheses

P(2) - Cl(21)	1.970(4)	P(6) - N(7)	1.569(8)
P(2) - Cl(22)	1.962(6)	P(8) - O(1)	1.579(7)
P(2) - N(1)	1.53(1)	P(8) - O(2)	1.555(7)
P(2) - N(3)	1.565(8)	P(8) - N(1)	1.55(1)
P(4) - Cl(41)	1.952(6)	P(8) - N(7)	1.550(7)
P(4) - Cl(42)	1.982(5)	O(1) - C(1)	1.43(1)
P(4) - N(3)	1.552(8)	O(2) - C(8)	1.43(1)
P(4) - N(5)	1.56(1)	C(1) - C(2)	1.35(2)
P(6) - Cl(61)	1.982(4)	C(6) - C(7)	1.49(1)
P(6) - Cl(62)	1.970(5)	C(7) - C(13)	1.50(1)
P(6) - N(5)	1.55(1)	C(8) - C(13)	1.38(2)

Cl(21) - P(2) - Cl(22)	102.8(2)	O(1) - P(8) - O(2)	105.3(4)
Cl(21) - P(2) - N(1)	109.1(3)	O(1) - P(8) - N(1)	104.7(5)
Cl(21) - P(2) - N(3)	105.2(4)	O(1) - P(8) - N(7)	112.9(4)
Cl(22) - P(2) - N(1)	108.4(4)	O(2) - P(8) - N(1)	108.8(4)
Cl(22) - P(2) - N(3)	109.3(4)	O(2) - P(8) - N(7)	105.5(5)
N(1) - P(2) - N(3)	120.5(5)	N(1) - P(8) - N(7)	118.9(5)
Cl(41) - P(4) - Cl(42)	102.2(3)	P(2) - N(1) - P(8)	141.9(5)
Cl(41) - P(4) - N(3)	111.8(5)	P(2) - N(3) - P(4)	134.4(6)
Cl(41) - P(4) - N(5)	105.7(4)	P(4) - N(5) - P(6)	131.4(6)
Cl(42) - P(4) - N(3)	104.1(4)	P(6) - N(7) - P(8)	140.0(7)
Cl(42) - P(4) - N(5)	110.2(4)	O(1) - C(1) -C(6)	116.8(9)
N(3) - P(4) - N(5)	121.2(5)	P(8) - O(1) -C(1)	127.7(6)
Cl(61) - P(6) - Cl(62)	101.0(2)	P(8) - O(2) -C(8)	127.5(6)
Cl(61) - P(6) - N(5)	104.8(4)	C(1) - C(6) -C(7)	123.8(9)
Cl(61) - P(6) - N(7)	110.3(4)	C(6) - C(7) -C(13)	116.4(8)
Cl(62) - P(6) - N(5)	110.1(4)	O(2) - C(8) -C(13)	116.6(8)
Cl(62) - P(6) - N(7)	105.3(4)	C(7) - C(13) -C(8)	124(1)
N(5) - P(6) - N(7)	123.2(5)		

molecule as well as in one of the *t*-butyl groups in the structure. The P-N distances are in the normal range [1.53(1)-1.569(8)] with a mean value of 1.55Å. Bond angles at phosphorus and nitrogen for the phosphazene ring average to 121(1) and 137(2)^{o} respectively; the angles at the ring nitrogen are thus larger than those generally observed for the trimeric compounds[12] as well as the aminophosphazenes $N_4P_4(NMe_2)_8$ [130.0(6)^{o}][105] and $N_4P_4(NC_4H_8)_8$ [131.7(4)^{o}][106] but are close to those observed in N_4P_4(O-C_6H_4-2-Me)$_8$ [mean 138.5^{o}].[107] The P-O bonds in the 1,3,2-dioxaphosphocin ring [mean 1.567(11) Å] are significantly shorter than those observed in the pentacoordinated phosphorus compound $(C_6H_{11}NH)P[(O\text{-}4,6\text{-}(t\text{-}Bu)_2C_6H_2)_2CH_2](1,2\text{-}O_2C_6H_4).1/2Et_2O$ [mean 1.632(3) Å] or in the tricoordinated derivative $(C_6H_{11}NH)P[O\text{-}4,6\text{-}(t\text{-}Bu)_2C_6H_2)_2CH_2]$ [mean 1.666(3) Å].[104c]

The phosphazene ring is nonplanar as expected and has a 'twisted' conformation. Interestingly, the eight membered 1,3,2-dioxaphosphocin ring in 1.**99** has a 'tub' conformation [Fig. 1.7] with atoms O(1), C(1), C(8) and C(13) coplanar to within ±0.026 Å while atoms P(8), O(2), C(6) and C(7) depart at the same side from this plane by 1.18, 1.00, 0.46 and 0.93 Å respectively. So far, such a conformation for this ring has been found only for pentacoordinated phosphoranes in which the ring spans *apical-equatorial* sites[104(C)] but not in tetra-[108] or tricoordinated[104(c), 109] phosphorus derivatives.

In compound 1.**100** [Fig.1.8, Table 1.3] the phosphazenic P-N bonds at P(8), which bears the 1,3,2-diazaphosphorinane ring, are longer than the rest; the next two [N(1)-P(2), N(7)-P(6)] are shorter, followed by longer [P((2)-N(3), P(6)-N(5)] and again by shorter [N(3)-P(4), N(5)-P(4)] bonds. It would be interesting to see whether other 2,2-diaminocyclotetraphosphazenes also exhibit such an alternating long-short-long-short array of bonds to know more about bonding in cyclotetraphosphazenes; to our knowledge, an X-ray structure is not available for any other compound till now.

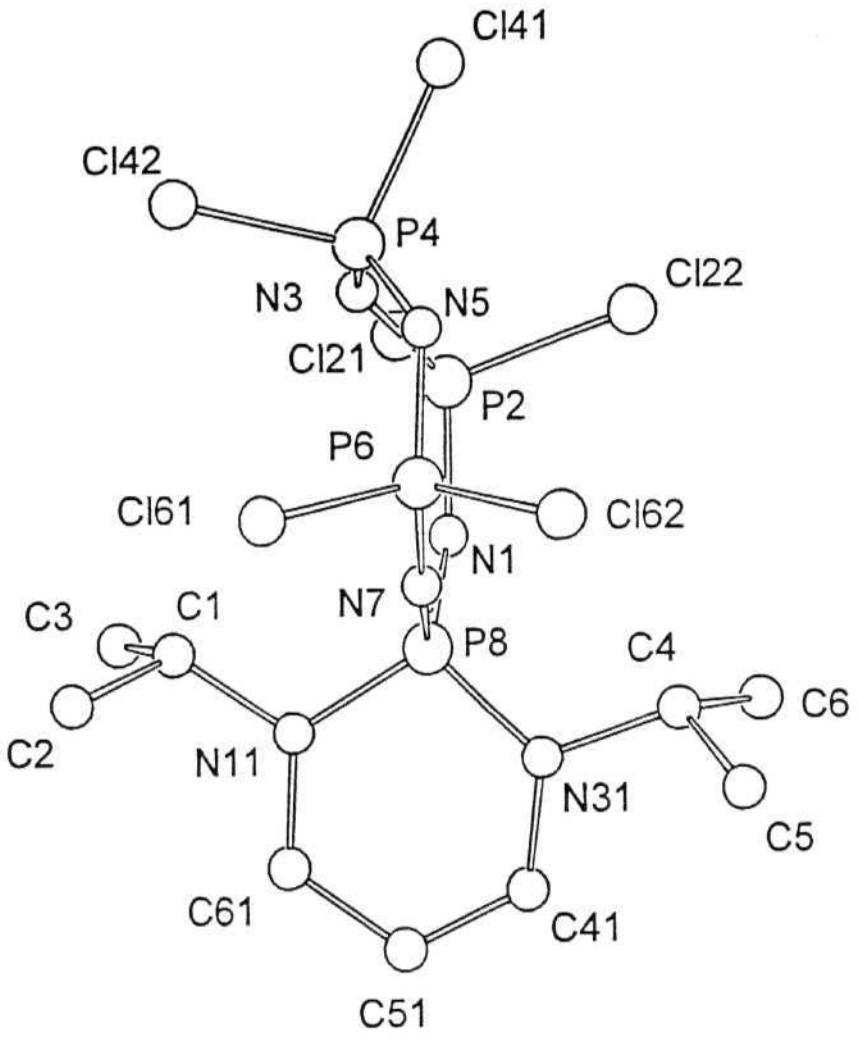


Fig 1.8 Molecular structure of 1.**100**; only non-hydrogen atoms are shown for clarity.

Another interesting point in the structure of 1.**100** is the unusual widening of the angle at N(7) [160.9(3)^{o}] towards linearity; even in the acyclic derivative 1.**103** [see below] the angle at nitrogen is much lower [140.5(2)^{o}]. Since at N(1), which is electronically equivalent to N(7), there is no significant widening, we attribute this observation to conformational effects. The phosphazene ring is nonplanar; if one considers the mean plane of the N_4P_4 ring, P(2), N(1) and N(5) are above this mean plane by 0.54, 0.30 and 0.12 Å whilst P(4), P(6), P(8), N(3) and N(7) are below this plane by

Table 1.3. Selected bond lengths (Å) and bond angles (deg) for 1.**100** with esd's in parentheses

P(2) - Cl(21)	1.987(2)	P(6) - N(5)	1.562(4)
P(2) - Cl(22)	2.012(2)	P(6) - N(7)	1.506(4)
P(2) - N(1)	1.527(4)	P(8) - N(1)	1.577(3)
P(2) - N(3)	1.567(4)	P(8) - N(7)	1.571(4)
P(4) - Cl(41)	1.991(2)	P(8) - N(11)	1.630(4)
P(4) - Cl(42)	1.988(2)	P(8) - N(31)	1.621(4)
P(4) - N(3)	1.552(4)	N(11) - C(61)	1.414(8)
P(4) - N(5)	1.542(3)	N(31) - C(41)	1.43(1)
P(6) - Cl(61)	1.994(2)	C(41) - C(51)	1.42(1)
P(6) - Cl(62)	1.994(2)	C(51) - C(61)	1.408(9)

Cl(21) - P(2) - Cl(22)	101.25(7)	N(5) - P(6) - N(7)	121.9(2)
Cl(21) - P(2) - N(1)	108.5(2)	N(1) - P(8) - N(7)	111.3(2)
Cl(21) - P(2) - N(3)	104.1(1)	N(1) - P(8) - N(11)	110.5(2)
Cl(22) - P(2) - N(1)	109.8(1)	N(1) - P(8) - N(31)	110.8(2)
Cl(22) - P(2) - N(3)	109.1(2)	N(7) - P(8) - N(11)	109.7(2)
N(1) - P(2) - N(3)	121.9(2)	N(7) - P(8) - N(31)	108.9(2)
Cl(41) - P(4) - Cl(42)	101.41(9)	N(11) - P(8) - N(31)	105.6(2)
Cl(41) - P(4) - N(3)	109.8(2)	P(2) - N(1) - P(8)	140.1(3)
Cl(41) - P(4) - N(5)	105.5(2)	P(2) - N(3) - P(4)	135.5(2)
Cl(42) - P(4) - N(3)	105.0(1)	P(4) - N(5) - P(6)	130.8(3)
Cl(42) - P(4) - N(5)	110.6(2)	P(6) - N(7) - P(8)	160.9(3)
N(3) - P(4) - N(5)	122.6(2)	P(8) - N(11) -C(61)	124.2(3)
Cl(61) - P(6) - Cl(62)	101.06(7)	P(8) - N(31) -C(41)	123.2(4)
Cl(61) - P(6) - N(5)	108.1(2)	N(31) - C(41) -C(51)	117.6(7)
Cl(61) - P(6) - N(7)	109.0(2)	C(41) - C(51) -C(61)	121.0(7)
Cl(62) - P(6) - N(5)	104.8(1)	N(11) - C(61) -C(51)	119.5(6)
Cl(62) - P(6) - N(7)	110.0(1)		

0.30, 0.18, 0.15, 0.28 and 0.22 Å respectively. The conformation of the 1,3,2-diazaphosphorinane ring is that of a flattened chair. Atoms P(8) and C(51) are above and below the mean plane containing N(11), N(31), C(41) and C(61) [coplanar to within 0.038 Å] by 0.18 and 0.31 Å respectively.

The exocyclic (to phosphazene ring) P-N bonds in 1.**100** [mean: 1.626(4) Å] are shorter than those observed in $N_4P_4(NMe_2)_8$ [1.69(1) Å][105] or $N_4P_4(NC_4H_8)_8$ [1.677(7) Å],[106] suggesting a greater π-character for such P-N bonds in 1.**100**. The sums of the angles at N(11) and N(31) are 358.4 and 359.0° respectively, suggesting that the lone pair on nitrogen is involved in further bonding interactions with phosphorus.

In the dispirocyclic compound 1.**101** (Fig. 1.9, Table 1.4), the P-N bonds in the phosphazene ring are longer for the phosphorus atoms bearing the 1,3,2-diazaphosphorinane ring than those at P(2) which has a PCl_2 group. Such a significant

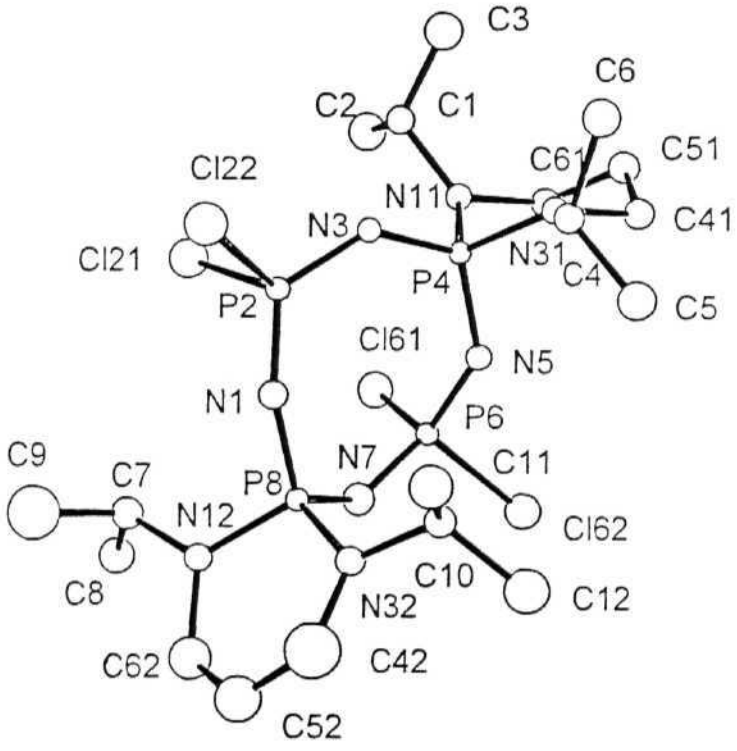


Fig 1.9 Molecular Structure of 1.**101**; only non-hydrogen atoms are shown for clarity.

Table 1.4. Selected bond lengths (Å) and bond angles (deg) for 1.**101** with esd's in parentheses

P(2) - Cl(21)	2.033(3)	P(8) - N(1)	1.578(5)
P(2) - Cl(22)	2.000(2)	P(8) - N(7)	1.569(5)
P(2) - N(1)	1.517(5)	P(8) - N(12)	1.624(5)
P(2) - N(3)	1.530(4)	P(8) - N(32)	1.631(5)
P(4) - N(3)	1.590(4)	N(11) - C(61)	1.469(8)
P(4) - N(5)	1.603(5)	N(31) - C(41)	1.466(7)
P(4) - N(11)	1.642(5)	C(41) - C(51)	1.517(10)
P(4) - N(31)	1.642(4)	C(51) - C(61)	1.513(9)
P(6) - Cl(61)	2.012(2)	N(12) - C(62)	1.440(9)
P(6) - Cl(62)	2.000(2))	N(32) - C(42)	1.393(9)
P(6) - N(5)	1.547(5)	C(42) - C(52)	1.342(14)
P(6) - N(7)	1.534(5)	C(52) - C(62)	1.413(12)

Cl(21) - P(2) - Cl(22)	100.23(14)	N(1) - P(8) - N(12)	110.1(2)
Cl(21) - P(2) - N(1)	109.2(2)	N(1) - P(8) - N(32)	108.9(3)
Cl(21) - P(2) - N(3)	107.1(2)	N(7) - P(8) - N(12)	109.7(3)
Cl(22) - P(2) - N(1)	106.5(2)	N(7) - P(8) - N(32)	111.5(3)
Cl(22) - P(2) - N(3)	104.95(19)	N(12) - P(8) - N(32)	103.2(3)
N(1) - P(2) - N(3)	125.9(3)	P(2) - N(1) - P(8)	151.3(4)
N(3) - P(4) - N(5)	116.7(2)	P(2) - N(3) - P(4)	131.5(3)
N(3) - P(4) - N(11)	111.1(3)	P(4) - N(5) - P(6)	137.0(3)
N(3) - P(4) - N(31)	107.4(2)	P(6) - N(7) - P(8)	134.5(4)
N(5) - P(4) - N(11)	108.7(2)	P(4) - N(11) -C(61)	112.5(4)
N(5) - P(4) - N(31)	107.6(3)	P(4) - N(31) -C(41)	114.1(4)
N(11) - P(4) - N(31)	104.6(2)	P(8) - N(12) -C(62)	124.2(3)
N(5) - P(6) - N(7)	122.6(3)	P(8) - N(32) -C(42)	123.1(6)
Cl(61) - P(6) - Cl(62)	98.61(13)	N(31) - C(41) -C(51)	111.6(6)
Cl(61) - P(6) - N(5)	111.9(2)	C(41) - C(51) -C(61)	113.7(5)
Cl(61) - P(6) - N(7)	107.9(3)	N(11) - C(61) -C(51)	112.0(5)
Cl(62) - P(6) - N(5)	106.5(2)	N(32) - C(42) -C(52)	123.2(9)
Cl(62) - P(6) - N(7)	106.5(3)	C(42) - C(52) -C(62)	123.0(7)
N(1) - P(8) - N(7)	113.0(3)	N(12) - C(62) -C(52)	115.5(7)

variation is absent in the aryloxy compound 2,2,6,6-N_4P_4(O-2,6-$Cl_2C_6H_3$)$_4Cl_4$.[22] The average P-N bond length of 1.559 Å in 1.**101** is close to that in the monospiro compound 1.**100** [mean 1.551 Å]. The N-P-N angles in the phosphazene ring at P(spiro) atoms P(4) and P(8) are narrower [116.7(2) and 113.0(3)] than at the PCl_2 ends [125.9(3) and 122.6(3)]; this feature is similar to that in 1.**100**. Angles at nitrogen vary more [131.5(3)-151.3(4)] possibly as a result of conformational constraints on the phosphazene ring. The P-N bonds in the six-membered rings are longer than the P-N bonds in the phosphazene ring, as expected.[54]

The phosphazene ring in 1.**101** has an irregular boat structure with the atoms P(8), N(1) and N(5) on the same side. The two six-membered rings show different conformations. The one at P(4) has a 'chair' conformation with P(4) and C(51) at -0.74 and 0.63 Å from the mean plane of the other four which are coplanar to within 0.01 Å. The corresponding ring at P(8) has a flattened 'boat' conformation with N(12) and C(42) at 0.37 and 0.09 Å above the mean plane of the remaining four [coplanar to within 0.03 Å]. This latter feature is similar to that found in the pentacoordinated phosphorane ($C_{14}H_8O_2$)(2,6-$Me_3C_6H_3O$)P[(Me)$NCH_2CH_2CH_2$ N(Me)].[110]

As is observed in other monospirocyclic diaminocyclotriphosphazenes,[12] the P-N bond lengths in 1.**102** (Fig. 1.10, Table 1.5) vary as P(spiro) - N-PCl_2 > Cl_2P-N-PCl_2 > P(spiro) - N-PCl_2. However, the interesting point in the structure of 1.**102** is that the P-N bonds to the 1,3,2-diazaphosphorinane ring [mean: 1.623 Å] are nearly of the same length as the phosphazenic P(spiro)-N bonds [mean: 1.623(4) Å]. The phosphazene N-P(spiro)-N angle is close to that observed for the analogous tetrameric derivative 1.**101**. The phosphazene ring is planar to within ±0.09 Å and the diazaphosphorinane ring has a chair conformation.

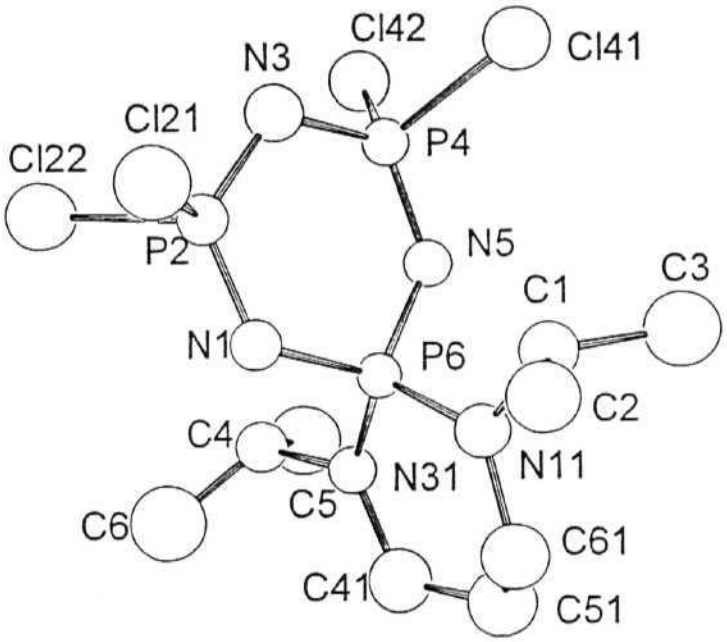


Fig 1.10 Molecular Structure of 1.**102**; only non-hydrogen atoms are shown for clarity.

The sums of the bond angles at N(11) and N(31) are, respectively, 359.8 and 359.3^{O} and are thus close to planarity; these deviate from the plane of the three atoms to which they are bonded by 0.03 Å and 0.08 Å respectively. In the compound 2,2-N_3P_3[(Me)NCH_2 CH_2CH_2N(Me)]Cl_4[44] reported by Shaw and coworkers, the corresponding sum of the angles is 351^{O} suggesting an appreciable amount of sp^3 character; this was the reason attributed to the lower coupling constants in the ^{13}C NMR of this compound.[44] However, in 1.**100** also ^{2}J(P-C) and ^{3}J(P-C) values are very low (< 3 Hz; only singlets observed) and hence we believe that other factors may also be operative which lead to this observation.

Table 1.5. Selected bond lengths (Å) and bond angles (deg) for 1.**102** with esd's in parentheses

P(2) - Cl(21)	1.994(2)	P(6) - N(5)	1.617(4)
P(2) - Cl(22)	2.016(2)	P(6) - N(11)	1.622(4)
P(2) - N(1)	1.545(4)	P(6) - N(31)	1.623(4)
P(2) - N(3)	1.574(4)	N(11) - C(1)	1.472(6)
P(4) - Cl(41)	2.0027(19)	N(31) - C(4)	1.470(6)
P(4) - Cl(42)	2.002(2)	N(31) - C(41)	1.443(6)
P(4) - N(3)	1.585(4)	C(41) - C(51)	1.426(8)
P(4) - N(5)	1.550(4)	C(51) - C(61)	1.419(9)
P(6) - N(1)	1.629(4)		

Cl(21) - P(2) - Cl(22)	99.54(10)	N(5) - P(6) - N(11)	109.2(2)
Cl(21) - P(2) - N(1)	108.84(17)	N(5) - P(6) - N(31)	110.7(2)
Cl(21) - P(2) - N(3)	107.7(2)	N(11) - P(6) - N(31)	105.6(2)
Cl(22) - P(2) - N(1)	110.13(17)	P(2) - N(1) - P(8)	124.9(2)
Cl(22) - P(2) - N(3)	107.67(19)	P(2) - N(3) - P(4)	117.1(2)
N(1) - P(2) - N(3)	120.9(2)	P(4) - N(5) - P(6)	125.1(2)
Cl(41) - P(4) - Cl(42)	99.58(10)	P(6) - N(11) -C(61)	124.2(3)
Cl(41) - P(4) - N(3)	106.58(19)	P(6) - N(11) -C(1)	118.1(3)
Cl(41) - P(4) - N(5)	110.66(16)	C(1) - N(11) -C(61)	118.2(4)
Cl(42) - P(4) - N(3)	108.7(2)	P(6) - N(31) -C(41)	123.2(4)
Cl(42) - P(4) - N(5)	108.97(18)	P(6) - N(31) -C(4)	117.5(3)
N(3) - P(4) - N(5)	120.4(2)	C(4) - N(31) -C(41)	117.4(4)
N(1) - P(6) - N(5)	110.35(18)	N(31) - C(41) -C(51)	117.6(7)
N(1) - P(6) - N(11)	111.6(2)	C(41) - C(51) -C(61)	121.0(7)
N(1) - P(6) - N(31)	109.3(2)	N(11) - C(61) -C(51)	119.5(6)

In the monocyclic derivative 1.**103** (Fig. 1.11, Table 1.6), the P=N distance is short but close to that in the parent compound $Cl_2P(O)$-N=PCl_3 (1.**3**) [mean 1.521 Å][111]

and $Cl_2P(O)$-N=P(O-2,6-$C_6H_3Cl_2)_3$ (1.**111**) [1.515(4) Å].[22] What is probably more significant is the $Cl_2P(O)$-N bond length of 1.560(3) Å; this is shorter than that in the

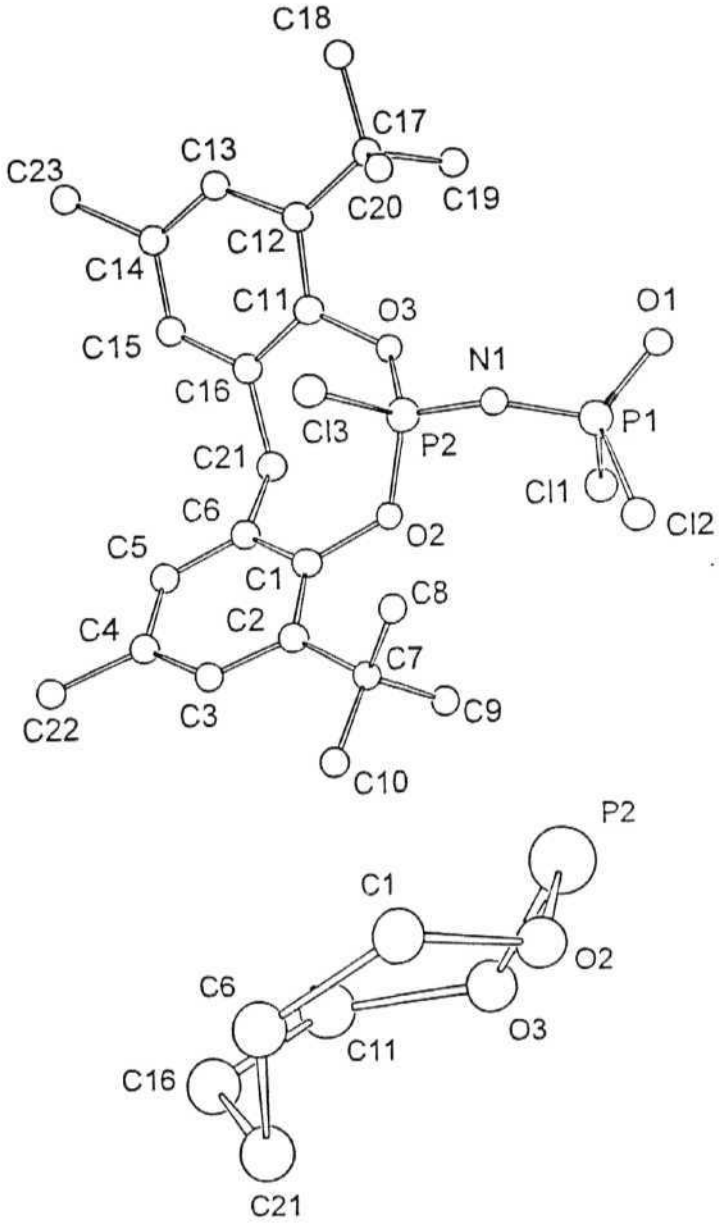


Fig 1.11 Molecular Structure of 1.**103**; only non-hydrogen atoms are shown for clarity. Also shown at the bottom is the conformation of the eight membered 1,3,2-dioxaphosphocin ring.

parent compound 1.**3** [mean 1.587 Å] but is close to that in 1.**111** [1.567(4) Å]. Noting that in this linear phosphazene there are no resonance forms available as in cyclotri- or cyclotetraphosphazenes, this P-N bond should be essentially a single bond for book keeping purposes, but still is considerably shorter than the P-N single bond distance of 1.769(19) Å in the phosphoramidate salt NaH_3NPO_3 and 1.800(4) Å in KH_3NPO_3.[112]

In contrast to the 'boat' conformation found in 1.**99** for the 1,3,2-dioxaphosphocin ring, a 'boat-chair' conformation[104(b)] is found for the same ring in 1.**103** [*cf.* Fig. 1.11]; the atoms C(1), C(6), C(11) and C(16) are coplanar to within ±0.02 Å while the atoms P(2), O(2), O(3) and C(2) are above this plane by 0.16, 0.67, 0.61 and 0.76 Å respectively.

Table 1.6. Selected bond lengths (Å) and bond angles (deg) for 1.**103** with esd's in parentheses

P(1) - O(1)	1.437(3)	P(2) - Cl(3)	1.9764(13)
P(1) - N(1)	1.560(3)	O(2) - C(1)	1.432(4)
P(1) - Cl(1)	2.020(2)	O(3) - C(11)	1.432(4)
P(1) - Cl(2)	2.003(2)	C(1) - C(6)	1.388(5)
P(2) - N(1)	1.526(3)	C(6) - C(21)	1.512(5)
P(2) - O(3)	1.558(2)	C(11) - C(16)	1.390(5)
P(2) - O(2)	1.560(2)	C(16) - C(21)	1.512(5)

O(1) - P(1) - N(1)	119.2(2)	O(3) - P(2) - Cl(3)	106.60(10)
O(1) - P(1) - Cl(2)	110.3(2)	O(2) - P(2) - Cl(3)	106.21(10)
N(1) - P(1) - Cl(2)	105.62(14)	P(2) - O(2) -C(1)	126.8(2)
O(1) - P(1) - Cl(1)	110.8(2)	P(2) - O(3) -C(11)	129.4(2)
N(1) - P(1) - Cl(1)	108.07(14)	P(1) - N(1) - P(2)	140.5(2)
Cl(1) - P(1) - Cl(2)	101.34(8)	O(2) - C(1) -C(6)	116.5(3)
N(1) - P(2) - O(3)	109.8(2)	C(1) - C(6) -C(21)	122.0(3)
N(1) - P(2) - O(2)	111.5(2)	O(3) - C(11) -C(16)	117.1(3)
O(3) - P(2) - O(2)	110.55(13)	C(11) - C(16) -C(21)	121.6(3)
N(1) - P(2) - Cl(3)	112.04(14)	C(6) - C(21) -C(16)	117.2(3)

1.23 *CONCLUSIONS*

To summarize, this study shows that the formation of spirocyclic derivatives in the reaction of $N_4P_4Cl_8$ (1.**2**) with diamines/ diols is a favoured pathway. The relatively greater stability of these compounds may be associated with steric factors that make sites close to P(spiro) hindered. The spirocyclic tetraphosphazenes 1.**99**-1.**101** represent the first members in this series to be studied by X-ray crystallography; these studies are likely to be useful in understanding the nature of the P-N bond in cyclic tri- *vs* tetraphosphazenes. While considering the bonding in cyclophosphazenes, often an sp^2 mixing of orbitals[113] for nitrogen is assumed; in view of the wide angles at nitrogen (~ 160^{O}) observed in the tetrameric series (eg: 1.**100**) it may be worth reconsidering this model.

1.3 *Experimental*

Chemicals and solvents were from Aldrich/ Fluka or from local manufacturers. Further purification was done according to standard procedures.[114] All operations, unless stated otherwise, were carried out under dry nitrogen atmosphere using standard Schlenck techniques.[115] ^{1}H, ^{13}C and ^{31}P (operating at 80.961 MHz) NMR spectra were recorded on a Brüker 200 MHz NMR spectrometer in $CDCl_3$ solutions with shifts referenced to $SiMe_4$ (^{1}H, ^{13}C; $\delta = 0$) and ext. 85 % H_3PO_4 ($\delta = 0$) respectively; J values are in Hz. IR spectra were recorded on either a Perkin-Elmer 1310 spectrophotometer or a JASCO FT-IR 5300 spectrophotometer. Elemental analyses were carried out on a Perkin-Elmer 240C CHN analyser. Melting points are uncorrected.

Syntheses:

a) 2,2-N_4P_4{[O-4,6-(*t*-Bu)$_2$-C_6H_2]$_2$$CH_2$}$Cl_6$.1/2$C_4H_8Cl_2$[**1.99**.1/2$C_4H_8Cl_2$].

Methylenebis(4,6-di-*t*-butyl-phenol)[116] (0.55 g, 1.3 mmol) was refluxed with excess of sodium leaves in dry THF (20 cm^3) for 3 d. Unreacted sodium was then removed by forceps. To the remaining suspension, $N_4P_4Cl_8$ (1.**2**) (0.6 g, 1.3 mmol) in THF (10 cm^3) was added dropwise (10 min) and the mixture refluxed for 1 d. Then THF was removed *in vacuo* and hexane was added to the residue. The insoluble material was filtered off and the solvent removed from the filtrate. The gummy residue was crystallized from cyclohexane at 25^{O}C to afford 1.**99**.1/2$C_4H_8Cl_2$ [*cf.* X-ray structure; the source of 1,4-dichlorobutane ($C_4H_8Cl_2$) is likely to be THF. It is known that HBr reacts with THF to give 1,4-$C_4H_8Br_2$.[117] In our case the reaction of THF with HCl is possibly mediated by $N_4P_4Cl_8$; formation of 1,4-dichlorobutane from THF has been found to occur in the presence of $P(O)Cl_3$ also.[118] We had earlier experienced facile chlorination of α-hydroxy phosphonates by $N_4P_4Cl_8$.[119]]

Yield :0.26 g (23%).

M. p. 178-179°C.

Found (after drying at 0.5 mm/ 4 h): C, 42.42; H, 5.28; N, 6.90. $C_{29}H_{42}Cl_6N_4O_2P_4$ requires C, 42.72; H, 5.19; N, 6.87%. $C_{31}H_{46}Cl_7N_4O_2P_4$ requires: C, 42.37; H, 5.28; N, 6.38%.

^{1}H NMR (after evacuating at 0.5mm/ 4h): 1.30, 1.42, 1.44, 1.47 (s each, 36H, *t*-Bu-*H*), 4.10 (br, 2H, CH_2), 7.20, 7.40 (s each, 4H, Ar-*H*). Two triplets of low intensity at 3.45 and 3.50 ppm, assignable to 1,2-dichlorobutane, were also observed.

^{31}P NMR: -25.2 (t, *P*(spiro), ^2J(P-P) = 72.0 Hz), -14.1 (dd, 2*P*Cl$_2$, ^2J(P-P) = 72.0, 26.4 Hz), -9.9 (t, *P*Cl$_2$, ^2J(P-P) = 26.4 Hz).

An analogous reaction using 2,2'-methylenebis(4-methyl-6-*t*-butyl-phenol) did not give any isolable product.

b) **2,2-N_4P_4[(*i*-Pr)NCH_2CH_2CH_2N(*i*-Pr)]Cl_6** (1.**100**). To a stirred solution of 1.**2** (0.59 g, 1.27 mmol) in CH_2Cl_2 (10 cm^3) at 5°C was added dropwise a solution of N,N'-diisopropyl-1,3-propanediamine (0.40 g, 2.54 mmol) in CH_2Cl_2 (10 cm^3). The mixture was stirred at 25°C for 4 h and the solvent removed *in vacuo*. Toluene was added and the insoluble amine hydrochloride filtered off. The filtrate was concentrated to a small volume (0.2 cm^3) and kept at -20°C to give crystals of 1.**100**; on evaporation of the mother liquor more compound was obtained.

Total yield: 0.46 g (66%).

M. p. 90-92°C.

Found: C, 19.82; H, 3.80; N, 15.48. $C_9H_{20}N_6P_4Cl_6$ requires C, 19.69, H, 3.67; N, 15.31%.

^{1}H NMR: 1.16 (d, 12H, ^{3}J(H-H) = 6.4 Hz, CH_3), 1.80 (qnt, 2H, ^{3}J(H-H) = 6.0 Hz, CCH_2), 3.05 (dt, 4H, ^{3}J(P-H) ~ 16 Hz, ^{3}J(H-H) = 6.0 Hz, NCH_2), 3.86 (m, 2H, NCHMe$_2$).

^{13}C NMR: 20.6, 27.2, 37.8, 46.5.

^{31}P NMR: -14.6 (t, ^{2}J(P-P) = 26.0 Hz, P(spiro)), -6.2 to -7.5 (m, Pcl$_2$).

c) **2,2,6,6-N$_4$P$_4$[(*i*-Pr)-NCH$_2$CH$_2$CH$_2$N(*i*-Pr)]$_2$Cl$_4$** (1.**101**). To compound 1.**100** (0.68 g, 1.23 mmol) in CH_2Cl_2 (10 cm^3), N,N'-diisopropyl-1,3-propanediamine (0.39 g, 2.47 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise (15 min) and the mixture stirred overnight at 30°C. The solvent was completely removed, and hexane (15 cm^3) was added to the residue. Filtration followed by concentration of the solution to *ca* 2 cm^3 afforded crystalline 1.**101**.

Yield: 0.4 g (51%).

M.p. 200-202°C.

Found: C, 33.98; H, 6.20; N, 17.60. $C_{18}H_{40}Cl_4N_8P_4$ requires C, 34.08; H, 6.35; N, 17.66%.

^{1}H NMR: 1.17 (d, 12H, CH_3), 1.81 (qnt, 2H, CCH_2), 3.10 (dt, 4H, ^{3}J(P-H) = 16.0 Hz, ^{3}J(H-H) ~ 6.0 Hz, NCH_2), 3.60 (m, 2H, NCHMe$_2$).

^{13}C NMR: 19.9, , 26.3, 38.2, 45.7.

^{31}P NMR: -19.4 (t, P(spiro), ^{2}J(P-P) = 25.6 Hz), -5.8 (t, ^{2}J(P-P) = 25.6 Hz, PCl$_2$).

d) **2,2-N$_3$P$_3$[(*i*-Pr)NCH$_2$CH$_2$CH$_2$N(*i*-Pr)]Cl$_4$** (1.**102**). This compound was prepared by a route analogous to that for 1.**100** using $N_3P_3Cl_6$ (1.**1**) (0.69 g, 2 mmol) and N,N'-diisopropyl-1,3-propanediamine (0.63 g, 4 mmol). Compound 1.**102** was crystallized from hexane.

Yield: 0.61 g (70%).

M. p. 150-152°C.

Found: C, 24.85,; H, 4.60; N, 16.05. $C_9H_{20}Cl_4N_5P_3$ requires C, 24.96, H, 4.65, N, 16.17%.

^{1}H NMR: 1.13 (d, 12H, ^3J(H-H) = 6.4 Hz, CH_3), 1.75 (qnt, 2H, CCH_2), 3.00 (dt, J = 16.0, 6.0 Hz, NCH_2), 3.95 (m, 2H, CHMe$_2$).

^{13}C NMR: 19.9, 26.3, 38.2, 45.7.

^{31}P NMR: 6.3 (t, ^2J(P-P) = 36.8 Hz), 20.6 (d, ^2J(P-P) = 36.8 Hz).

e) $Cl_2P(O)$-N=P[(O-4-Me-6-*t*-Bu-$C_6H_2)_2CH_2$]Cl (1.**103**). To $Cl_2P(O)N{=}PCl_3$ (1.**3**) (0.78 g, 2.9 mmol) in toluene (25 cm^3), a solution of 2,2'-methylene-bis(4-methyl-6-*t*-butyl phenol) (0.99 g, 2.9 mmol) and triethylamine (0.58 g, 5.8 mmol) in toluene (10 cm^3) was added dropwise at 25°C (15 min). The mixture was stirred overnight, filtered and the filtrate concentrated to *ca* 10 cm^3. An oily material separated, which was extracted with hot benzene. Cooling the benzene solution to 25°C afforded 1.**103**.

Yield: 0.9 g (52%).

M. p. 188°C.

Found: C, 49.85; H, 5.37; N, 2.40. $C_{23}H_{30}Cl_3NO_4P_2$ requires C, 49.97; H, 5.47; N, 2.53%.

^{1}H NMR: 1.40 (s, 18H, *t*-Bu-*H*), 2.30 (s, 6H, CH_3), 3.60 (d, 1H, $^2J(H_A\text{-}H_B)$ = 18.0 Hz, ArCH_AH$_B$), 4.32 (d, ^{2}J = 18.0 Hz, ArCH$_A$$H_B$), 7.15, 7.20 (s each, 4H, Ar-*H*).

^{31}P NMR: -15.4, -13.8 [AB quartet; J(AB) ~ 60 Hz].

f) N_3P_3[O-4-Me-6-*t*-Bu-C_6H_2-CH_2-4-Me-6-*t*-Bu-C_6H_2OH]Cl_5 (1.**105**). A procedure similar to (**a**) above was followed using the diol (1.08 g, 3.1 mmol) and 1.**1** (1.06 g, 3.11 mmol). The reaction mixture was chromatographed (hexane, CH_2Cl_2) to

remove the unreacted diol and the residue was heated at 100°C/ 0.5 mm to remove most of unreacted 1.**1** (*ca* 0.2 g) to afford 0.3 g of a gummy material. ^{31}P NMR: a) 21.7 (d, 2P, ^{2}J(P-P) = 61.0 Hz, 8.2 (t, 1P, ^{2}J(P-P) = 61 Hz, assigned to 1.**105**, *ca* 80%); b) 19.3 (assigned to unreacted 1.**1**, *ca*. 10 %), c) 21.1 (d, ^{2}J(P-P) ~ 72 Hz), -7.63 (t, ^{2}J(P-P) ~ 72 Hz (unassigned, *ca* 10%). Pure 1.**105** could be obtained as a semisolid by column chromatography using dichloromethane/ hexane as eluant.

Found: C, 42.61; H, 4.91; N, 6.55. $C_{23}H_{31}Cl_5N_3O_2P_3$ requires C, 42.39; H, 4.79; N, 6.45%).

^{1}H NMR: 1.42, 1.50 (s each, 18H, t-bu-*H*), 2.22, 2.32 (s each, 6H, Ar-CH_3), 4.20 (s, 2H, ArCH_2), 6.65, 6.80, 7.20,7.30 (s each, total 4H, Ar-*H*).

^{31}P NMR: 21.7 (d, 2P, ^{2}J(P-P) = 61.0 Hz, 8.2 (t, 1P, ^{2}J(P-P) = 61 Hz.

MS: m/z 649 [M(^{35}Cl)]$^{+}$, 613 [M(^{35}Cl) - HCl]$^{+}$.

g) N_3P_3[(*i*-Pr)NCH$_2$CH$_2$CH$_2$N(*i*-Pr)]F_4 (1.**106**). To a stirred solution of 1.**102** (0.52 g, 1.2 mmol) in methyl cyanide (20 cm^3) was added KF (dried at 120°C for 2 d, 1.04 g, 18 mmol) in one portion at 25°C. The mixture was heated under reflux for 36 h, cooled and filtered. Removal of solvent gave a solid that was crystallized from toluene to give compound 1.**106**.

Yield: 0.35 g (80%).

M. p. 64-66°C.

Found: C, 28.95; H, 5.20; N, 18.58. $C_9H_{20}F_4N_5P_3$ requires C, 29.43; H, 5.45; N, 19.07%.

^{1}H NMR: 1.16 (d, J = 6.0 Hz, 12H, CH_3), 1.88 (qnt, J = 6.0Hz, 2H, CCH_2), 3.07 (td, 4H, J = 14.1, 6.6 Hz, NCH_2), 3.56-3.65 (m, 2H, $NCHMe_2$).

^{13}C NMR: 20.1, 26.5, 37.9, 45.7.

^{31}P NMR: 15.4 (1P, P(spiro), ^{2}J(P-P) ~ 90 Hz), 11.4 (2P, ^{1}J(P-F) ~ 965 Hz, PF_2).

h) Fluorination of 1.100. Procedure was the same as in (**g**) above using 1.**100** (0.66 g, 1.2 mmol) and KF (1.04 g, 18 mmol). A very hygroscopic solid (0.35 g), probably $N_4P_4F_5(OH)[N(i\text{-}Pr)CH_2CH_2CH_2N(i\text{-}Pr)]$ (1.**107**, see mass spectrum below), was isolated.

^{1}H NMR: 1.10-1.30 (br m, ~12H, CH_3), 1.60-1.90 (br, 2H, CCH_2), 2.80-3.20 (br, 4H, NCH_2), 3.80-4.20 (br, 2H, $NCHMe_2$).

^{31}P NMR: -14.6 (tt, $1J$(P-F) ~ 850 Hz, ^2J(P-P) ~ 81 Hz, PF_2), 0.1 (m, P(spiro)), -11.0 (m, unassigned).

MS: 434 [80%, $\{M\text{-}CH_3+H\}^+$], 349 [10%], 334 [25%], 293 [25%, $N_4P_4HF_5(OH)^+$; this type of ion with phosphazene skeleton intact is typical for fluorocyclotriphosphazenes $N_3P_3(X\text{-}Y)F_4$;[50] the latter compounds show peaks at m/z corresponding to $\{N_3P_3HF_4\}^+$].

i) Reaction of 1.100 with methylamine: Formation of 1.108 and 1.109

To a stirred solution of excess of methylamine (*ca* 1 g, 33 mmol) and triethylamine (2 cm^3) in chloroform (10 cm^3) maintained at -60°C was added 1.**100** (0.4 g, 0.7 mmol) all at once with continuous stirring. After the reaction mixture reached 25°C, it was refluxed (using acetone slush on the top) for 2 h. The solvent was removed and toluene (10 cm^3) was added to the residue. Filtration followed by concentration of the solution gave a solid. Yield ~ 0.26 g. From this, compound 1.**109**, m. p. 214-216°C (*ca* 50 mg) was isolated in a pure state using CH_2Cl_2 solvent.

Found: C, 34.68; H, 8.14; N, 31.82. $C_{14}H_{39}N_{11}P_4$ requires C, 34.63; H, 8.11, N, 31.74%.

^{1}H NMR: 1.08 (d, J = 6.7 Hz, 6H, $CHCH_3$), 1.15 (d, J = 6.6 Hz, 6H, $CHCH_3$), 1.72 (qnt, J = 6.2 Hz, CCH_2), 2.10 (br, ~2H, $NHMe$), 2.50-2.75 (complex, 11 lines, 15H, NCH_3), 3.00 (two qrt , 4H, NCH_2), 4.20 (m, 2H, NCH).

^{31}P NMR: 19.8 (dd or t, 2P, J = 40 Hz), 17.1 (t, 1P, J ~ 40 Hz), 14.7 (t, 1P, J ~ 40 Hz).

MS: 485 [M^+], 473, 442, 426, 411, 384, 361, 330 [100%, {M-(*i*-Pr)NCH_2CH_2 CH_2N(*i*-Pr) + H}$^+$]. Two peaks of low intensity at m/z 538 and 516 were also observed.

^{1}H NMR (residue from the mother liquor; 1.**108** + 1.**109**, *ca* 1:1 based on ^{31}P NMR): 1.10 (d, J ~ 6.0Hz, $CH(CH_3)_2$), 1.70 (m, CH_2), 2.45 (d, ^{3}J(P-H) ~ 20 Hz, NCH_3), 2.60 (m, NCH_3), 2.80-3.20 (m, NCH_2) 3.90 - 4.20 (m, $CHMe_2$).

^{31}P NMR (excluding peaks for 1.**109**): 8.0 (t or dd, 1P, ^2J ~ 34 Hz), 6.2 (t, 1P, ^2J ~ 27 Hz), -1.92 (t, 1P, ^2J ~27 Hz).

An attempt to isolate pure 1.**108** by reacting 1.**2** with excess of methylamine in diethyl ether was not successful; only the bicyclic derivative 1.**109** was isolated as a crystalline solid.

(j) 2,2,6,6-N_4P_4[(*i*-Pr)-$NCH_2CH_2CH_2N$(*i*-Pr)]$_2$$(NHMe)_4$ (1.110)

To methylamine (*ca* 1 cm^3; taken in excess) in dichloromethane (10 cm^3) maintained at -78°C, compound 1.**101** (0.19 g, 0.3 mmol) in dichloromethane (10 cm^3) was added and the mixture was stirred at this temperature for 4 h. Then the contents were allowed to attain room temperature while stirring (8 h). Solvent was removed, toluene (10 cm^3) was added to the residue. Filtration followed by concentration afforded 1.**110** as a crystalline solid.

Yield: 0.1 g (53%).

M. p. 163°C.

Found: C, 43.94; H, 9.45; N, 26.49. $C_{22}H_{56}N_{12}P_4$ requires C, 43.12; H, 9.21; N, 27.4%).

^{1}H NMR: 1.06 (d, J = 14.0 Hz, 24H, CHCH_3), 1.61 (qnt, J = 6.2 Hz, 4H, CCH_2), 2.50 (d, J = 20.0 Hz, 12H, NCH_3), 3.05 (two qrt, 8H, NCH_2), 4.20 (m, 4H, NC*H*).

^{13}C NMR: 21.2, 27.3, 28.5, 39.2, 45.7.

^{31}P NMR: 1.8 (t, 2P, ^{2}J = 33 Hz), 4.1 (t, 2P, ^{2}J = 33 Hz).

X-Ray Crystallography

Suitable crystals were mounted inside a capillary (1.**99**.1/2$C_4H_8Cl_2$, 1.**100**, 1.**101**, 1.**103**) or on a glass fibre (1.**102**). Data were collected on an Enraf-Nonius CAD4 [1.**99**.1/2$C_4H_8Cl_2$, 1.**101**, 1.**103**] or MACH3 [1.**99**, 1.**102**] diffractometer using MoK_α [λ = 0.7107 Å] radiation. The details pertaining to data collection and refinement are listed in Table 6. The structures were solved by conventional methods.[120] Refinement was done on F for 1.**99**.1/2$C_4H_8Cl_2$ and 1.**100** (Xtal3)[121] and on F^2 fo 1.**101**-1.**103** [SHELX93, SHELX97].[119] Only in the case of 1.**103** an absorption correction based on psi scans was applied. All non-hydrogen atoms were refined anisotropically. H atoms were placed at calculated positions and not refined [U(H) = 0.035Å^2] for 1.**99**.1/2$C_4H_8Cl_2$, whereas for 1.**100** H-atoms were refined isotropically except H611 and H612. For 1.**101**-1.**103** H atoms were included at idealized positions using a riding model and not refined. In the structure of 1.**99**.1/2$C_4H_8Cl_2$ there is some high residual density in the neighbourhood of two chlorine atoms Cl(01) and Cl(61); this is a consequence of poor quality of the crystals and hence the data. There was 8.5% decay during data collection for 1.**99**.1/2$C_4H_8Cl_2$; in the structure there is a highly disordered 1,4-dichlorobutane (half molecule in the asymmetric unit) in addition to a disordered *t*-butyl group. Hence the R value for this compound is rather high.

Table 1.7: Crystal data for 1.**99**.1/2 $C_4H_8Cl_2$ and 1.**100**-1.**103**.

Compound	1.**99**.1/2$C_4H_8Cl_2$	1.**100**	1.**101**	1.**102**	1.**103**
Empirical Formula	$C_{29}H_{42}Cl_6N_4O_2P_4$. 1/2$C_4H_8Cl_2$	$C_9H_{20}C1_6N_6P_4$	$C_{18}H_{40}Cl_4N_8P_4$	$C_9H_{20}Cl_4N_5P_3$	$C_{23}H_{30}Cl_3NO_3P_2$
M	880.80	568.91	634.26	433.01	536.77
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$	$P2_1/n$	Pbca
a /Å	11.154 (14)	11.373(3)	10.058(11)	12.449(3)	11.188(2)
b /Å	11.703 (2)	16.955(6)	16.7959(14)	11.725(3)	17.743(2)
c /Å	17.428 (5)	12.570(4)	18.0196(18)	13.366(3)	26.405(2)
α/ deg	106.34 (2)	90.0	90	90	90
β/ deg	104.25 (5)	111.28(2)	90	90.67(2)	90
γ/ deg	89.85 (4)	90.0	90	90	90
V /Å^3	2110.9 (9.7)	2259(6)	3044(3)	1950.8(7)	5241.6(12)
Z	2	4	4	4	8
D_{calc} /g cm^{-3}	1.383	1.614	1.384	1.474	1.360
λ /Å	0.7107	0.7107	0.7107	0.7107	0.7107
T /K	293	173	293	293	293
μ/ mm^{-1}	0.59	1.06	0.623	0.852	0.497

contd...

Table 1.7 contd...

$F(000)$	910	1112	1328	888	2240
Cryst. size [mm]	0.7 x 0. 5 x 0.3	0.8 x 0.4 x 0.3	0.4 x 0.3 x 0.3	0.5 x 0.4 x 0.3	0.42 x 0.42 x 0.4
$\theta_{max.}$	25	25	25	25	25
Reflect coll	7632	4304	3051	3576	4539
Indep reflect	7367	3953	3051	3418	4536[d]
R_{int}	0.043	0.022	0.000	0.0402	0.0065
Data	3850[I>2 (I)]	3806[I>2 (I)]	2655[I>2 (I)]	2228[I>2 (I)]	3059[I>2 (I)]
Parameters	433	298	315	194	301
R[a]	0.106[I>4 (I)][b]	0.048[I>2 (I)][b]	0.0457[I>2 (I)][c]	0.0567[I>2 (I)][c]	0.0562[I>2 (I)][c]
wR[a]	0.062	0.036	0.1187	0.1426	0.1311
S	2.27	2.60	1.058	1.028	1.082
Max. /min peak in diff. map [eÅ^{-3}]	1.3/ -1.6	0.55/ -0.59	0.567/ -0.434	0.535/ -0.354	0.414/ -0.615

[a] $R = \Sigma \big| \, |F_O| - |F_C| \, \big| \, / \, \Sigma |F_O|$; $wR = \{\Sigma[w(F_O^2 - F_C^2)^2] / \Sigma[w(F_O)^2]\}^{1/2}$;

[b] Refinement on F;

[c] Refinement on F^2;

[d] Absorption correction based on psi scans [T_{max} 0.9998; T_{min} 0.9903] applied. Extinction Coefficient: 0.0044.

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PART 2. CYCLODIPHOSPHAZANES

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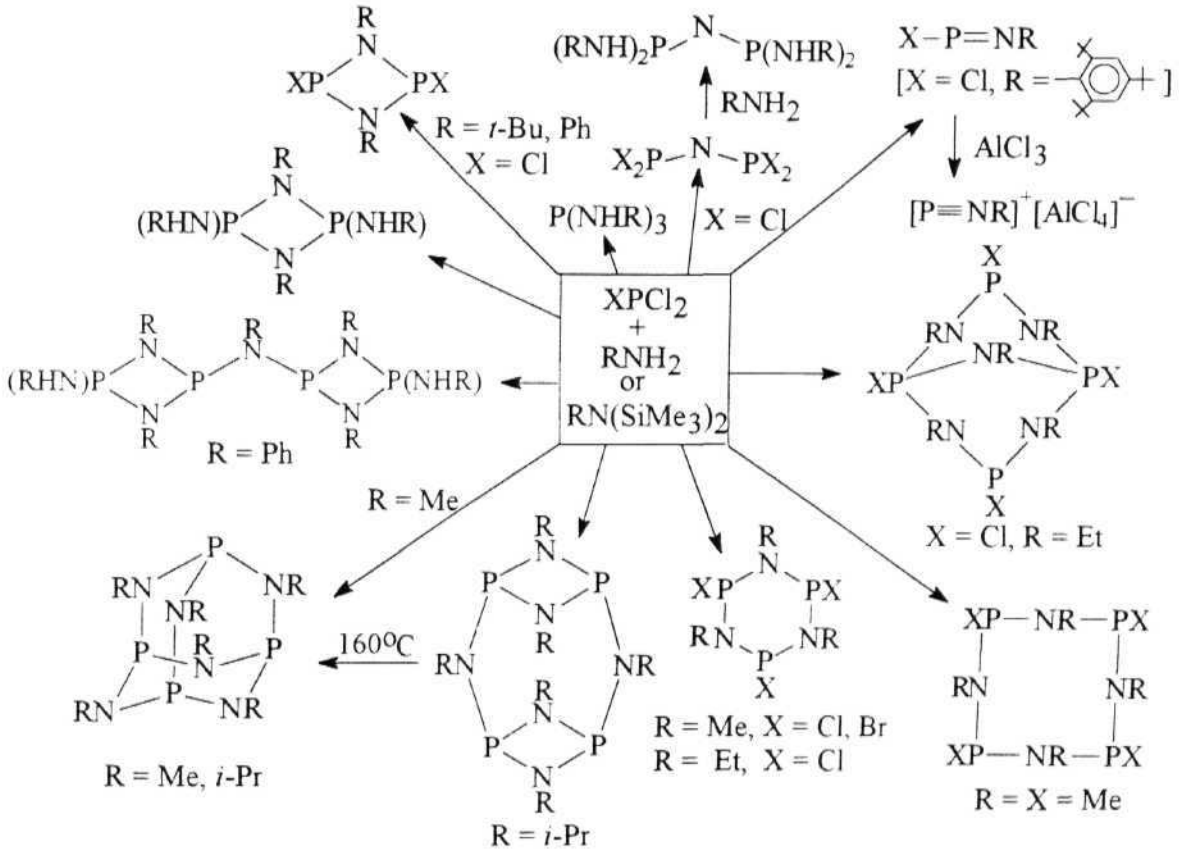
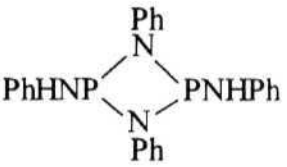
2.1 *Introduction (Literature survey)*

Phosphorus and nitrogen, in contrast to any pair of adjacent elements of the same group in the periodic table, are unique in forming numerous linear and cyclic compounds.[1,2] The important types of compounds with a formal P(III)-N single bond are shown in Scheme 2.1.[3]

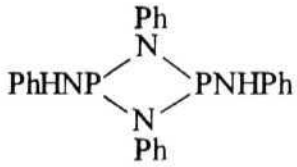
Scheme 2.1



Among these, λ^3-cyclodiphosphazanes (diazadiphosphetidines) constitute an important class; their synthesis, structure and reactivity have been a subject of considerable interest.[4-15] Several synthetic routes, in addition to those shown in Scheme 2.1, are available:

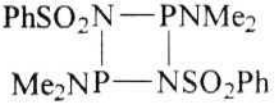
a) $4PhNH_2 + 2(Et_2N)_3P \longrightarrow 6Et_2NH +$ 

2.3 (ref. 13)

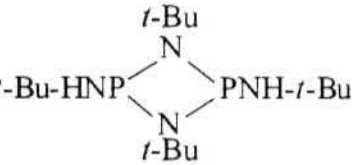
b) $2(PhNH)_3P \xrightarrow{\Delta}$ 

$\delta(P)$: 74.1

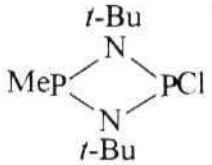
2.3 ($\delta(P)$: 104.4; ref. 16)

c) $PhSO_2NH_2 + (Me_2N)_2PCl \xrightarrow{\text{Pyridine}}$ 

2.4 (ref. 18)

d) $O\{SiMe_2N(t\text{-Bu})H\}_2 + PCl_3 \xrightarrow[-\ (Me_2SiO)_3]{Et_3N}$ 

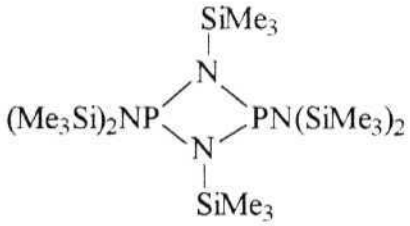
2.5 (*cis*; ref. 19)

e) $(Me_3Si)NP(t\text{-Bu})=Nt\text{-Bu} \xrightarrow{MePCl_2}$ 

2.6 (ref. 19)

f) $(t\text{-Bu})\text{-}N(SiMe_3)Li + PCl_3 \longrightarrow [ClPNt\text{-Bu}]_2$

2.1 (ref. 20)

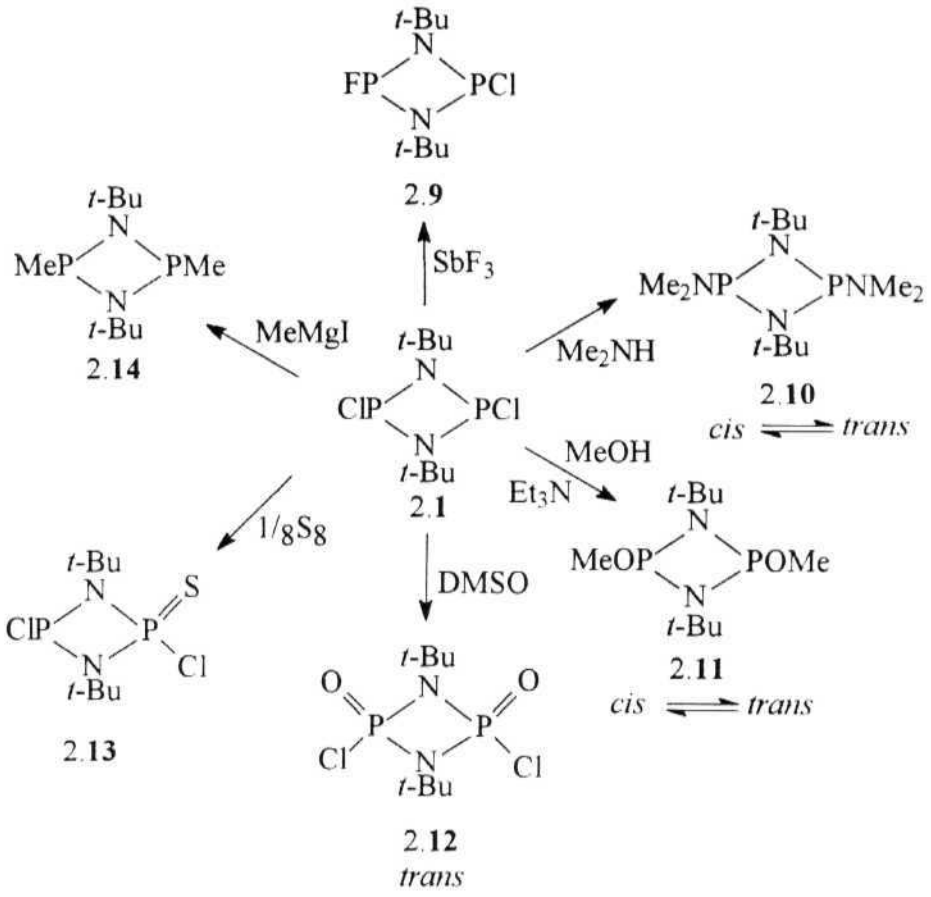
g) $(Me_3Si)_2NP=NSiMe_3 \xrightarrow{25^oC}$ 

2.7

2.8 (ref. 21)

The compounds $(XPNR)_2$ [X = Y = Cl; R = *t*-Bu (**2.1**), Ph (**2.2**)] are the most studied and the discussion that follows relates to mainly these two derivatives. Some reactions of **2.1** are shown in Scheme 2.2.[22]

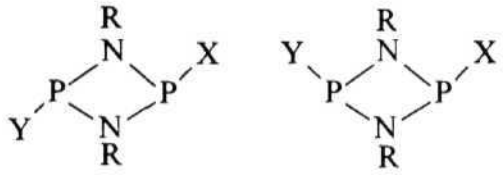
Scheme 2.2



Some of the interesting features in these cyclodiphosphazanes are (i) the relative orientation of the groups X and Y (*cis* and *trans*), (ii) synthetic routes to compounds with X and Y as different groups, (iii) structural chemistry of compounds in which X and Y form a part of the difunctional reagent HX---YH, (iv) behaviour towards oxidation and (v) co-ordination behaviour. These points are discussed below.

2.11 *Relative orientation of* [XP-$(NR)_2$-PY]

In general two geometrical isomers, *cis* and *trans*, which differ in the orientation of the substituents X and Y with respect to the plane of the four-membered N_2P_2 ring (**A** and **B**), are possible. Distinction between the two is best made by ^{31}P NMR (solution) or by X-ray crystallography. Selected ^{31}P NMR data are presented in Table 2.1.



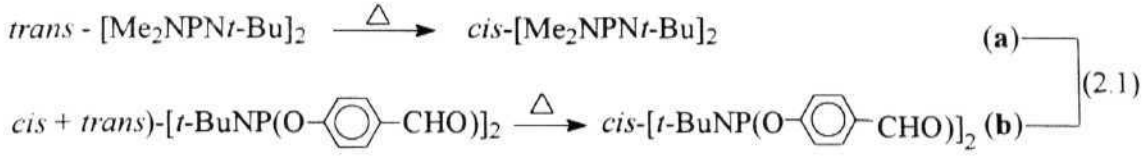
A **B**

Table 2.1. ^{31}P NMR data for the compounds [RNP(X)NRP(Y)]

Sl.No	X, Y	δ(*cis*)	δ(*trans*)	Ref.
		R = *t*-Bu		
1	X = Y = Cl	207.9	-	23
2	X = Y = OMe	133.7	220.4	24
3	X = Y = OCH_2CF_3	143.3	222.9	25
4	X = Y = O*t*-Bu	129.6	-	25
5	X = Y = $O(C_6H_4CHO\text{-}p)$	144.7	235.6	26
6	X = Y = F	165.6	-	27
7	X = Y = NH*t*-Bu	89.4	-	28
8	X = Y = NHMe	98.1	172.4	29
9	X = Y = NMe_2	95.0	184.7	29
10	X = Y = NEt_2	91.3	-	29
11	X = Y = $N(Me)(SiMe_3)_2$	89.9	-	29
12	X = Y = NC_5H_{10}	91.9	182.3	29
13	X = Y = $NMe(PPh_2)$	116.7 (X-ray)	205.7	30
		R = Ph		
14	X = Y = Cl	199.5	-	8
15	X = Y = OMe	137.2	187.2	28
16	X = Y = OCH_2CF_3	142.2	189.8	31
17	X = Y = NPh_2	-	169.0	8
18	X = Y = NH-*i*-Pr	97.7	150.5 (trans: cis 11: 1)	8
19	X = Y = NMe_2	101.0	166.5 (trans: cis 10: 1)	27, 28
20	X = Y = N-(n-Bu)$_2$	-	164.4	8
21	X = Y = NEt_2	-	162.2	28
22	X = NPh_2, Y = NHPh	104.9, 100.9 J = 12.2Hz	not obsd.	8
23	X = Y = NHPh	104.4	not obsd.	13

It is clear from Table 2.1 that for a given pair, the signal for the *trans* isomer is observed 45-90 ppm downfield to the *cis* isomer in the ^{31}P NMR.

In several cases *trans* → *cis* isomerization is favoured,[12,32,33] particularly when traces of amine hydrochloride is present (*cf* eq. 2.1).[28] On the basis of the equilibrium



isomer composition of several compounds in this series Norman and coworkers have made the following generalizations:[12]

The N(ring)-aryl diazadiphosphetidines prefer the *trans* isomers when both the *exo*-amino groups are relatively bulky. With smaller substituents the *cis* form becomes more stable. For N(ring)-alkyl-substituted diazadiphosphetidines *cis* isomers are preferred for 2,4-dihalo, 2,4-dialkoxy and 2,4-diamino derivatives.[8] The 2,4-dichloro derivatives $[RNPCl]_2$ [R = Ph or *t*-Bu] exist as *cis* isomers with no evidence of the *trans* form.

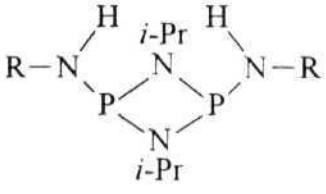
Norman and co-workers have also performed a detailed study of (a) *cis*/ *trans* isomerism and (b) conformational properties of 2,4-bis(primaryamino)-1,3,2,4-diazadiphosphetidines. The equilibrium constants $K_{cis/\ trans}$ {= [cis]/ [trans]} for several compounds thus obtained are given in Table 2.2. It can be seen that in most cases the *cis* isomer is preferred thermodynamically.[12]

The orientation of the substituents on the exocyclic group is also of some interest. For example, in *cis*-$[i\text{-Pr-NHPN}(i\text{-Pr})]_2$ three possible conformers (**C-E**) based on P-N bond rotation are possible.[12] The ^{31}P NMR spectrum of this compound shows a singlet at

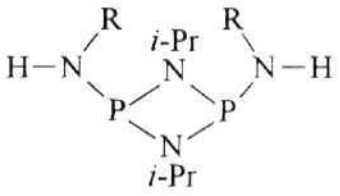
Table 2.2 Equilibrium constants (K) for the *cis*/ *trans* isomer equilibration

Compound	K
$[(i\text{-PrNH})PN\text{-}i\text{-Pr}]_2$	15 ± 1
$[Me_2NPN\text{-}t\text{-Bu}]_2$	10
$[t\text{-BuNHPN-}t\text{-Bu}]_2$	∞
$[Et_2NPN\text{-}t\text{-Bu}]_2$	∞
$[EtNHPNEt]_2$	8 ± 1
$[MeNHPNMe]_2$	3 ± 0.5

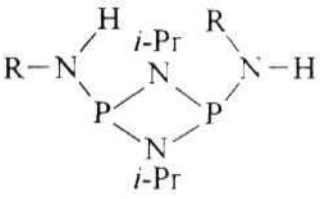
95.4 ppm at 27°C. At -90°C a pair of equal area singlet resonances at δ 96.0 and 83.3 and a singlet at δ 80.4 ppm are observed. Based on this and the ^2J(P-N-H) values, the authors have assigned these resonances to the presence of conformers **E** (unsymmetrical) and **D** (symmetrical). The *trans* isomer does not show temperature dependence.



C) Symmetrical



D) Symmetrical



E) Unsymmetrical

It is interesting in this context to note that with smaller alkoxy groups (OMe, OEt, OCH_2CF_3) the kinetically favoured *trans* isomer is converted to its *cis* counterpart on standing in solution,[25] whereas with a more bulky group such as O-*t*-Bu only the *cis* isomer is isolated.[34] Certainly, more experimental data is required to unravel the details.

However later studies by Shreeve and coworkers have thrown open some more questions. Instead of using an alcohol or phenol with triethylamine as a base, they used the lithium salts of alcohols.[11] Thus when $[t\text{-BuNPCl}]_2$ (2.**1**) was reacted with two mole equivalents of $LiOCH_2CF_3$, the *trans*-isomer (δ(P) = 223.0) was obtained in more than 8-

fold excess relative to the *cis* isomer (δ(P): 143.3).[7] In earlier studies where triethylamine was used as base, the product was almost entirely the *cis* isomer.[25]

Thus the *trans* isomer appeared to be the thermodynamically favoured one. No change in isomer distribution occurred when *trans*-[*t*-BuNP(OCH_2CF_3)]$_2$ was either allowed to stand for a long time at 25°C or when it was heated to 60°C for 12h. Since the use of triethylamine gives $Et_3N.HCl$ as a reaction product, the authors suggest that it could acid-catalyze the isomerization of the *trans* isomer to the *cis* isomer. When the lithiated alcohol was used, the LiCl formed did not play a similar catalytic role; thus, it was concluded that the *trans* isomer is both the kinetically and thermodynamically stable product.

However when sterically more demanding nucleophiles C_6F_5OLi and $(F_3C)_2CHOLi$ are used, *cis* isomers are the predominant products. To add to the confusion, reaction of the bulky $(Me_3Si)_2NLi$ with (*t*-BuNPCl)$_2$ led to the *trans* isomer as the major product.[7] Perhaps studies on molecular mechanics may reveal more details on these compounds.

2.12 *Synthesis of diazadiphosphetidines with X and Y as different groups*

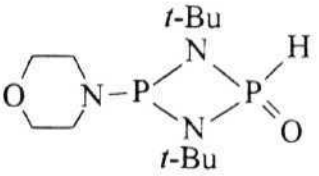
The interest in compounds of this type, particularly when X = Cl and Y = amino, alkoxy or aryloxy stems from the fact that the residual functionality could later be utilized for further reactions (like reaction with Na or $AlCl_3$ to get new P-P bonded species or phosphenium cations respectively).[19,35] It can be expected that by suitably controlling the stoichiometry of the nucleophile with respect to $(RNPCl)_2$ partially substituted products [XPNRPY-NR] will be formed. Some known examples of such derivatives are listed in Table 2.3.

Table 2.3. Mixed derivatives [X-PNRPY-NR] with their ^{31}P NMR data

S.No	R	X	Y	P_X	P_Y	J(P-P)	Ref.
1	*t*-Bu	Cl	OMe	188.0	137.8	37.2	25, 27
2	*t*-Bu	Cl	O-*t*-Bu	191.8	163.8	49.7	25
3	*t*-Bu	Cl	F	197.1	180.3	49.6	27
4	*t*-Bu	Cl	NMe_2	186.6	131.5	32.5	27, 29
5	*t*-Bu	F	NMe_2	145.9	116.3	14.0	27
6	Ph	Cl	NMe_2	178.6	136.3	-	13
7	*t*-Bu	Cl	NH-*t*-Bu	199.0	138.2	45.0	23
8	*t*-Bu	NC_4H_8O	P(O)H	75.5	-	-	29
9	*t*-Bu	O-*t*-Bu	P(O)H	105.1	-3.2	12.1	25
10	*t*-Bu	NMe_2	NHMe	170.1	184.3	-	29

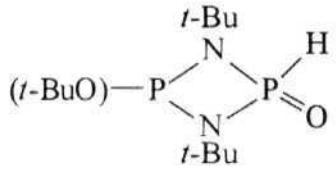
All the compounds listed in Table 2.3 can be considered to be *cis* isomers on the basis of the δ(P) values as discussed earlier.

When phosphorus trichloride is treated with four molar equivalents of *t*-butylamine, the unsymmetrically substituted compound ClPN(*t*-Bu)P(NH-*t*-Bu)N(*t*-Bu) (entry no.7 in Table 2.3) is obtained as one of the products.[23] The reactions of chlorocyclophosphazanes with amines in a few cases leads to products in which there is partial hydrolysis. For example, compound **2.15** is a minor product along with $[(OC_4H_8N]PN(t\text{-Bu})]_2$ in the reaction of morpholine with $[ClPN(t\text{-Bu})]_2$; the yield of this



2.15

product increases upon heating the reaction mixture.[29] An explanation based on water induced cleavage of an exocyclic P-N bond is offered for this observation. In the reaction of *t*-butanol with $[ClPN(t\text{-}Bu)]_2$ the expected product $[(t\text{-}BuO)PNt\text{-}Bu]_2$ could not be obtained in a pure state. On standing at ambient temperature or heating under reduced pressure the unsymmetrically substituted compound 2.**16** formed by butene elimination is isolated.[25]

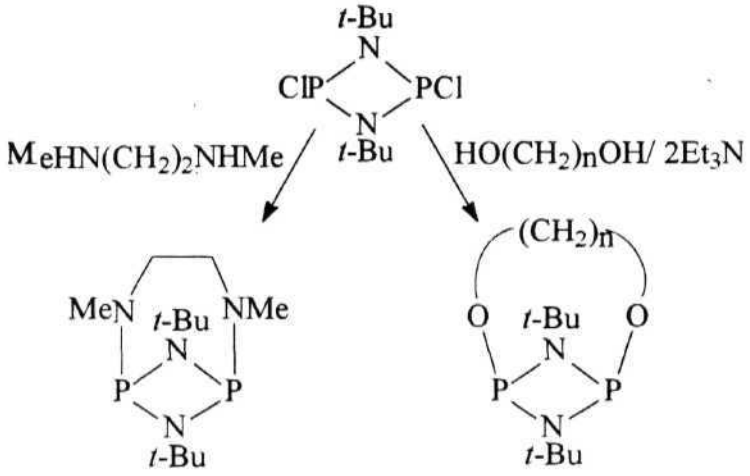


2.**16**

It is of interest to note that an attempt to prepare $(MeO)P(NPh)_2P(NMe_2)$ by reacting *cis* $[PhNPCl]_2$ with one mole equivalent of methanol in the presence of Et_3N followed by treatment with an excess of Me_2NH at low temperature led only to an equimolar mixture of $[PhNP(OMe)]_2$ [δ(P) = 193.0 (s)] and $[PhNP(NMe_2)]_2$ [δ(P) = 166.5 (s)].[4]

2.13 *Structural chemistry of diazadiphosphetidines in which X and Y form part of the difunctional reagent HX----YH.*

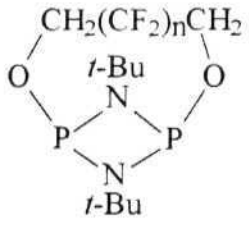
Keat and Thompson isolated the bicyclic compounds 2.**17**-2.**19** as solids by reacting $[ClPN(t\text{-}Bu)]_2$ (2.**1**) with the corresponding diamine/ diol (Scheme 2.3).[36] Interestingly, in the reaction using N,N'-dimethyl-1-3-propanediamine no bicyclic compound similar to 2.**17** could be isolated.



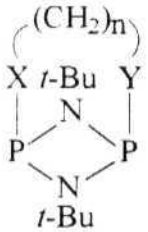
2.**17**; δ(P): 155.0

n = 2, 2.**18**; δ(P): 177.5
n = 3, 2.**19**; δ(P): 135.4

Reaction of 2.**1** with lithiated polyfluorodiols $HOCH_2(CF_2)_nCH_2OH$ (n = 2, 3) proceed smoothly to give bridged compounds 2.**20** and 2.**21** as liquids.[7] Interestingly the ^{31}P NMR chemical shift at δ ~ 220 (s) for 2.**20** - 2.**21** is well outside the range reported for the other bridged compounds. Later Krishnamurthy and coworkers isolated bicyclic compounds 2.**22** - 2.**25** using $[ClPNPh]_2$ as the precursor. They were also successful in characterizing 2.**24** and 2.**25** in the solid state by X-ray crystallography.[4]



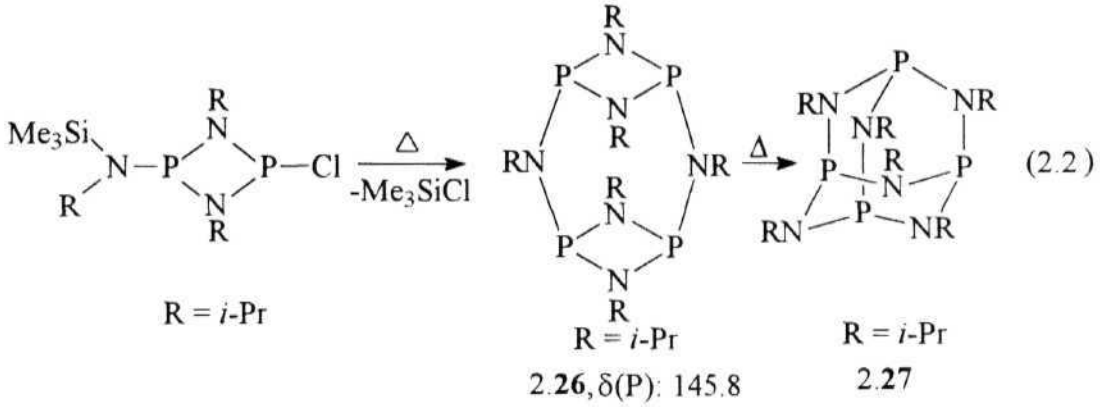
2.**20** (n = 2; δ(P): 221.5)
2.**21** (n = 3; δ(P): 222.3)



2.**22** (n = 2, X = Y = O; δ(P): 172.3)
2.**23** (n = 2, X = Y = NMe; δ(P): 151.9)
2.**24** (n = 2, X = O, Y = NMe;
δ(P): 158.9, 164.4 [J = 25.5Hz]
2.**25** (n = 3, X = Y = O; δ(P): 137.3)

The tricyclic compound 2.**26** is formed by heating the unsymmetrical phosphazane in refluxing acetonitrile solution. A fascinating aspect of compound 2.**26** is that it is

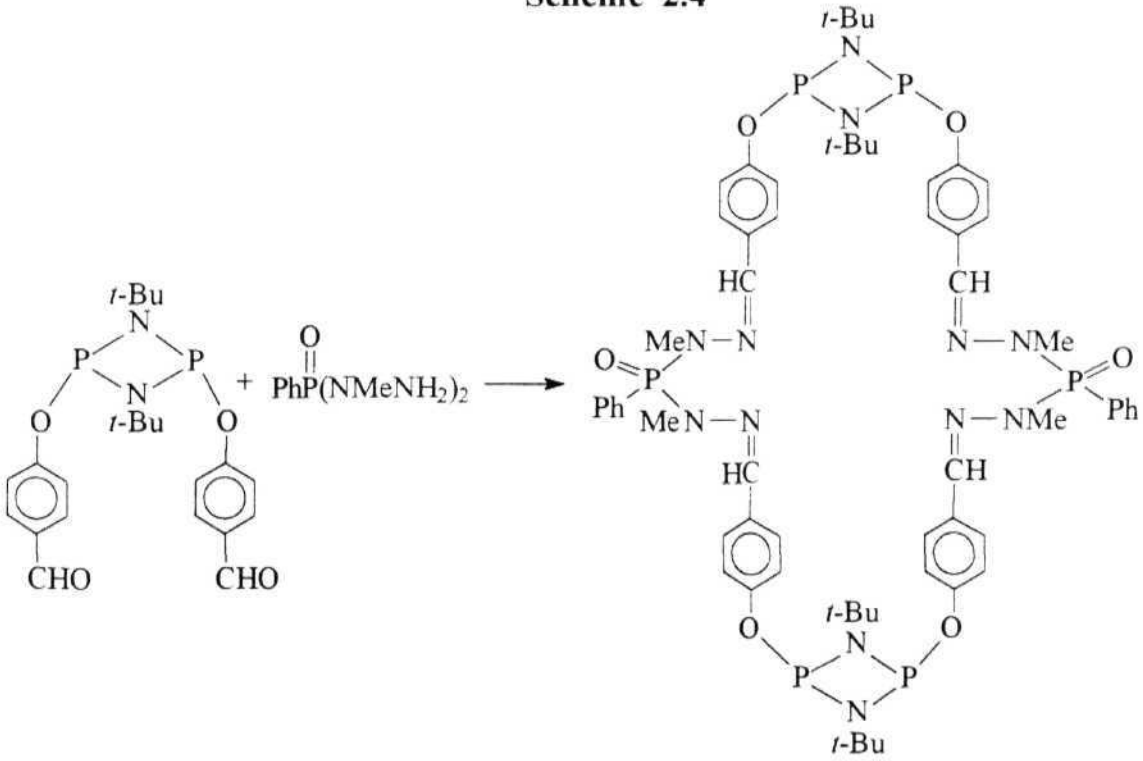
thermodynamically unstable with respect to the adamantane-like compound 2.**27**; the latter is obtained by heating 2.**27** at 156-158°C for several days (eq 2.2).[37]



(2.2)

It is not always necessary to use the difunctional reagent HX--YH to obtain the polycycles with cyclodiphosphazane skeleton. An elegant approach has been developed by Majoral and coworkers for the synthesis of macrocycles (Scheme 2.4).[26]

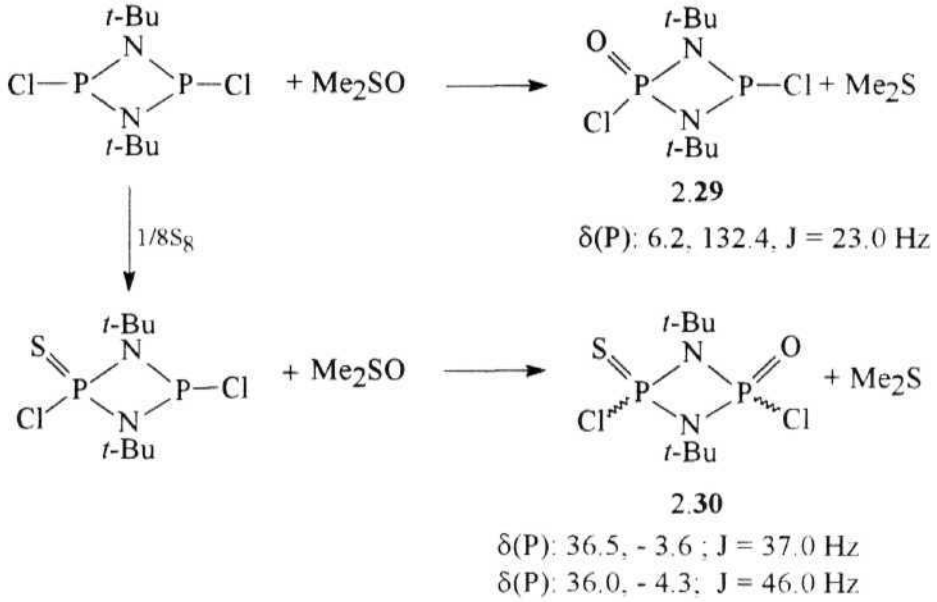
Scheme 2.4



2.14 *Oxidative addition reactions*

In compound $(XPNR)_2$, the phosphorus is trivalent and is susceptible to oxidation in several cases.[38] The simplest is the addition of oxygen, sulfur, selenium etc. Some reactions are shown in Scheme 2.5.[23] The dimethylamino derivative $[Me_2NPN(t\text{-Bu})]_2$ is unreactive towards DMSO; however *t*-butylhydroperoxide converts it to the dioxide 2.**31** smoothly (eq. 2.3).[25]

Scheme 2.5

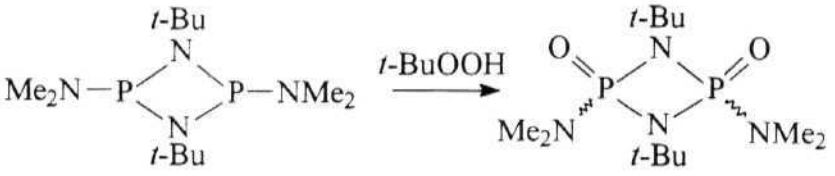


2.**29**

δ(P): 6.2, 132.4, J = 23.0 Hz

2.**30**

δ(P): 36.5, - 3.6 ; J = 37.0 Hz
δ(P): 36.0, - 4.3; J = 46.0 Hz



(2.3)

2.**31**

cis isomer δ(P): 4.0
trans isomer δ(P): 1.6

In general, it is found that the *trans* isomers are more reactive than the *cis* isomers towards oxidation.[24] For example reaction of a 1:1 mixture of isomers of [Me_2NPN-(*t*-

Bu)]$_2$ with half mole equivalent of sulfur, selenium or methyl iodide results in the formation of the *trans* - mono oxidation products [$Me_2NP(Z)$-N-(*t*-Bu)]$_2$ (Z = S, Se, MeI) from the *trans* isomer, leaving the *cis* isomer unchanged.[39] The reaction is stereospecific; the stereospecificity is also confirmed in the oxidation of *cis*-[Me_2NPN(*t*-Bu)]$_2$ with sulfur wherein only *cis*-[$Me_2NP(S)N$(*t*-Bu)]$_2$ (X-ray) was obtained.

The diselenium derivatives [$Me_2NP(Se)N$-(*t*-Bu)]$_2$ are very labile; this behaviour can be made use of in the preparation of the monoselenides as shown in eq. 2.4.[40]

$$[Me_2NPNt\text{-}Bu]_2 + [Me_2NP(Se)Nt\text{-}Bu]_2 \longrightarrow 2\,[Me_2NP(Se)(Nt\text{-}Bu)_2NMe_2] \qquad (2.4)$$

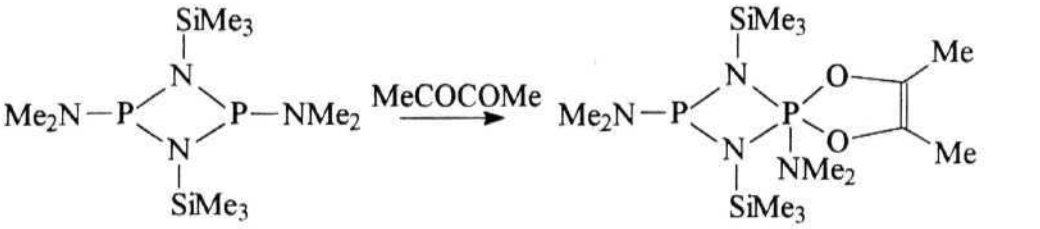
cis δ(P): 39.8
trans δ(P): 48.9

cis δ(P): 90.0, 36.2; ^1J(P-Se) = 812.4 Hz
^2J(P-P) = 9.4 Hz
trans δ(P): 117.7, 61.0; ^1J(P-Se) = 829.8 H
^2J(P-P) = -10.1 Hz

The bicyclic derivative [*t*-BuNPN(Me)CH_2CH_2N(Me)PN-*t*-Bu] undergoes ready oxidation with selenium to give the monoseleno derivative [*t*-BuNP(Se)N(Me)CH_2CH_2N (Me)PN-*t*-Bu]. However the bicyclic compounds 2.**22** - 2.**25** failed to react with sulfur or with diketones.[41]

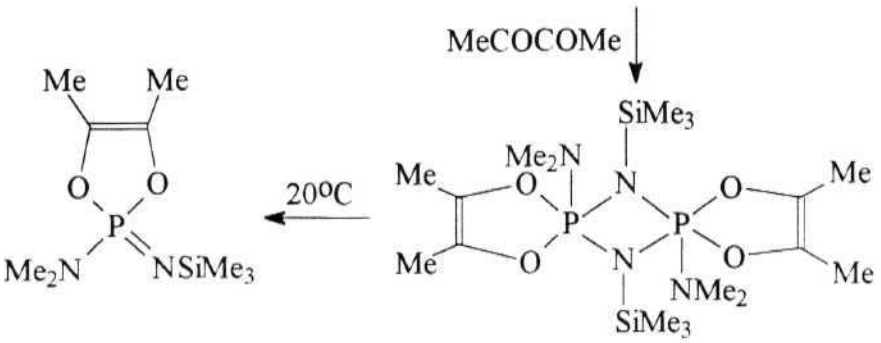
Diketones can oxidatively add to P(III) compounds leading, most often, to pentacoordinated phosphorus compounds. When the diazadiphosphetidine $(Me_2NPNSiMe_3)_2$ is treated with a diketone, the initially formed pentacoordinated compound breaks up into monomeric phosphazenes (Scheme 2.6).[42] Similarly benzil reacts with [(EtO)PNPh]$_2$ to yield the phosphorane which breaks down to 2.**36** (eq 2.5).[43] Schmidpeter and coworkers have been able to obtain the stable pentacoordinated compound 2.**37** by reacting [ClPNPh]$_2$ with benzilmonoanil (eq 2.6).[44]

Scheme 2.6



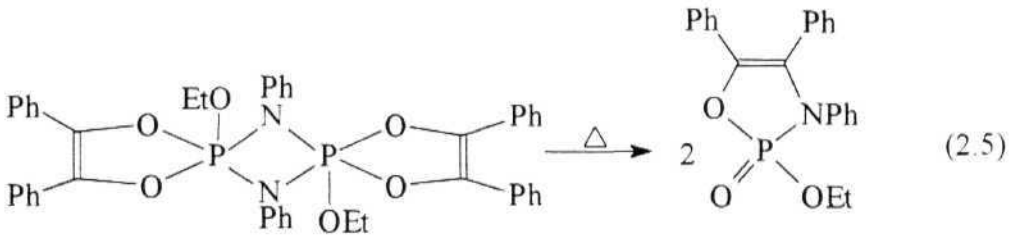
2.**32**, δ(P): 107.6

2.**33**, δ(P): 84.3, - 40.6; ^2J(P-P) = 15.0 Hz



2.**35**, δ(P): 15.9

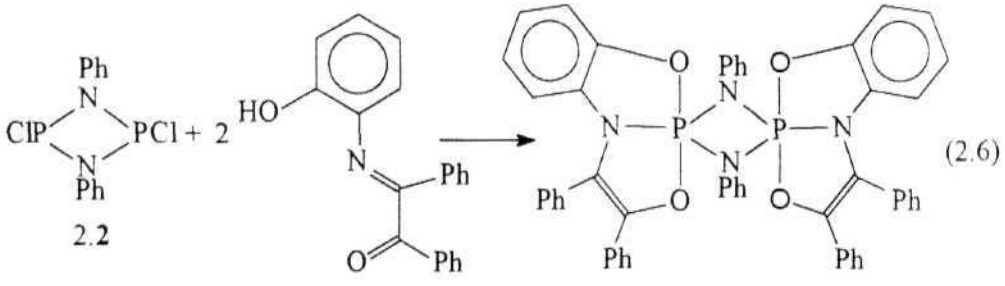
2.**34**, δ(P): - 53.1



δ(P): 62.8

2.**36**

(2.5)



2.**2**

2.**37**, δ(P): - 50.5

(2.6)

2.15 *X-ray structural studies*

Solid state structures of several diazadiphosphetidines are known. This data is summarized in Table 2.4. In most cases the N_2P_2 ring is planar; significant puckering is observed only for the *cis* compounds $[C_5H_{10}NP\text{-}N\text{-}t\text{-}Bu]_2$ and $[Ph_2P(Me)N\text{-}P\text{-}N\text{-}t\text{-}Bu]_2$. Destabilizing interaction between the lone pairs on nitrogen and phosphorus in the *cis* isomers is reduced by the twisting of the cyclodiphosphazane ring.[24] The P-N bonds are in the range 1.69-1.73Å and the ring nitrogen is close to planarity in all the cases.

2.16 *OBJECTIVES OF THE PRESENT WORK*

The main objectives of this part of the work are:

(i) To check whether *cis* and *trans*-$[(ArO)PN\text{-}t\text{-}Bu]_2$ are the major products in the reaction of $[ClPN\text{-}t\text{-}Bu]_2$ with phenols in the light of available literature

(ii) To isolate unsymmetrically substituted phosphazanes of the type $[ClP(N\text{-}t\text{-}Bu)_2\text{-}P(OAr)]$ for further use

(iii) To introduce large-size rings by reacting $[ClPN\text{-}t\text{-}Bu]_2$ with difunctional reagents, and

(iv) To check the oxidative addition reactions (with S, Se) of cyclodiphosphazanes.

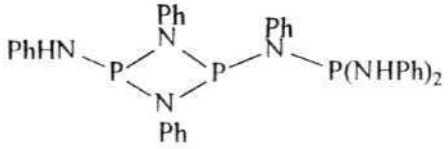
Table 2.4. Structural data on diazadiphoshetidines

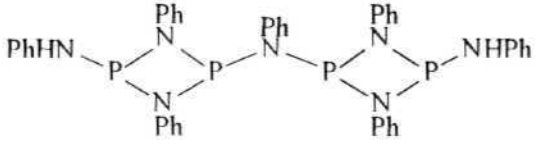
Compound	P-N	P-N-P	N-P-N	Σ N(ring)	Comments	Ref.
cis [ClPN-*t*-Bu]$_2$	1.689(4)	97.3(4)	82.4(4)	356.4	N_2P_2 ring: planar, C_s	45
cis [ClPNPh]$_2$	1.695(10)	99.7(4)	80.3(4)	359.9	N_2P_2 ring: planar, C_s	8
cis [C_5H_{10}NPN-*t*-Bu]$_2$	1.735	96.8(1)	80.3(1)	346.3	N_2P_2 ring: puckered ± 0.138Å; exocyclic P-N 1.679(2) Å	24
cis [Ph_2P(Me)NPN-*t*-Bu]$_2$	1.723(11)	96.9(8)	80.1(6)	359	Puckered	30
cis [*t*-BuNHPN-*t*-Bu]$_2$	1.733	98.0	80.7	347.6	endocyclic P-N 1.685	18
cis {PhNHPNPhP[NPhP(NHPh)$_2$]NPh}[a]	1.721(8)	100.2(4)	79.3(4)	359.1	Planar	13
cis [PhNHP(NPh)$_2$P]NPh [b]	1.722(6), 1.718(7)	100.3(3) 99.8(3)	79.1(3) 79.5(3)	356	P-N(exo): 1.714(7)[c] 1.667(8)[d]	46
{$Mo_2(CO)_8$[μ-*cis*-(Me-4-C_6H_4OPNPh)$_2$]$_2$}[e]	1.712(4)	98.7	80.9	360	Puckered	14
[PhNP]$_2$[-N(Me)CH_2CH_2O-]	1.722(7)	99.9(1)	79.34(2)	360	Exocyclic P-N 1.661(4) Puckered ring	4
[PhNP]$_2$[-O$CH_2CH_2CH_2$O-]	1.714	99.9(1)	79.6(3)	359.3	Planar	4
trans [MeOPNPh]$_2$	1.721, 1.734(4)	99.9(2)	80.1(2)	360	Planar	47
trans [PhNP(O-C_6H_4-4-Me]$_2$	1.717	115.3	79.8	360	Planar	5
trans [(Me_3Si)$_2$NPNSiMe_3]$_2$	1.727	97.5	82.5	360	Planar exocyclic P-N 1.712Å	22

contd..

Table 2.4 contd..

trans $[(F_3CCH_2O)PNPh]_2$	1.716(3)	100.2(2)	79.8(2)	359.8	Planar	33
trans $[PhNP(NPh)]_2$	1.713(9)	101.1	78.9(5)	359.9	Exocyclic P-N 1.709(9)	8
trans $[t\text{-BuNHPN-}t\text{-Bu}]_2$	1.685(3)	96.4	83.5	354.7	Exocyclic P-N 1.631(3)	12
trans $[EtNHP(S)NEt]_2$	1.674(3)	97.0(2)	83.0(2)	356.8	Exocyclic P-N 1.616(4)	12

a 

b 

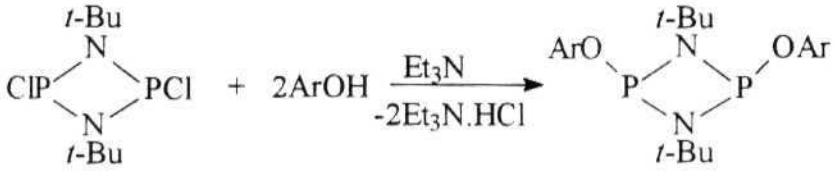
[c] P-N-Ph-P [d] P-NHPh [e] δ(P): 155.5

2.2 *Results and Discussion*

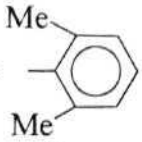
The precursors [ClPN-*t*-Bu]$_2$ [2.**1**; δ(P): 207.9] and [ClPNPh]$_2$ [2.**2**; δ(P): 199.5] were prepared by reacting phosphorus trichloride with *t*-butylamine and aniline hydrochloride respectively, following literature procedures.[48,49] For most of the reactions in the present study compound 2.**1** has been utilized because of the ease of its isolation in a pure state.

2.21 *Bis aryloxy/ alkoxy derivatives* [(RO)PN-*t*-Bu]$_2$

We shall first consider the *bis* aryloxy / alkoxy derivatives [(R'O)PNR]$_2$. We have used the reaction of [ClPN*t*-Bu]$_2$ with phenols in the presence of triethylamine (eq. 2.7) to prepare these compounds. Compounds 2.**38**-2.**43** have been assigned the *cis*-geometry based on their ^{31}P NMR chemical shifts [Section 2.11] as well as the single crystal X-ray structure performed on 2.**38**. The δ(P) values are upfield to *cis*-[(C$_6$F$_5$O)PN*t*-Bu]$_2$



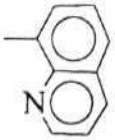
2.**1** 2.**38**-2.**43** (2.7)

Ar =  [2.**38**, δ(P): 156.3]

Ar =  [2.**41**, δ(P): 142.2]

 [2.**39**, δ(P): 142.2]

 [2.**42**, δ(P): 142.5]

 [2.**40**, δ(P): 141.9]

 [2.**43**, δ(P): 142.9]

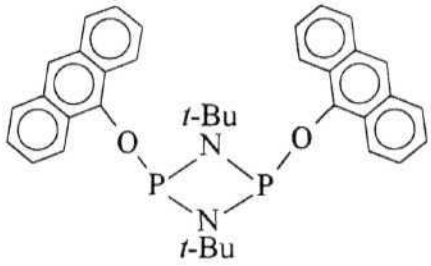
[δ(P): 162.6] as can be expected due to the lower group electronegativity of these -OAr groups relative to $-OC_6F_5$.[50] Other points of observation are given below:

(i) Analogous reaction of 2.**2** with 2,6-dimethylphenol / Et_3N afforded a product mixture exhibiting two ^{31}P NMR peaks at 153.3 and 222.2 ppm in the tricoordinated region in the ratio 4:1; these are assigned to *cis*- and *trans*-$[(2,6\text{-}Me_2C_6H_3O)PN(Ph)]_2$ (2.**44**) respectively.

(ii) In the reaction mixture using 4-methoxyphenol, a small quantity (~3%) of the *trans*-isomer [δ(P): 231.0 ppm] was observed.

(iii) The reaction of 2.**1** with 2,6-$Me_2C_6H_3ONa$ or 4-MeC_6H_4ONa also gave *cis*-$[(2,6\text{-}Me_2C_6H_3O)PN(t\text{-}Bu)]_2$ or $[(4\text{-}Me\text{-}C_6H_4O)PN(t\text{-}Bu)]_2$ as the only product. However in the reaction of 2,6-$Me_2C_6H_3OLi$ [prepared by treating n-BuLi with the phenol] with 2.**1** in THF no *cis* isomer was detected; only one major peak (>85%) at 214.8 ppm was observed in the ^{31}P NMR. This is probably due to *trans*-$[(2,6\text{-}Me_2C_6H_3O)PN(t\text{-}Bu)]_2$; this δ(P) value can be compared with that of *trans*-$[(C_6F_5O)PN(t\text{-}Bu)]_2$ [δ(P): 252.0 ppm].[11] However we were not successful in obtaining this compound in a pure state because of hydrolysis [^{31}P NMR: peaks at +10 to -3 ppm].

(iv) The reaction of 2.**1** with sodium anthryloxide in THF afforded *cis*-[(1-anthryloxy) P-N(*t*-Bu)]$_2$ (2.**45**); [δ(P): 166.8]. This assignment is based on the closeness of its δ(P) value to the *cis* isomers 2.**38**-2.**43** (eq. 2.7).



2.**45**

Although we have not been able to monitor these reactions with respect to time or temperature because of limited accessibility, two points appear to be clear:

a) *Cis*-isomers are the preferred products in the reactions of 2.**1** with phenols in the presence of Et_3N or as their sodium salts. In contrast to the isolation of *trans*-[(4-Me-C_6H_4O)PNPh]$_2$ in the reaction of 2.**2** with 4-MeC_6H_4ONa, we could isolate only *cis*-[(4-MeC_6H_4O)PN-*t*-Bu]$_2$ in the reaction of 2.**1** with 4-MeC_6H_4ONa. This observation does indicate that for the sterically more demanding *t*-butyl precursor 2.**1** *cis*-isomers are favoured.

b) Reaction using lithium aryloxides may lead to the preferential formation of the *trans* isomer as noted by Shreeve and coworkers.[7]

In contrast to the reaction of 2.**1** with phenols, the reaction with two mole equivalents of 9-anthracene methanol using triethylamine as a base apparently takes a different course. Although a crystalline solid, m.p 214°C, was isolated, the ^{31}P NMR spectrum ($CDCl_3$) showed three singlets [Fig.2.1] at 135.2, 84.1 and 4.7 ppm. The intensities of these signals were variable in several batches checked; hence they must arise from different compounds. The signal at 4.7 ppm must arise from a tetracoordinated phosphorus, thus suggesting a rearrangement of P-OCH_2Ar to P(O)CH_2Ar. Whether the peaks at 84.1 and 135.2 ppm are due to *cis* and *trans*-{(RO)PN-*t*-Bu}$_2$ (2.**46**) is difficult to say but at least the one at 135.2 ppm must be due to one of the isomers. The ^{1}H NMR spectrum also showed the presence of more than one compound; although one AX quartet corresponding to OCH_ACH_XAr [δ(A): 5.80, δ(X): 6.40, ^2J(AX) = 10.0 Hz] was present, no peak corresponding to P(O)<u>H</u> was observed. The analytical (CHN) values were also not very helpful and suggested partial chlorination of the anthracenyl residue or hydrolysis. We attempted to get an X-ray structure of the compound but did not succeed due to its instability in air. In the reaction of 2.**1** with 1-naphthalene methanol an oily material was isolated; this showed mainly three peaks at δ 135.0, 84.4, and 1.7 ppm in the ^{31}P NMR; however some hydrolyzed products [^{1}H NMR: P(O)<u>H</u> resonances centred at

7.0 (^1J = 720 Hz) and 7.7 (^1J = 600 Hz)] were also present and hence further analysis was not attempted.

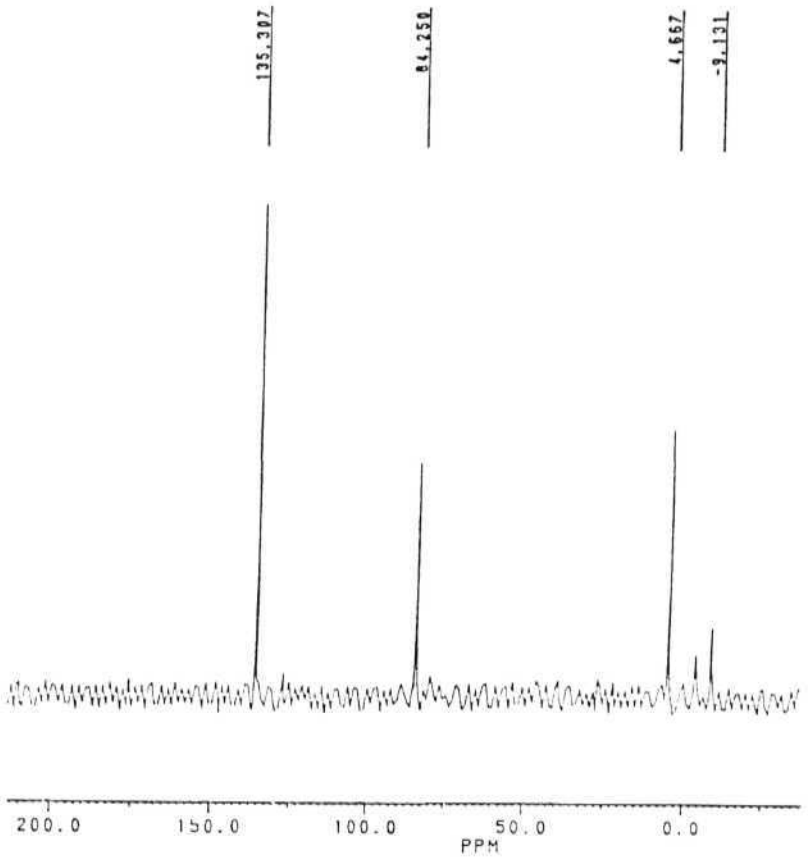


Fig 2.1 ^{31}P NMR spectrum of the product from the reaction of 2.**1** with two mole equivalents of 9-anthracenemethanol.

2.22 *Reaction of* [ClPN-*t*-Bu]$_2$ (2.**1**) *with diols*

As regards to the reaction of 2.**1** with difunctional reagents, three products (**F**)-(**H**) are possible. Since in the reaction of 2.**1** with a phenol / Et_3N, the *cis* isomer of (**F**) [(ArO)PN-*t*-Bu]$_2$ is overwhelmingly favoured, it should be possible to isolate these compounds preferentially in good yields. We chose the following diols:

(a) 2,2'-methylenebis(4-methyl-6-*t*-butyl-phenol)

(b) bis(2-hydroxy-1-naphthyl)methane[51]

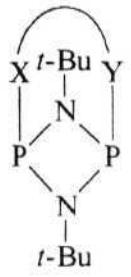
(c) 2,2'-biphenyldimethanol

(d) 1,4-butanediol

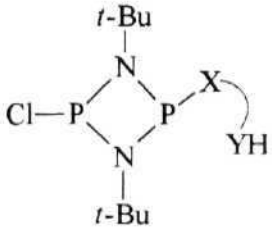
(e) 2,2'-methylenebis(4-chlorophenol)

(f) 2,2'-dimethylpropane-1,3-diol

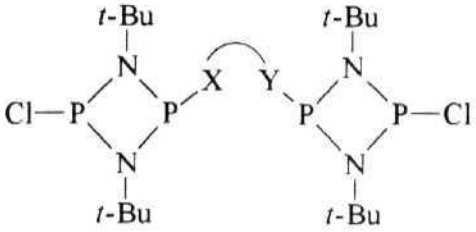
(g) 2,2'-biphenol



(F)

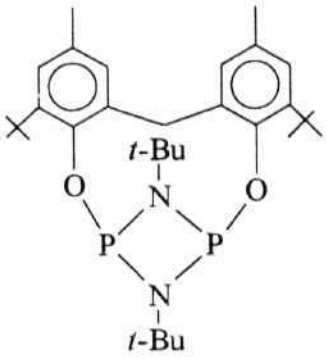


(G)

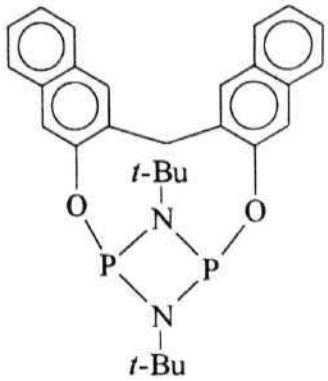


(H)

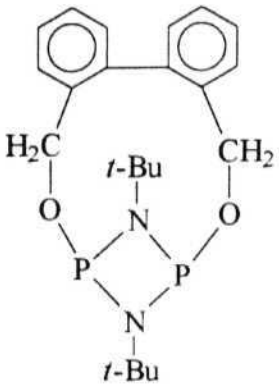
The choice of these reagents was dictated by our desire to introduce large rings into the phosphazane skeleton. We were successful in isolating compounds 2.**47**-2.**49** in pure state; compounds 2.**50**-2.**53** were identified only by NMR. Although compounds 2.**47** and 2.**49** are fairly stable, 2.**48** is not. The yields of 2.**47**-2.**49** are good (65-85%). An interesting point to be noted about these compounds is the variation in the ^{31}P NMR chemical shifts. For example, although all the three compounds 2.**47**, 2.**48** and 2.**51** have the same number of atoms (seven) in the bridging loop the chemical shift range span nearly 40 ppm. The δ(P) values for 2.**47**, 2.**48** and 2.**51** are significantly more upfield than for Shreeve's compound 2.**54** [δ(P): 222.3],[11] which contains a fluorinated dioxy bridging group; all of these have a bridging loop of seven atoms. Deshielding by fluorine atoms thus appears to be considerable.



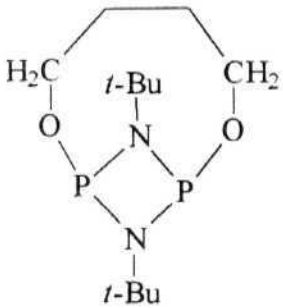
2.**47** [δ(P): 143.9; X-ray]



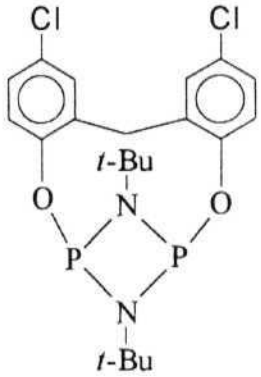
2.**48** [δ(P): 181.4; X-ray]



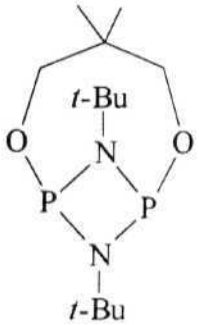
2.**49** [δ(P): 125.6]



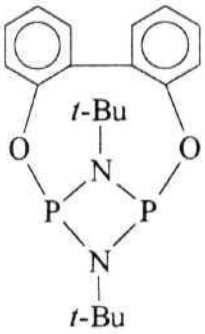
2.**50** [δ(P): 131.2]



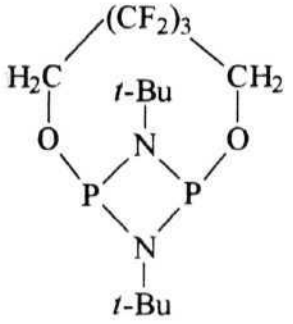
2.**51** [δ(P): 162.1]



2.**52** [δ(P): 139.4]



2.**53** [δ(P): 167.2]



2.**54** [δ(P): 222.3]

Compound 2.**49** represents the first example of a bicyclic phosphazane with an eight atom bridging loop. Its δ(P) value is the most upfield among all the bicyclic derivatives. Interestingly in the ^{1}H NMR the methylene protons of the $ArCH_2$ group show up as two doublets [δ(A): 4.49, δ(B): 4.67] with a $^{3}J(\underline{P}\text{-}\underline{H})$ value of ~18 Hz [Fig 2.2] [it is also possible that the two geminal protons are non equivalent ($ArC\underline{H}_AC\underline{H}_B$). However in such a case we expect both $^{3}J(\underline{P}\text{-}\underline{H})$ and $^{2}J(H_A\text{-}H_B)$ leading to more peaks; see structural diagrams below], suggesting that they are in slightly different environments.

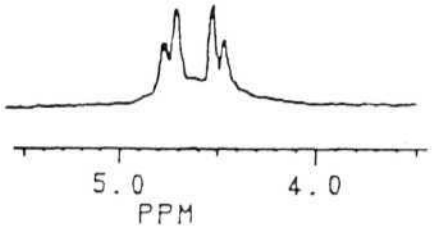
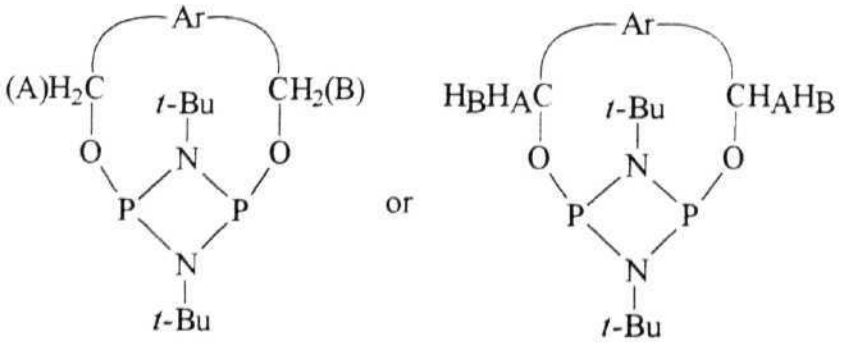
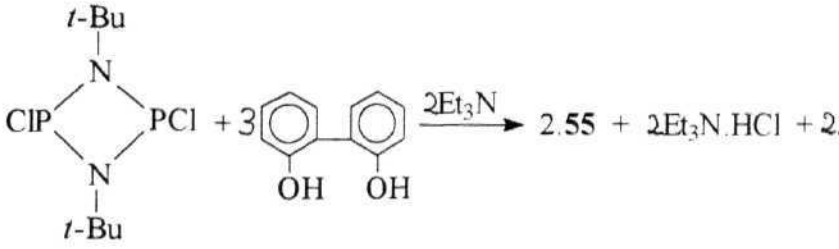


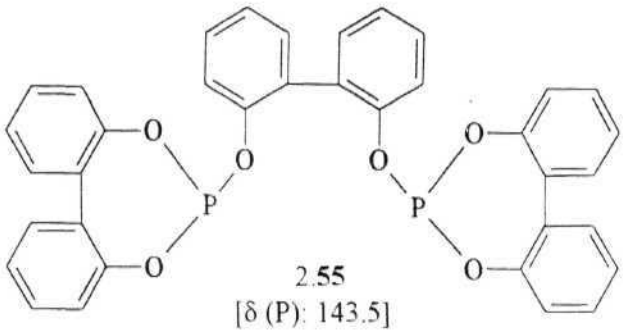
Fig 2.2 ^{1}H NMR of 2.**49** in the -OCH_2Ar region.



Unexpectedly, in the reaction of 2.**1** with 2,2'-biphenol, in addition to the bicyclic derivative 2.**53** we also observed the formation of $[2,2'\text{-}(C_6H_4O)_2P]_2[2,2'\text{-}(OC_6H_4)_2]$ (eq. 2.8) 2.**55**; the identity of this compound is also confirmed by the unit cell measurements of a single crystal.[52] The yield of this compound can be increased by using more biphenol. Although at first look its formation appears serendipitous, replacement of an amino group from a phosphine with an alkoxy/ aryloxy group is an established procedure.[53]



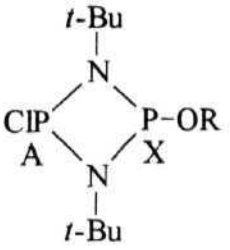
2.**1**



2.**55**
[δ (P): 143.5]

2.23 *Unsymmetrically substituted cyclodiphosphazanes*

The monosubstituted derivatives [ClPN(*t*-Bu)-P(OR)N(*t*-Bu)] can be useful precursors for further reactions because of the presence of only one replaceable chlorine which can avoid complications. We have utilized 2,6-dimethylphenol, 2-naphthol and 1-anthracenemethanol for these reactions. Although pure products could not be obtained, the partially substituted derivatives 2.**56**-2.**58** are readily identified by ^{31}P NMR; the impurities include the starting material or the *bis* derivative $[(RO)PNt\text{-}Bu]_2$. In the case of 2.**56**, repeated vacuum distillation (109-111°C/ 0.5 mm) afforded a fraction containing 2.**56** upto 90% purity. The ^{31}P spectra of two samples, one containing 2.**1** as impurity



OR = 2,6-$Me_2C_6H_3O$ (2.**56**)
2-$C_{10}H_7O$ (2.**57**)
1-$OCH_2C_{14}H_9$ (2.**58**)

and the other containing 2.**38** as impurity are shown in Fig 2.3. The ^2J(P-N-P) value of 45.6 Hz is close to that for [ClPN(*t*-Bu)$_2$P(O *t*-Bu)] (^2J = 49.3 Hz).[25]

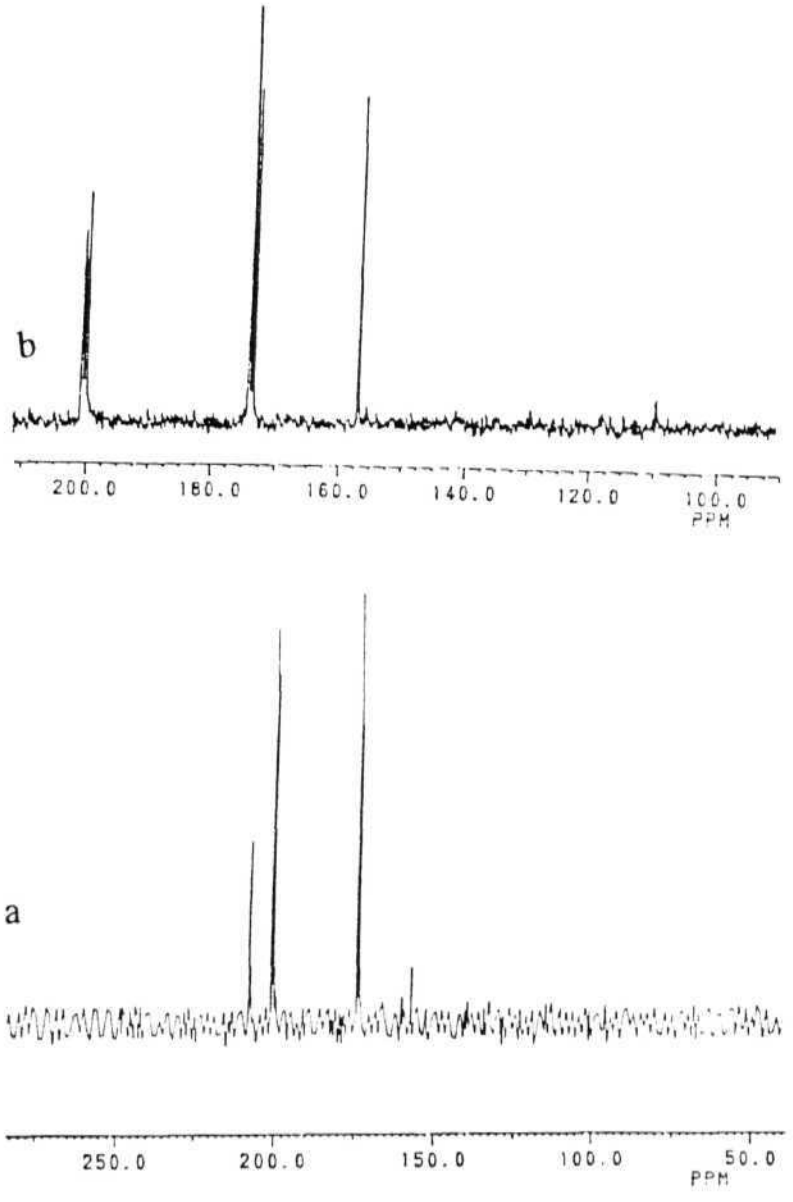
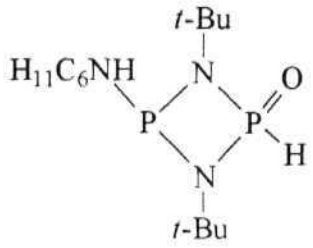


Fig 2.3 ^{31}P NMR spectra of 2.**56** a) containing 2.**1** as impurity b) containing 2.**38** as impurity.

Compounds 2.**56**-2.**58** were unstable in $CDCl_3$ solutions in our hands; over a period of 2-3 days complete decomposition had occurred [^{31}P NMR evidence]. Suspecting that the residual chlorine was the problem, we attempted to replace it with a cyclohexylamino group by treating 2.**56** with excess of cyclohexylamine. However the compound that could be isolated was 2.**59** (X-ray) in which the phenoxy group was absent. Although ^{31}P NMR showed a broad resonance, ^{1}H NMR showed the presence of a P(O)H group [δ(H): 7.35, $^{1}J(\underline{P}\text{-}\underline{H})$ = 580 Hz]. Difficulties in isolating mixed derivatives have been alluded to by Krishnamurthy and coworkers before;[4] formation of compounds similar to 2.**59** has also been noted before by Keat and coworkers in the reaction of morpholine with 2.**1**.[29]



2.**59** (X-ray)

The above reaction shows that the instability of the mixed chloro derivatives 2.**56**-2.**58** is associated with hydrolysis at both the chlorine and aryloxy/ alkoxy ends. In view of this problem we did not proceed further in studying the reaction of 2.**56** and 2.**57**.

2.24 *Oxidative addition reactions*

Reaction of 2.**47** with 3/8 mole equivalents of sulfur in toluene at 80°C for 12 h gives the mono substituted derivative 2.**60** in *ca* 23% yield; the ^{31}P NMR of this compound [Fig 2.4(a)] shows two closely spaced doublets at 104.7 [P(III)] and 48.4 [P(V)] ppm [$^{2}J(PNP) \approx 16.0$ Hz]. The ^{1}H NMR [Fig 2.4(b)] spectrum shows mainly the mono substituted product with the *t*-butyl and methyl groups connected to the aromatic residue showing two resonances each. What is significant in this result is that under

analogous conditions selenium reacted with 2.**47** to give the *bis* seleno derivative 2.**61**. Thus it appears that in these addition reactions selenium is more reactive than sulfur.

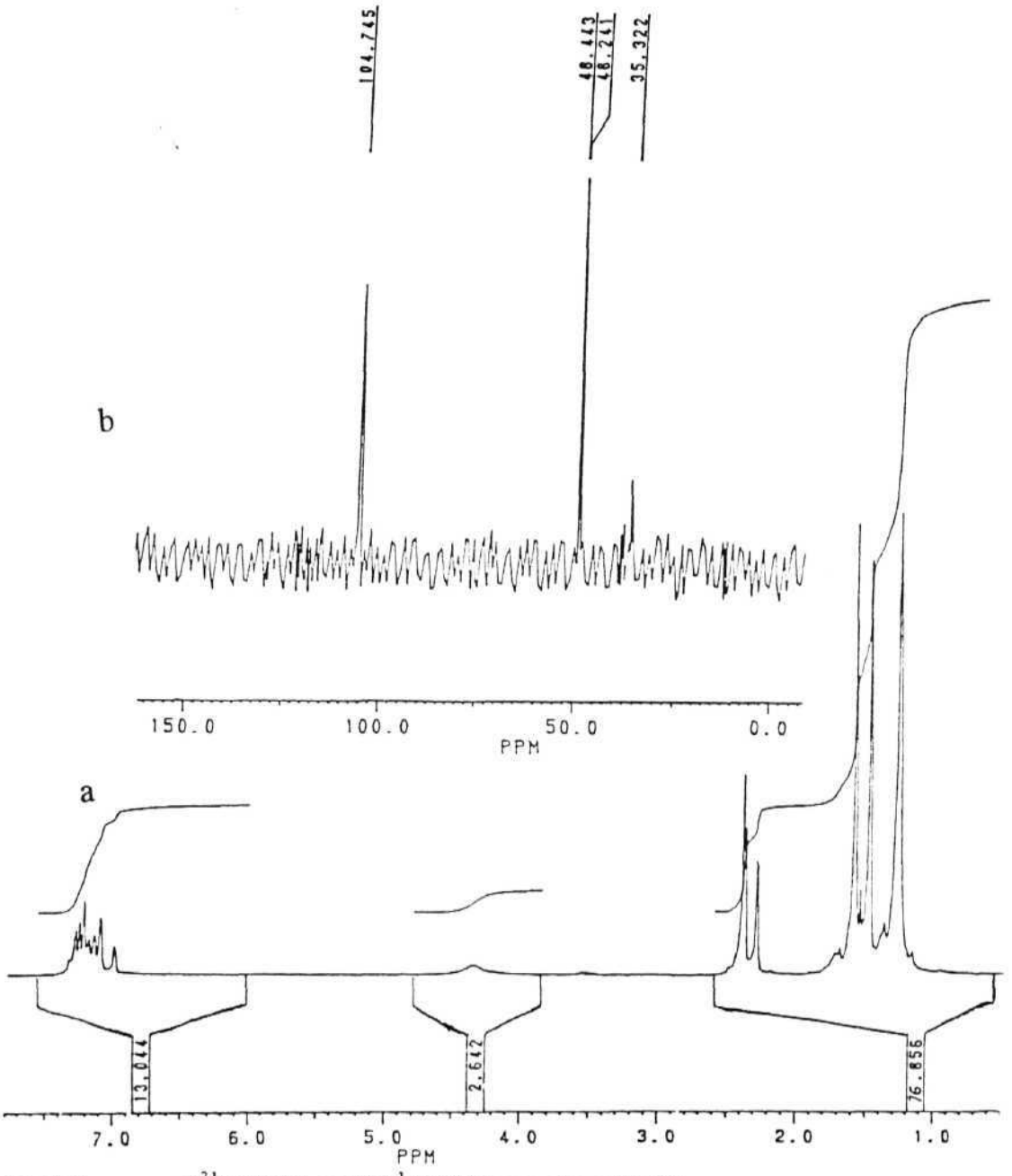
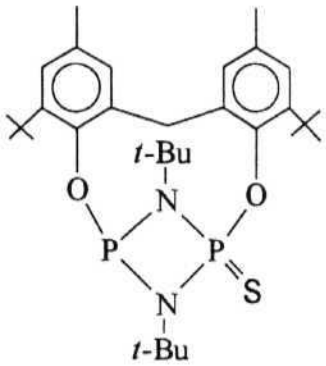
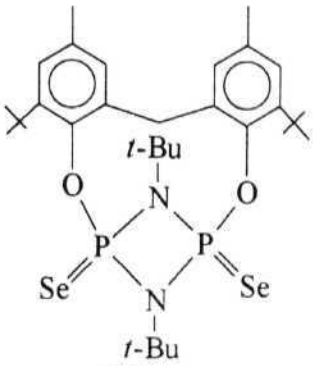


Fig 2.4 a)^{31}P NMR and b) ^{1}H NMR spectra of 2.**60**.

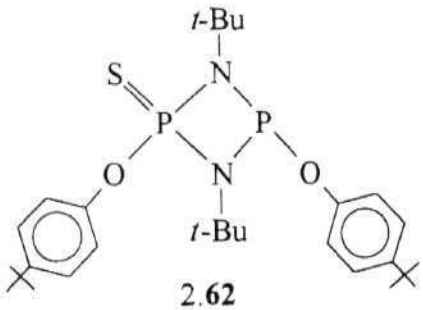


2.**60**

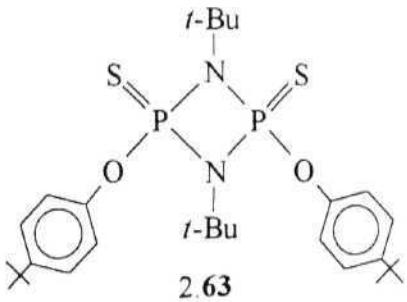


2.**61** [δ(P): 21.7; X-ray]

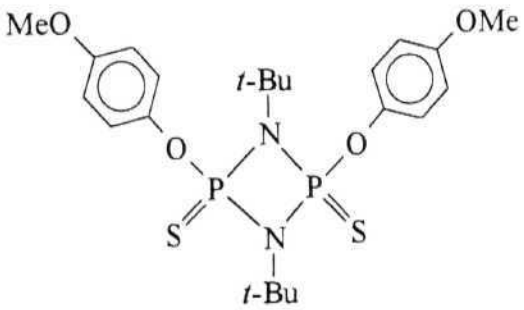
We also reacted the *bis*-aryloxy derivatives 2.**41** and 2.**42** with sulfur under similar conditions. Whereas the reaction mixture on using 2.**42** gave a mixture of both the mono (2.**62**) and bis (2.**63**) derivatives in a ratio of *ca* 2:1 as shown by ^{31}P NMR [Fig 2.5(a)] the reaction mixture using 2.**41** gave mainly the bis derivative [(4-MeO-C_6H_4O)P(S)(N-*t*-Bu)]$_2$ [2.**64**, δ(P): 45.6] is the major product [Fig 2.5(b)]. This difference is probably due



2.**62**



2.**63**



2.**64**

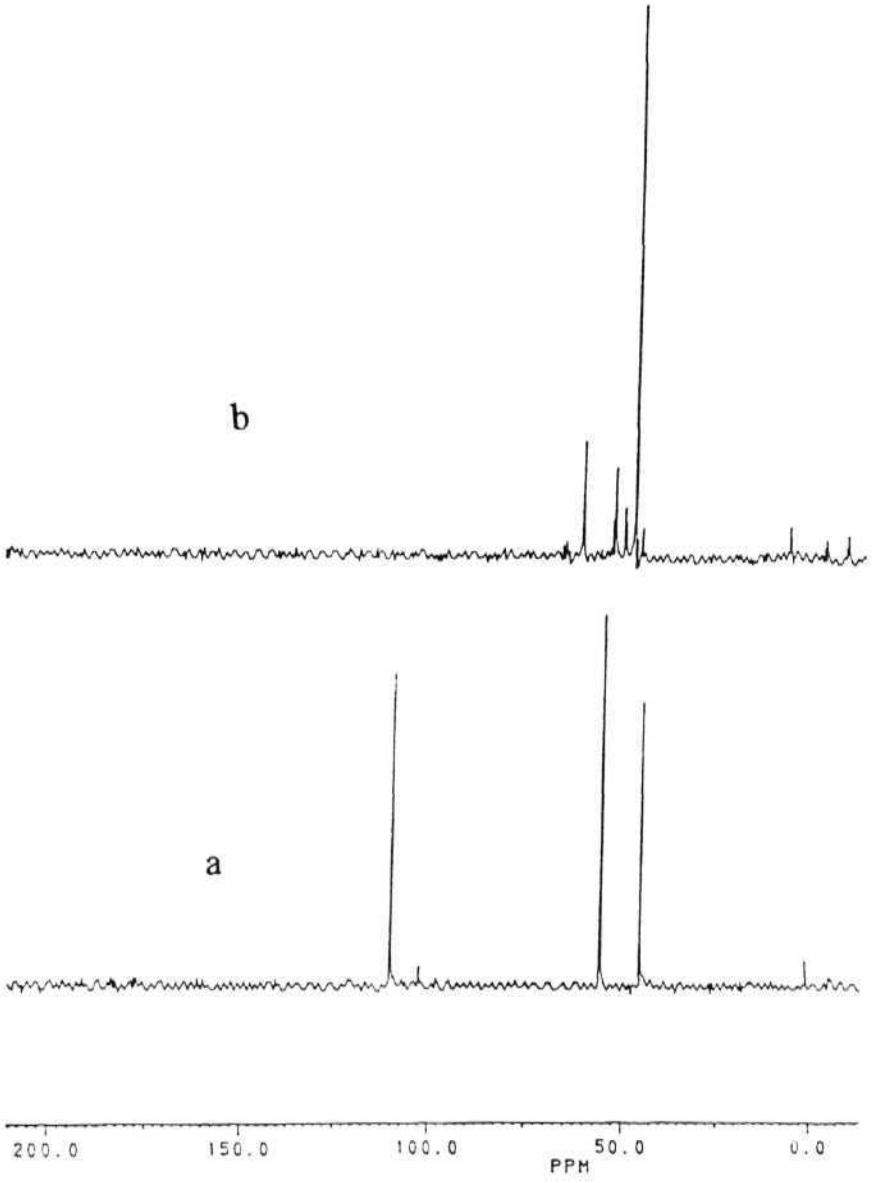


Fig 2.5 a) ^{31}P NMR spectrum of both mono (2.**62**) and bis (2.**63**) derivatives in a ratio of 2:1. b) ^{31}P NMR spectrum of 2.**64**.

to an electronic effect [Caution:Despite having used selenium inside the fume hood and worn gloves the author had swelling of the hands.[54] Hence no further reactions were conducted using selenium].

For all the three compounds 2.**47**, 2.**48** and 2.**51**, the $ArC\underline{H}_2$ protons show a broad signal in the ^1H NMR suggesting that the 10-membered ring is nonrigid. This behaviour contrasts the cases in which the two oxygens are connected to the same phosphorus as in the spirocyclic phosphazene 1.**99** discussed in Part 1; in these cases we obtain sharper signals (a doublet or an AB quartet).

Finally it should be mentioned that the *bis*-aryloxy derivative 2.**38** reacts with *o*-chloroanil to give a pentacoordinated product with a δ(P) of -53.9 ppm which is consistent with the formula $[(2,6\text{-}Me_2C_6H_3O)(1,2\text{-}O_2C_6Cl_4)PN\text{-}t\text{-}Bu]_2$ (2.**64**). This result contrasts those obtained with 2.**32** alluded to in the introduction, wherein mainly tetracoordinated phosphorus products were obtained.

2.25 *X-ray structural studies*

Single crystal X-ray analyses have been performed for compounds 2.**38**, 2.**47**.$1/2C_6H_6$, 2.**59** and 2.**61**.

An ORTEP drawing of a molecule of 2.**38** is shown in Fig. 2.6, selected structural parameters are given in Table 2.5. The methyl carbons of the *t*-butyl group at N(2) are disordered, but in Fig 2.6 only one of the possible orientations is shown. This compound to our knowledge represents the second bis-*cis*-aryloxy diazadiphosphetidine to be structurally characterized.[50] Earlier, only the structures of *trans*-$[PhNP(OR)]_2$ (OR = OMe[28], OCH_2CF_3[31], O-4-Me-C_6H_4[55]) were known.

The P-N distances to a particular phosphorus atom in 2.**38** are unequal; the longer P-N bond to one P atom is associated with the shorter bond to the second. Although such a feature is also seen in *trans*-$[PhNP(O\text{-}4\text{-}MeC_6H_4]_2$[55], it is more pronounced in 2.**38**. However all the P-N distances are in the normal range (1.71-1.73Å) found for analogous compounds (see also Table 2.4).[50] The P-O distances in 2.**38** (mean: 1.664Å) lie in

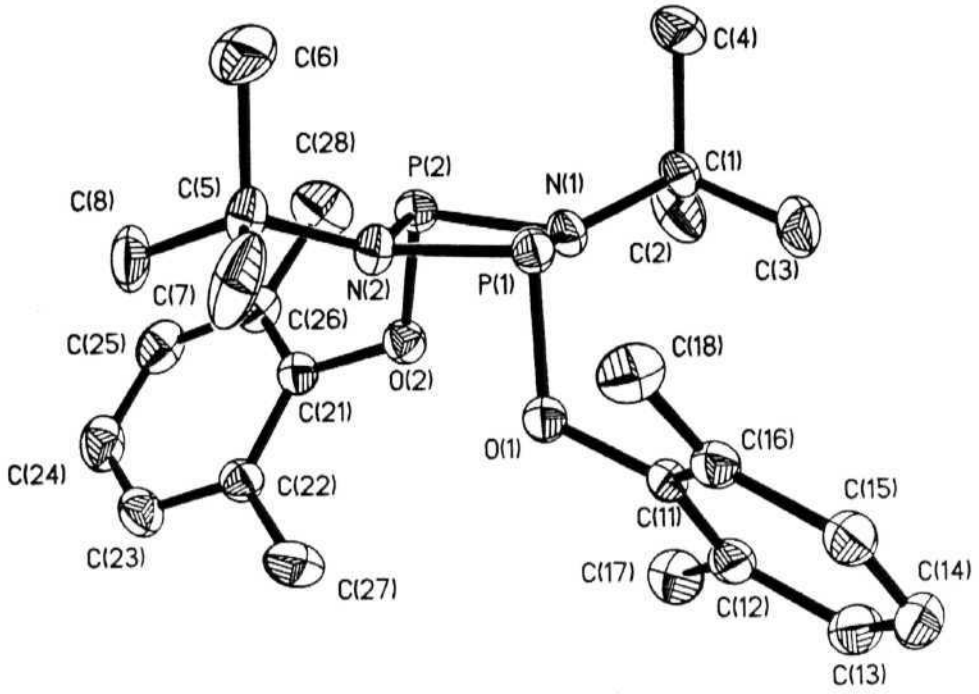


Fig 2.6 Molecular structure of 2.**38**; only non-hydrogen atoms are shown for clarity.

between those of $[PhNP(O\text{-}4\text{-}MeC_6H_4]_2$ (mean: 1.637Å) and *cis*-$[C_6F_5OPNt\text{-}Bu]_2$ (mean 1.685 Å); only slight puckering of the diphosphazane ring as in the case of *cis*-$[C_6F_5OPNt\text{-}Bu]_2$ is observed.[50] The atoms P(1) and P(2) deviate from the mean plane containing the four atoms [P(1), P(2), N(1), N(2)] in the same direction to an extent of 0.05Å - 0.06Å respectively, whereas N(1) and N(2) deviate in the other direction by -0.06 and -0.05Å respectively. The planes of the two aromatic rings are (nearly) mutually perpendicular to each other (dihedral angle 88°).

In contrast to the *trans*-$[PhNP(OR)]_2$ where the ring nitrogens are virtually planar (sum of bond angles = 360°), in 2.**38** these are clearly *nonplanar* with the sum of bond angles at N(1) and N(2) being 349.6 and 352.3° respectively. However such a feature is also observed for *cis*-$[(C_5H_{10}N)PN\text{-}t\text{-}Bu]_2$ (sum = 346.3°).[24]

Table 2.5 Selected bond lengths [Å] and angles [°] for 2.**38** with esd's in parentheses

P (1) - O (1)	1.6644 (14)	P (1) - N (2)	1.700 (2)
P (1) - N (1)	1.718 (2)	P (1) - P (2)	2.5635 (7)
P (2) - O (2)	1.664 (2)	P (2) - N (1)	1.704 (2)
P(2) - N (2)	1.716 (2)	O (1) - C (11)	1.399 (2)
O (2) - C (21)	1.396 (2)	N (1) - C (1)	1.493 (2)
N (2) - C (5)	1.485 (3)		

O (1) - P (1) -N (2)	97.92 (8)	O (1) - P (1) - N (1)	105.55 (8)
N (2) - P (1) - N (1)	82.39 (8)	O (2) - P (2) - N (2)	105.81 (8)
O (2) - P (2) - N (1)	97.94 (8)	C (21) - O (2) - P (2)	121.39 (13)
N (1) - P (2) - N (2)	82.33 (8)	C (1) - N (1) - P (1)	125.70 (14)
C (11) - O (1) - P (1)	120.68 (11)	C (5) - N (2) - P (1)	126.77 (14)
C (1) - N (1) - P (2)	126.87 (14)	P (1) - N (2) - P (2)	97.28 (8)
P (2) - N (1) -P (1)	97.05 (8)	N (1) - C (1) - C (4)	110.6 (2)
C (5) - N (2) - P (2)	128.21 (14)		

In the structure of 2.**47**·1/2C_6H_6, [Fig 2.7; Table 2.6 for structural parameters] the compound crystallizes in the space group $P\bar{1}$ with the unit cell having one molecule of benzene in addition to two molecules of the cyclodiphosphazane. In contrast to [PhNP(-O $(CH_2)_3$O-)]^{4}, the N_2P_2 ring is severely puckered in 2.**47**·1/2.C_6H_6. The two phosphorus atoms P(2) and P(4) are above the mean plane of the N_2P_2 ring by 0.13 and 0.09Å respectively while the nitrogen atoms N(1) and N(3) are below the plane by 0.16 and 0.02 Å respectively. All the four P-N distances are close (1.710Å) in this compound but the two P-O distances vary more (by > 0.03Å). Interestingly, these P-O distances are much longer than those found in the phosphazene derivatives N_4P_4\{[O-4,6-(*t*-Bu)$_2C_6H_2$]$_2CH_2$\}Cl_6 (mean: 1.567Å) and $Cl_2P(O)N=P$[\{O-4-Me-6-*t*-Bu-C_6H_2\}$_2CH_2$] (mean: 1.559Å) which contain analogous aromatic residues on the two oxygens [see

section **1.23**]. Both the ring nitrogens in 2.**47** are significantly nonplanar as shown by the sum of the bond angles [351.4° at N(1) and 346.9° at N(3)].

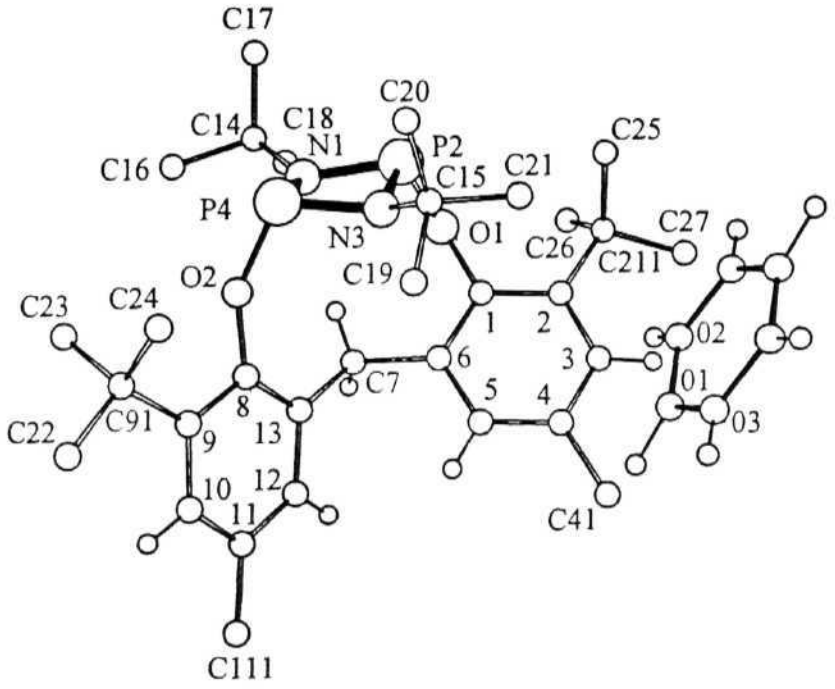


Fig 2.7 Molecular structure of 2.**47**·1/2C_6H_6; only non-hydrogen atoms are shown for clarity.

Table 2.6 Selected bond lengths [Å] and angles [°] for 2.**47**·1/2 C_6H_6 with esd's in parentheses

P (2) - O (1)	1.664 (2)	P (2) - N (1)	1.706 (2)
P (2) - N (3)	1.715 (2)	P (4) - O (2)	1.631 (2)
P (4) - N (1)	1.710 (2)	P (4) - N (3)	1.717 (2)
O (1) - O (1)	1.400 (3)	O (2) - C (8)	1.390 (2)
N (1) - C (14)	1.483 (4)	N (3) - C (15)	1.496 (4)
C (1) - C (6)	1.393 (3)	C (6) - C (7)	1.522 (4)
C (7) - C (13)	1.504 (3)	C (8) - C (13)	1.381 (3)

contd..

Table 2.6 contd..

O (1) - P (2) - N (1)	105.19 (9)	O (1) - P (2) - N (3)	107.69 (9)
N (1) - P (2) - N (3)	81.5 (1)	O (2) - P (4) - N (1)	107.81 (9)
O (2) - P (4) - N (3)	109.19 (9)	N (1) - P (4) - N (3)	81.3 (1)
P (2) - O (1) - C (1)	125.4 (2)	P (4) - O (2) - C (8)	150.2 (2)
P (2) - N (1) - P (4)	97.3 (1)	P (2) - N (1) - C (14)	126.7 (1)
P (4) - N (1) - C (14)	127.4 (1)	P (2) - N (3) - P (4)	96.7 (1)
P (2) - N (3) - C (15)	126.9 (2)	P (4) - N (3) - C (15)	123.3 (2)
O (1) - C (1) - C (6)	118.6 (2)	C (1) - C (6) - C (7)	119.4 (2)
C (6) - C (7) - C (13)	118.1 (2)	O (2) - C (8) - C (13)	121.8 (2)
C (7) - C (13) - C (8)	123.1 (2)		

In the structure of 2.**48**, each molecule is an enantiomer and the unit cell contains two molecules as shown in Fig 2.8; selected bond lengths and bond angles are given in Table 2.7. The P-N and P-O distances are in the same range as in 2.**47**·1/2C_6H_6. Of the two enantiomers, the first one [shown in Fig 2.8] has a perfectly planar N_2P_2 ring whereas the second one is slightly nonplanar (deviation from the plane ~ 0.07-0.08Å), the deviation from planarity being much less pronounced than that found in 2.**47**·1/2C_6H_6. The sums of the bond angles at N(1A) and N(3A) are 359.5 and 349.4° respectively whereas those at N(1B) and N(3B) are 357.9 and 347.2° respectively; these data show that one of the nitrogen atoms of the four membered ring in each enantiomer of 2.**48** [N(3A) and N(3B)] is more pyramidal than the other.

Compound 2.**59** [ORTEP in Fig 2.9, bond distances and angles in Table 2.8] represents a unique example of a molecule bearing a P(III) and a P(V) centre. Although there is appreciable disorder for the methyl carbons of both the *t*-butyl groups, the structure is well-refined. Of the two possible dispositions for the phosphoryl oxygen (*cis*

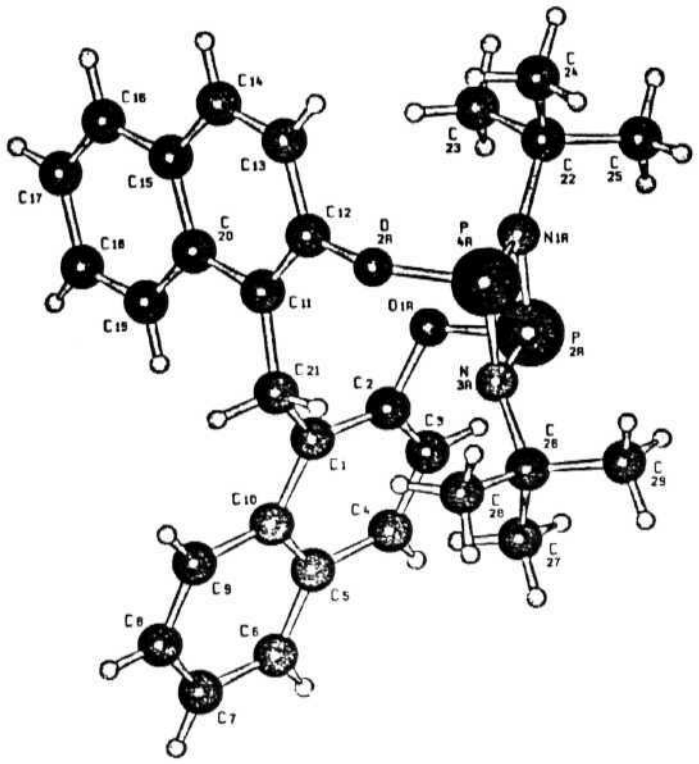


Fig. 2.8 Molecular structure of 2.**48**; only non-hydrogen atoms are shown for clarity.

Table 2.7 Selected bond lengths [Å] and angles [°] for 2.**48**·with esd's in parentheses

P (2A) - O (1A)	1.678 (6)	P (2A) - N (1A)	1.689 (7)
P (2A) - N (3A)	1.709 (7)	P (2A) - P (4A)	2.545 (3)
P (4A) - O (2A)	1.646 (7)	P (4A) - N (1A)	1.698 (7)
P (4A) - N (3A)	1.709 (7)	P (2B) - O (1B)	1.667 (6)
P (2B) - N (3B)	1.696 (7)	P (2B) - N (1B)	1.700 (7)
P (4B) - O (2B)	1.653 (7)	P (4B) - N (1B)	1.705 (7)
P (4B) - N (3B)	1.707 (7)	O (1A) - C (2)	1.400 (9)
O (2A) - C (12)	1.402 (11)	O (1B) - C (2B)	1.388 (9)
O (2B) - C (12B)	1.401 (10)	N (1A) - C (22)	1.476 (11)
N (3A) - C (26)	1.497 (11)	N (1B) - C (22B)	1.471 (12)

contd..

Table 2.7 contd..

N (3B) - C (26B)	1.512 (11)	C (1) - C (2)	1.362 (11)
C (1) - C (21)	1.508 (10)	C (11) - C (12)	1.361 (11)
C (11) - C (21)	1.502 (11)	C (1B) - C (2B)	1.359 (11)
C (1B) - C (21B)	1.531 (12)	C (11B) - C (12B)	1.382 (12)
C (11B) - C (21B)	1.497 (12)		

O (1A) - P (2A) - N (1A)	97.7 (3)	O (1A) - P (2A) - N (3A)	102.0 (3)
N (1A) - P (2A) - N (3A)	83.3 (3)	O (2A) - P (4A) - N (1A)	107.4 (4)
O (2A) - P (4A) - N (3A)	104.3 (4)	N (1A) - P (4A) - N (3A)	83.0 (3)
O (2A) - P (4A) - P (2A)	111.5 (2)	C (2) - O (1A) - P (2A)	117.6 (5)
C (12) - O (2A) - P (4A)	129.8 (5)	C (22) - N (1A) - P (2A)	129.1 (6)
C (22) - N (1A) - P (4A)	133.0 (6)	P (2A) - N (1A) - P (4A)	97.4 (4)
C (26) - N (3A) - P (4A)	125.2 (6)	P (2A) - N (3A) - P (4A)	96.3 (4)
C (22B) - N (1B) - P (2B)	128.9 (6)	C (22B) - N (1B) - P (4B)	132.7 (6)
P (2B) - N (1B) - P (4B)	96.3 (4)	C (26B) - N (3B) - P (2B)	127.6 (6)
C (26B) - N (3B) - P (4B)	123.2 (6)	P (2B) - N (3B) - P (4B)	96.4 (4)
C (2) - C (1) - C (21)	122.9 (7)	C (12) - C (11) - C (21)	122.3 (9)
C (11) - C (12) - O (2A)	123.6 (9)	C (11) - C (21) - C (1)	119.3 (7)
C (2B) - C (1B) - C (10B)	119.0 (8)	C (12B) - C (11B) - C (21B)	121.3 (9)
C (11B) - C (12B) - O (2B)	123.6 (9)	C (11B) - C (21B) - C (1B)	119.1 (7)

and *trans*) with respect to the amino group (**I**, **J**) the former is observed. The ring P-N distances in this compound (mean: 1.760Å) are quite long when compared to the previously discussed structures 2.**38**, 2.**47**·1/2C_6H_6 and 2.**48**; this distance in 2.**59** is pretty close to the accepted single P-N bond distance of 1.780(5)Å.[56] The exocyclic P-N distance, however is short and is close to that found in $(C_6H_{11}NH)P[O\text{-}(4,6\text{-}(t\text{-}Bu)_2C_6H_2)_2CH_2]$ (1.635(3)Å).[57] The P-H distance is close to the expected distance of 1.32Å.[58] The four membered N_2P_2 ring is planar to within 0.06Å with the phosphorus atoms above the mean plane and the nitrogens below.

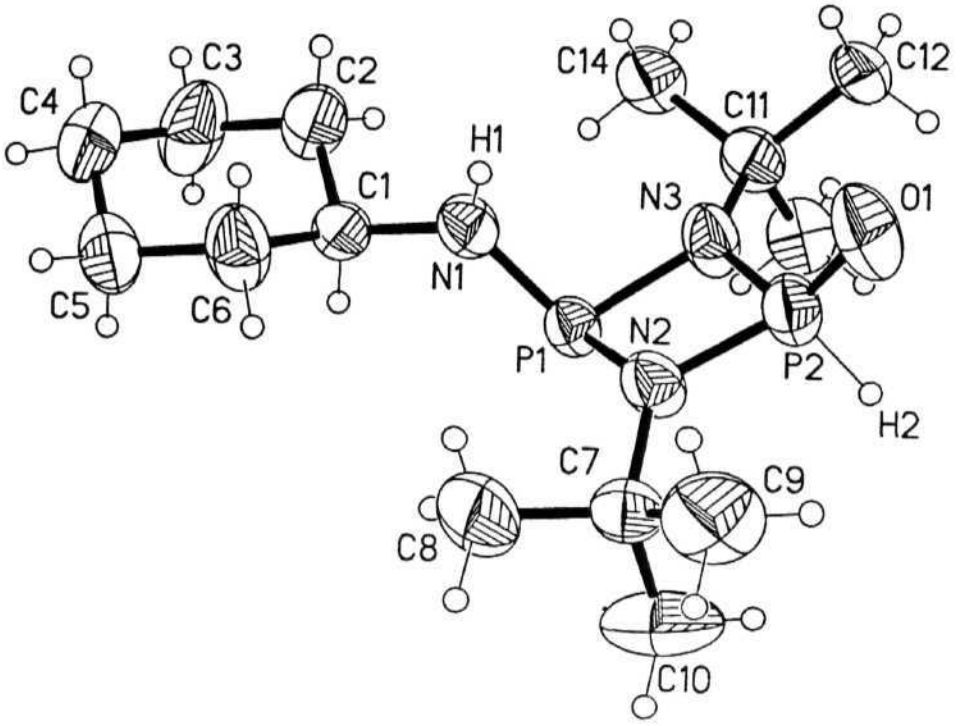
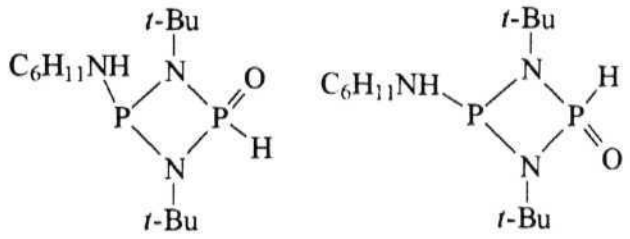


Fig 2.9 Molecular structure of 2.**59**; only non-hydrogen atoms are shown for clarity.

Table 2.8 Selected bond lengths [Å] and angles [°] for 2.**59**·with esd's in parentheses

P (1) - N (1)	1.637 (2)	P (1) - N (3)	1.752 (2)
P (1) - N (2)	1.767 (2)	P (1) - P (2)	2.5579 (7)
P (2) - O (1)	1.468 (2)	P (2) - N (3)	1.645 (2)
P (2) - N (2)	1.650 (2)	N (1) - C (1)	1.464 (2)
N (2) - C (7)	1.488 (2)	N (3) - C (11)	1.482 (2)

N (1) - P (1) - N (3)	104.51 (9)	N (1) - P (1) - N (2)	107.86 (9)
N (3) - P (1) - N (2)	79.01 (8)	N (1) - P (1) - N (2)	115.60 (7)
O (1) - P (2) - N (3)	120.85 (11)	O (1) - P (2) - N (2)	121.59 (10)
N (3) - P (2) - N (2)	85.58 (8)	C (1) - N (1) - P (1)	122.99 (14)
C (7) - N (2) - P (2)	130.07 (14)	C (7) - N (2) - P (1)	127.17 (14)
P (2) - N (2) - P (1)	96.88 (8)	C (11) - N (3) - P (2)	130.63 (14)
C (11) - N (3) - P (1)	130.1 (2)	P (2) - N (3) - P (1)	97.65 (9)



(I) (J)

Compared to 2.**47**·1/2C_6H_6, the ring P-N distances in the diselenium derivative 2.**61** [ORTEP in Fig 2.10; bond parameters in Table 2.9] are shorter by *ca* 0.03Å. The P-O distances (mean: 1.577Å) are also short and are comparable to those found in phosphazenes with a similar aromatic residue (section **1.23**). The P=Se bond distances (mean: 2.093Å) are in the same range as expected.[59] The N_2P_2 ring is nonplanar with P(1) and P(2) below the mean plane by 0.07 and 0.08Å respectively; the selenium atoms

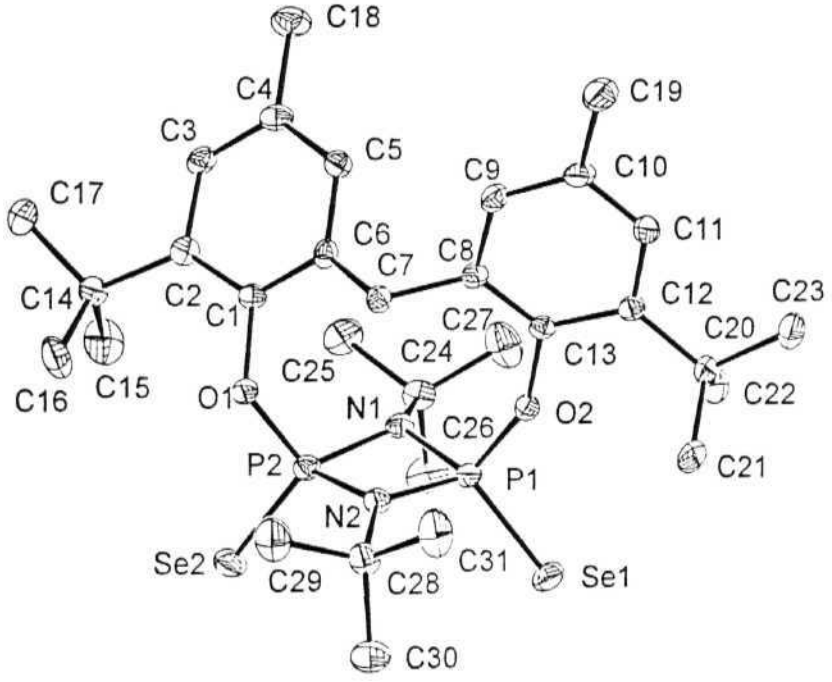


Fig 2.10 Molecular structure of 2.**61**; only non-hydrogen atoms are shown for clarity

Table 2.9 Selected bond lengths [Å] and angles [°] for **2.61** with esd's in parentheses

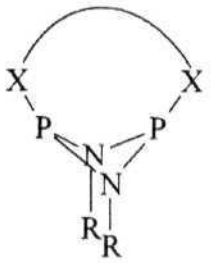
Se (1) - P (1)	2.0714 (16)	Se (2) - P (2)	2.0658 (15)
P (1) - O (2)	1.565 (4)	P (1) - N (2)	1.673 (4)
P (1) - N (1)	1.680 (4)	P (1) - P (2)	2.4861 (19)
P (2) - O (1)	1.590 (4)	P (2) - N (1)	1.680 (4)
P (2) - N (2)	1.677 (4)	O (1) - C (1)	1.432 (6)
O (2) - C (13)	1.417 (6)	N (1) - C (24)	1.520 (7)
N (2) - C (28)	1.512 (7)	C (1) - C (6)	1.391 (7)
C (6) - C (7)	1.524 (7)	C (7) - C (8)	1.505 (7)
C (8) - C (13)	1.378 (7)		

O (2) - P (1) - N (2)	112.8 (2)	O (2) - P (1) - N (1)	112.1 (2)
N (2) - P (1) - N (1)	83.6 (2)	O (2) - P (1) - Se (1)	107.80 (14)
N (2) - P (1) - Se (1)	118.19 (16)	N (1) - P (1) - Se (1)	120.91 (16)
O (1) - P (2) - N (1)	111.0 (2)	O (1) - P (2) - N (2)	109.6 (2)
N (1) - P (2) - N (2)	83.5 (2)	O (1) - P (2) - Se (2)	109.15 (14)
N (1) - P (2) - Se (2)	123.29 (16)	N (2) - P (2) - Se (2)	117.87 (16)
C (1) - O (1) - P (2)	130.1 (3)	C (13) - O (2) - P (1)	153.0 (3)
C (24) - N (1) - P (2)	130.9 (4)	C (24) - N (1) - P (1)	127.6 (4)
P (2) - N (1) - P (1)	95.4 (2)	C (28) - N (2) - P (1)	129.6 (4)
C (28) - N (2) - P (2)	132.3 (4)	P (1) - N (2) - P (2)	95.8 (2)
C (6) - C (1) - O (1)	118.6 (4)	C (1) - C (6) - C (7)	120.1 (4)
C (8) - C (7) - C (6)	118.2 (4)	C (13) - C (8) - C (7)	124.5 (4)
C (8) - C (13) - O (2)	121.6 (4)		

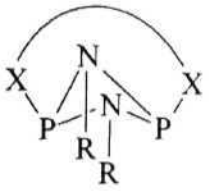
are on the same side of the mean plane as the P atoms. The two nitrogens N(1) and N(2) are above the mean plane by 0.09 and 0.05Å respectively.

As explained by Krishnamurthy and coworkers, for the *cis* disposition of substituents in cyclodiphosphazanes there are two possible conformers (**K** and **L**). In **K** the two atoms X and P are on the same side with respect to the N_2P_2 mean plane whereas in **L**

atoms X and P are on opposite sides of the mean plane.[4] It is likely that the non bonded X----X distances vary in these possibilities; a comparison is made in Table 2.10.



(K)



(L)

Table 2.10. Nonbonded X---X and P---P distances in selected *cis*-diazadiphosphetidines.[a]

Compound	X---X(non-bonded distances)	Disposition of X and P w.r.t. N_2P_2 mean plane	Nonbonded P---P distances
2.38	3.750	opposite	2.5635(7)
2.48·1/2C_6H_6	4.32	opposite	2.564(1)
2.49	3.539(2)(A)	opposite	2.546(A)
	3.576(4)(B)	opposite	2.535(B)
2.59	4.422	opposite	2.5579(7)
2.61	4.332	opposite	2.4861(19)
$(PhNP)_2[MeN(CH_2)_2O]$[4]	3.272	same	2.64 +/- 0.01
$[(PhNP)_2[O(CH_2)_3O-]$[4]	3.863	opposite	-

[a]calculated using a hpplot programme.

From Table 2.10 it is clear that for the compounds studied in this work, conformation **L** is the favoured one; in fact conformation **K** is so far found only for $(PhNP)_2[MeN(CH_2)_2O]$.[4] It is to be noted here that the substituents R on the two

nitrogens are always on the same side. The nonbonded X---X distance is most likely determined by the bridging ring size and steric constraints. As far as P---P nonbonded distances are concerned, it is mainly a matter of planarity or the puckering of the N_2P_2 ring; geometrically in the puckered ring we can expect the P---P distance to be shorter than in the planar ring. Since it is the *cis* isomers which are most often puckered, the P---P distance in them can be expected to be shorter than in the *trans* isomers.

2.26 *CONCLUSIONS*

(i) The reaction of [ClPN-*t*-Bu]$_2$ (2.**1**) with two mole eqs. of phenols in the presence of triethylamine gives *cis*-[(ArO)PN-*t*-Bu]$_2$ as isolable products.

(ii) Treatment of [ClPN-*t*-Bu]$_2$ with aromatic diols affords the *ansa* type of derivatives (O-Ar-O)(PN-*t*-Bu)$_2$. In addition, these reactions may lead to the cleavage of the phosphazane ring.

(iii) Attempts to prepare *pure* monosubstituted derivatives [ClP(N-*t*-Bu)$_2$P(OAr)] were not successful.

(iv) Under similar experimental conditions, reactions of 2.**47** with excess of selenium gives the bis seleno derivative 2.**61** whereas with sulfur only the monosubstituted derivative 2.**60** is obtained, suggesting that sulfur is less reactive than selenium in these reactions.

2.3 *Experimental*

The general experimental techniques used are as described in Part 1 (section 1.**3**).

A) Preparation of 2-*cis*-4-dichloro-1,3-di-*t*-butyldiazadiphosphetidine, *cis*-[ClPN-*t*-Bu]$_2$ (2.1)[48]

To phosphorus trichloride (13.9 g, 0.1 mol) in diethylether (100 cm^3), *t*-butyl amine (22 g, 0.3 mol) was added dropwise at -78°C over a period of 1 h. The reaction mixture was allowed to come to room temperature, stirred overnight and filtered. The precipitate was washed with diethylether (3 X 25 cm^3) and the washings added to the filtrate. Solvent was completely removed from the filtrate and the residue distilled *in vacuo* to afford 2.**1**.

Yield: 20.4 g (81.6%).

B.p. 111°C/ 3 mm (lit:[48] 110°C/ 3 mm.).

M.p. 40-42°C (lit:[48] 42-44°C).

^{31}P NMR: 206.9.

(B) Preparation of 2-*cis*-4-dichloro-1,3-diphenyl-diazadiphosphetidine, *cis*-[ClPNPh]$_2$ (2.2)[49]

Freshly crystallized aniline hydrochloride (25 g, 193 mmol) was dissolved in a refluxing solution of phosphorus trichloride (75 g, 546 mmol) in *sym*-tetrachloroethane (50 cm^3) during 24 h. The solution was filtered hot through a frit and evaporated to dryness *in vacuo* at *ca* 110°C; the white residue was extracted with hot benzene and slowly cooled to 20°C to yield 2.**2**.

Yield: 14 g (48%).

M.p. 150°C (lit: 153-155°C).[49]

^{31}P NMR: 200.4.

C) Preparation of 2-*cis*-4-*bis*(aryloxy)-1,3-di-*t*-butyldiazadiphosphetidines [(ArO)PN-*t*-Bu]$_2$ [ArO = 2,6-dimethylphenoxy (2.38), 2-naphthoxy (2.39), oxinato (2.40), 4-methoxyphenoxy (2.41), 4-*t*-butylphenoxy (2.42)] and 4-methylphenoxy (2.43). Typical procedure for 2.**38** is given below [Note: Analytical data for selected compounds only were taken, an X-ray structure is available for 2.**38**].

To compound 2.**1** (0.42 g, 1.7 mmol) in toluene (20 cm^3) was added a solution of 2,6-dimethylphenol (0.42 g, 3.41 mmol) and triethylamine (0.34 g, 3.41 mmol) in toluene (15 cm^3) over a period of 20 min. Stirring was continued overnight. Filtration followed by concentration (to ~ 10 cm^3) afforded 2.**38** as a crystalline material.

Yield: 0.39 g (79%).

M.p. 158°C.

^{1}H NMR: 1.25 (s, 18H, *t*-Bu-*H*), 2.50 (s, 12H, C*H*$_3$), 6.80-7.10 (m, 6H, Ar-*H*).

^{31}P NMR: 156.3.

Found: C, 64.55; H, 8.13; N, 6.27. $C_{24}H_{36}O_2N_2P_2$ requires C, 64.32 H, 7.95 N, 6.14 %.

The same compound was obtained in the reaction of 2.**1** with two mole equivalents of NaO-2,6-$Me_2C_6H_3$ [^{31}P NMR]; but reaction of 2.**1** with LiO-2,6-$Me_2C_6H_3$ [prepared from *n*-BuLi and 2,6-dimethylphenol] in THF led to a product mixture having a ^{31}P NMR peak at 214.8 ppm (*ca* 75%.) assigned to the *trans*-[(2,6-$Me_2C_6H_3O$)PN-*t*-Bu]$_2$. No *cis* isomer was observed.

Reaction of 2.**2** with two mole equivalents of 2,6-dimethylphenol/ Et_3N afforded a solid that showed two peaks in the ^{31}P NMR at δ 153.3 (*ca* 60%) and 222.2 (15%) ppm along with some hydrolyzed products [δ(P): -3.0 to +2.5ppm] (*ca* 25%). No pure product could be isolated.

Compounds 2.**39**-2.**43** have been prepared similarly using Et_3N as a base.

Compound 2.**39**: Quantities used: 2.**1** (3.45 g, 13.9 mmol), 2-naphthol (4.09 g, 28 mmol), Et_3N (2.82 g, 28 mmol).

Yield: 3.89 g (87.6%).

M.p. 162°C.

^1H NMR: 1.44 (s, 18H, *t*-Bu-*H*), 7.10-7.90 (m, 14H, Ar-*H*).

^{13}C NMR: 31.5 (t, J = 6Hz, CH_3), 50.8 (m, CMe_3), 116.2, 121.9, 124.4, 125.4, 126.2, 127.2, 127.7, 128.3, 129.0, 130.2, 134.3, 151.5.

^{31}P NMR: 142.2.

Found: C, 68.56; H, 6.58; N; 5.70. $C_{28}H_{32}N_2O_2P_2$ requires C, 68.32; H, 6.43; N, 5.35%.

Compound 2.**40**: Quantities used: 2.**1** (2.25 g 10 mmol), 8-hydroxyquinoline (3.00 g, 20 mmol) and Et_3N (2.00 g, 20 mmol).

Oily liquid; solid could not be obtained. A minor impurity (*ca* 6%) of a hydrolyzed product (^{31}P NMR: -4.2 ppm) was present and could not be removed; hence elemental analysis was not obtained.

Yield : 2.97g (90%).

^1H NMR: 1.45 (s, 9H, *t*-Bu-*H*), 1.47 (s, 9H, *t*-Bu-*H*), 7.32-8.94 (m, 12H, Ar-*H*).

^{13}C NMR: 31.4, 31.5, 50.8 (m), 120.1, 121.2, 122.2, 126.6, 129.6, 135.7, 136.0, 148.9.

^{31}P NMR: 141.9.

Compound 2.**41**: Quantities used: 2.**1** (0.99 g, 4 mmol), 4-methoxyphenol (0.99g, 8 mmol) and Et_3N (0.81 g, 8 mmol).

Yield: 1.47 g (87%).

M.p. 110-112°C.

^1H NMR: 1.40 (s, 18H, *t*-Bu-*H*), 3.80 (s, 6H, OCH_3), 6.80-7.10 (m, 8H, Ar-*H*).

^{31}P NMR: 142.2. The reaction mixture showed ~ 3% of a peak at 231 ppm (probably the *trans* isomer) was seen.

Found: C, 58.65; H, 7.16; N, 6.72. $C_{22}H_{32}N_2O_4P_2$ requires C, 58.15; H, 7.25; N, 6.18%.

Compound 2.**42**: Quantities used: 2.**1** (0.53 g; 2.15 mmol), 4-*t*-butylphenol (0.64 g, 4.3 mmol) and Et_3N (0.44 g, 4.3 mmol)

Yield: 0.99 g (84%).

M.p . 150°C.

^{1}H NMR: 1.30 (s, 18H, *t*-Bu-*H*), 1,40 (s,18H, *t*-Bu-*H*), 6.90-7.20 (m, 8H, Ar-*H*)

^{31}P NMR: 142.5.

Found: C, 66.91; H, 8.82; N, 5.57. $C_{28}H_{44}N_2O_2P_2$ requires C, 66.68; H, 8.27, N; 5.40%.

Compound 2.**43**: Quantities used: 2.**1** (0.39 g, 1.58 mmol), 4-methylphenol (0.34g, 3.15 mmol) and Et_3N (0.32 g, 3.15 mmol).

Yield: 0.49 g (80%).

M.p. gummy.

^{1}H NMR: 1.40 (s, 18H, *t*-Bu-*H*), 2.39 (s, 6H, C*H*$_3$), 7.05-7.20 (m, 8H, Ar-*H*).

^{31}P NMR: 142.9.

Reaction of 2.**1** with two mole equivalents of the LiO-4-*t*-Bu-C_6H_4 led to a mixture. ^{31}P NMR: 232.1 (*ca* 15%, assigned to *trans*-[(4-*t*-Bu-C_6H_4O)PN-*t*-Bu)$_2$, 142.4 [*cis* isomer, 2.**42**] and 136.7 (unassigned).

D) Preparation of 2-*cis*-4-*bis*-(1-anthryloxy)-1,3-di-*t*-butyl-diazadiphosphetidine [(1-$C_{14}H_9O$)PN-*t*-Bu]$_2$ (2.**45**)

A solution of 2.**1** (0.43 g, 1.74 mmol) in THF (10 cm^3) was added slowly to a stirred solution of sodium anthryloxide [prepared by using NaH (0.088 g, 3.67 mmol) and

anthrone (0.68 g, 3.49 mmol)] in THF (25 cm^3) at room temperature. The mixture was heated at reflux for 24 h and then cooled to room temperature. Filtration followed by removal of the solvent from the filtrate afforded a solid product (2.**45**) which was purified by crystallization from benzene (10 cm^3).

Yield: 0.49 g (76%).

M.p. 220°C (dec).

^{1}H NMR: 1.30 (s, 18H, *t*-Bu-*H*), 7.20-8.40 (m, 18H, Ar-*H*).

^{13}C NMR: 31.4, 52.0, 124.9, 124.9, 125.4, 125.7, 127.3, 128.3, 129.1, 134.1.

^{31}P NMR: 166.8.

Found: C, 66.91; H, 8.82; N, 5.57. $C_{28}H_{44}N_2O_2P_2$ requires C, 66.45 H, 7.92 N, 4.97%.

E) Attempted preparation of [(RO)PN-*t*-Bu]$_2$ [RO = 9-anthracenemethoxy (2.46) and 1-naphthalenemethoxy]

A solution of 2.**1** (1-2 mmol) in toluene (10 cm^3) was added slowly at room temperature to a stirred solution of two mole equivalents each of alcohol and Et_3N in toluene (25 cm^3). The reaction mixture was stirred overnight, filtered and the filtrate concentrated to afford an oil (with naphthalenemethanol) or a solid (with 9-anthracene methanol).

a) Reaction with anthracenemethanol:

Quantities used:

Solid (crystalline), m. p. 214°C.

^{1}H NMR: (1.30, major peak, ~18H, *t*-Bu-*H*), 5.80 (d, ^{2}J = 10Hz, 1H, OCH_2(A)), 6.40 (d, ^{2}J = 10Hz, 1H, OCH_2(B)), 7.00 - 8.60 (m, ~18H, Ar-*H*)

^{31}P NMR: 135.2 (35%), 84.1 (35%), 4.6 (30% hydrolyzed); the peak at 135.2 is assigned to *cis*-[ROPN-*t*-Bu]$_2$ (2.**46**).

Found: C, 69.92; H, 6.08; N, 4.05. $C_{38}H_{40}O_2P_2N_2$ requires C, 73.76; H, 6.50; N, 4.52%. The lower values indicate partial hydrolysis.

b) Reaction with naphthlenemethanol:

Quantities used:

Oil. ^{31}P NMR (major peaks): 135.0 (35%), 84.4 (15%), 1.7 (35%, hydrolyzed), -8.9 (10%, hydrolyzed). Hydrolysis was also apparent from ^{1}H NMR which showed a doublet at 7.7 ppm ($^{1}J(P-H)$ = 600 Hz). The peak at 135.0 may be assigned to *cis* [ROPN-*t*-Bu]$_2$.

F) Synthesis of the bicyclic derivatives a) {[(*t*-BuN)P]$_2$[O-6-*t*-Bu-4-Me-C$_6$H$_2$]$_2$CH$_2$} (2.47), b) {[(*t*-BuN)P]$_2$[2-O-1-C$_{10}$H$_6$]$_2$CH$_2$} (2.48) and c) {[(*t*-BuN)P]$_2$[2-OCH$_2$C$_6$H$_4$]$_2$} (2.49)

a) A solution of 2.1 (0.672 g, 2.72 mmol) in toluene (10 cm^3) was added dropwise with stirring to a mixture of 2,2'-methylenebis(6-*t*-butyl-4-methylphenol) (0.92 g, 2.92 mmol) and triethyl amine (0.55 g, 5.44 mmol) in toluene (10 cm^3) at 0°C during 10 min. The stirring was continued overnight. Filtration, removal of solvent and crystallization of the residue from benzene (*ca* 10 cm^3) gave 2.47 [**caution**: benzene is a carcinogen. All operations involving this solvent must be conducted inside the hood].

Yield: 0.97 g (86%).

M.p. 188°C.

^{1}H NMR: 1.11 (s, 18H, *t*-Bu-*H*), 1.48 (s, 18H, *t*-Bu-*H*), 2.34 (s, 6H, C*H*$_3$), 4.30 (br, 2H, C*H*$_2$), 7.04-7.38 (m, 4H, Ar-*H*).

^{13}C NMR: 21.3, 31.0, 31.2, 32.0, 35.0, 52.0, 125.8, 128.3, 128.8, 131.3, 133.4, 141.3.

^{31}P NMR: 143.9.

Found: C, 68.61; H, 8.91; N, 5.20. $C_{31}H_{48}N_2O_2P_2$ requires; C, 68.50; H, 8.85; N, 5.16%.

(b) For the synthesis of 2.**48**, bis-(2-hydroxy-1--naphthyl)methane (0.42 g, 1.4 mmol), 2.**1** (0.35 g, 1.4 mmol) and triethylamine (0.28 g, 2.8 mmol) in THF (15 cm^3 in all) were used. The crystals of 2.**48** were separated from the oily residue. The crystals were rather unstable in various solvents and hence a clear NMR spectrum could not be obtained. After two days in $CDCl_3$ solution the main peak in the ^{31}P NMR was at 5.9 ppm which is most likely a hydrolyzed product.

Yield: 0.44 g, (67%).

M.p. 194°C.

^1H NMR: 1.23 (s, 18H, *t*-Bu-*H*), 4.94 (br s, 2H, CH_2), 7.20 - 8.20 (m, 12H, *Ar-H*).

Residual peaks of variable intensity at 1.40 ppm (*t*-Bu-*H*), 3.00 and 3.82 (probably THF) were found.

^{31}P NMR: 181.4.

(c) For the synthesis of 2.**49**, 2.**1** (0.8 g, 3.7 mmol), 2,2'-biphenyldimethanol (0.69 g, 3.2 mmol) and triethylamine (0.65 g, 6.4 mmol) were used in a procedure similar to that for 2.**47**.

Yield: 0.98 g, (78%).

M.p. 165°C.

^1H NMR: 1.08 (s, 18H, *t*-Bu-*H*), 4.49 (d, J = 18.0Hz, 2H, CH_2(A)), 4.67 (d, J = 18.0Hz, 2H, CH_2(B)), 7.10-7.30(m, 8H, Ar-*H*).

^{31}P NMR: 125.7.

Found:. C, 63.35; H, 7.30; N, 6.78. $C_{22}H_{30}N_2O_2P_2$ requires; C, 63.43; H, 7.25; N, 6.75%.

(G) Reaction of 2.1 with other diols

These did not yield sufficiently pure products; however the bicyclic P(III) products were identified by ^{31}P NMR. These results are summarized below.

Diol	Product	δ(P)	Other peaks in ^{31}P NMR
1,4-butanediol	**2.50**[a]	131.2	-8.6, 5.1, 81.4 (total intensity ~20%)
2,2'-methylenebis-(4-chlorophenol)	**2.51**	162.1	188.4 (*ca* 30%)
2,2-dimethylpropane-1,3-diol	**2.52**	139.4	3.6 (≈ 60%)[b]
2,2'-biphenol	**2.53**	167.2	153.6, 143.5 (**2.55**)[c] (total intensity of two peaks is 20%, the rest is for **2.53**)

[a] A crystalline material, m.p. 200°C, was isolated; but it could not be separated free of oil because of solubility and hydrolysis problems.

[b] ^{1}H NMR spectrum shows hydrolysis [P(O)H at 6.85 ppm $^{1}J(P-H) \approx 620Hz$]

[c] This is the bridged compound $\{2,2'-(C_6H_4O)_2P\}_2(2,2'-OC_6H_4)_2$ (**2.55**) [X-ray evidence].[52]

H) Identification of the monoaryloxy derivatives [ClPN-*t*-Bu-P(OR)-N-*t*-Bu] [R = 2,6-Me_2-C_6H_3O (2.56), 2-$C_{10}H_7O$ (naphthyloxy) (2.57), 1-anthracenemethoxy (2.58)]

These compounds were identified mainly by ^{31}P NMR. A typical procedure is given for (**2.56**).

A mixture of 2,6-dimethylphenol (1.43 g, 60 mmol) and triethylamine (6.13 g, 60 mmol) in toluene (50 cm^3) was added dropwise to **2.1** (16.6 g, 67.3 mmol) in toluene (250 cm^3) at 0°C over a period of 30 min. After stirring at room temperature for 12 h the

solvent was stripped off and the residue analysed by ^{31}P NMR which showed *ca* 80% of 2.**56** along with a total of 20% of 2.**1** (δ(P): 206.9 ppm) and 2.**38** (δ(P): 156.3 ppm).

^{31}P NMR data for 2.**56** to 2.**58** are given below:

a) 2.**56**: 173.2 [d, $^{2}J(\underline{P}\text{-}\underline{P})$ = 45.6 Hz, P(OAr)], 199.9 [d, $^{2}J(\underline{P}\text{-}\underline{P})$ = 45.6 Hz, P-Cl]

b) 2.**57**: 162.9 [d, $^{2}J(\underline{P}\text{-}\underline{P})$ = 46.0 Hz, P(OAr)], 190.8 [d, $^{2}J(\underline{P}\text{-}\underline{P})$ = 46.0 Hz, P-Cl]

c) 2.**58**: 135.9 [d, $^{2}J(\underline{P}\text{-}\underline{P})$ = 32.0 Hz, P(OAr)], 190.3 [d, $^{2}J(\underline{P}\text{-}\underline{P})$ = 32.0 Hz, P-Cl]

The reaction mixture containing 2.**56**, when subjected to vacuum sublimation (109-111°C/ 0.5 mm) afforded fractions rich in 2.**56** (*ca* 90%) but containing either 2.**1** or 2.**38** as impurity (*ca* 10%). This spectrum is illustrated in the Results and Discussion section [Fig: 2.3].

Compounds 2.**56**-2.**58** appeared to be very unstable in $CDCl_3$ solutions; over a period of 2 days, the original mixture containing 2.**56**-2.**58** showed almost no 2.**56**-2.**58** remaining. Even repeated and careful fractional vacuum distillation did not help.

We also attempted to prepare mixed aryloxy derivatives by heated together equimolar quantities of 2.**38** and 2.**39** at *ca* 90°C in toluene for several hours but no exchange occurred (^{31}P NMR). Treatment of one mole equivalent each of 2.**1**, 2,6-dimethylphenol and 2-naphthol in the presence of triethylamine gave only symmetrically substituted products [^{31}P NMR evidence].

I) Synthesis of the mixed derivative $(C_6H_{11}NH)P(N\text{-}t\text{-}Bu)_2P(O)H$ (2.59)

To 2-chloro-4-(2,6-dimethylphenoxy)-1,3-di-*t*-butyl-diazadiphosphetidine (2.**56**) (0.69 g, 1.92 mmol) in benzene (25 cm^3), cyclohexylamine (0.39 cm^3, 0.57 g, 5.76 mmol) in benzene (5 cm^3) was added dropwise over 10 min while stirring at room temperature. The mixture was stirred overnight and the salt formed was filtered off. The filtrate was concentrated to ≈ 10 cm^3 from which crystals of 2.**59** appeared.

Yield: 0.48 g (60%).

M.p. 156°C.

^{1}H NMR: 1.37 (s, 18H, *t*-Bu-*H*), 1.00-2.20 (m, 10H, C_6H_{11}), 2.95 (brd, 1H, ^{3}J(P-H) = 12Hz, NC*H*), 3.10 - 3.30 (br, 1H, N*H*), 7.35 (d, 1H, ^{1}J(P-H) ≈ 58.0 Hz, P*H*).

I.R: 3230 (ν (NH)), 2358 (ν (P-H)) cm^{-1}.

^{31}P NMR: -9.1 (br); (the P(III) signal was probably too broad).

(J) Reaction of {[(*t*-BuN)P]$_2$[O-6-*t*-Bu-4-Me-C$_6$H$_2$]$_2$CH$_2$} (2.47) with sulfur

To compound 2.**47** (0.3 g, 0.55 mmol) in toluene (10 cm^3), sulfur (0.056 g, 1.75 mmol) was added and the mixture heated overnight at 80°C. Upon concentration a white solid along with some unreacted sulfur precipitated out. The large yellow crystals of unreacted sulfur were removed by hand-picking.

Yield: 0.080 g [contains *ca* 95% [(*t*-BuN)P(S)(O-4-Me-6-*t*-Bu-C$_6$H$_2$)$_2$CH$_2$P] (2.**60**) and <5% of {[(*t*-BuN)P(S)]$_2$[O-4-Me-6-*t*-Bu-C$_6$H$_2$]$_2$CH$_2$}.

M. p. 206 - 208°C.

^{1}H NMR:1.26 (br s, 18H, N-*t*-Bu-*H*), 1.47 (s, 9H, C-*t*-Bu-*H*), 1.57 (s, 9H, *t*-Bu-*H*), 2.35, 2.37 (s each, 6H (in all), C*H*$_3$), 4.30 (br, 2H, ArC*H*$_2$), 7.00 - 7.40 (m, 4H, Ar-*H*).

^{31}P NMR: 104.74, 48.4, ^{2}J (P-N-P) ≈16 Hz. A minor peak (< 5%) at 35.3 was also observed.

Analytically pure sample could not be isolated.

(K) Reaction of 2.47 with selenium: Synthesis of {(*t*-BuN)P(Se)}$_2${O-6-*t*-Bu-4-Me-C$_6$H$_2$}$_2$CH$_2$} (2.61)

To a solution of the bicyclic compound 2.**47** (0.37 g, 0.68 mmol) in toluene (10 cm^3) selenium (0.107 g, 1.36 mmol) was added and the mixture refluxed for 24 h.

Filtration followed by the evaporation of the solvent from the filtrate afforded a solid. From this pure 2.**61** was isolated by crystallization from CH_2Cl_2.

Yield: 0.05g, (13%).

M.p: 260°C (dec).

^{1}H NMR: 1.30 (s, 18H, *t*-Bu-*H*), 1.52 (s, 18H, *t*-Bu-*H*), 2.40 (s, 6H, Ar-CH_3), 4.40 (br, 2H, Ar-CH_2), 7.20 (s, 4H, Ar-*H*).

^{31}P NMR: 21.7. In principle ^{77}Se (7% natural abundance) satellites should be observed. However in these compounds if the signal / noise ratio is not high, which is the case for 2.**61**, these satellites may not be observed because they will be the AB part of an ABX [X = Se; A, B are the two phosphorus atoms that are chemically but not magnetically equivalent.[60]

Found: C, 53.14; H, 6.91; N, 4.00. $C_{31}H_{48}N_2O_2P_2Se_2$ requires C, 53.05; H, 6.30; N, 3.95%.

(L) Reaction of 2.**41** and 2.**42 with sulfur**

Compounds 2.**41** and 2.**42** were heated with 7/8 mole equivalents of sulfur and the reaction mixture checked by ^{31}P NMR: (a) 2.**41** + 7/8 S_8: ^{31}P NMR: 46.2 (70%), 51.4, 59.7 (together ≈30%). Other peaks of low intensity were also seen. (b) 2.**42** + 7/8 S_8: ^{31}P NMR: 109.7 and 55.3 (d each, ^{2}J(P-N-P) ≈ 17 Hz), 45.0 (s). [^{1}H NMR: (2 sets): Set 1 (30%): 1.30 (s, 18H, N-*t*-Bu-*H*), 1.64 (s, 18H, C-*t*-Bu-*H*); Set 2 (70%): 1.33 (s, 18H, N-*t*-Bu-*H*), 1.50 (s, 18H, C-*t*-Bu-*H*); 6.90-7.60 (m, combined intensity *ca* 16 H, Ar*H*)].

(M) Reaction of 2.38 with *o*-chloroanil. Synthesis of the penta-coordinated derivative [(2,6-$Me_2C_6H_3O$)(1,2- $O_2C_6Cl_4$)P-N-*t*-Bu]$_2$ (2.**64**)

Compound 2.**38** (0.15 g, 0.35 mmol) was heated upto 150°C and *o*-chloroanil (0.16 g, 0.65 mmol) was added in small quantities (10 min). The addition was continued

till a light yellow colour persisted. The residue was extracted with toluene, and the solution concentrated to obtain 2.**64** as a gummy material.

Yield: 0.172 g, (73%).

^{1}H NMR: 1.42 (s, 9H, *t*-Bu-*H*), 2.60 (s, 6H, C*H*$_3$), 6.95-7.30 (m, 6H, Ar-*H*).

^{31}P NMR: -53.9. An impurity peak at -3.2 ppm (*ca* 5%) was also observed.

X-ray Crystallography

Data were collected on Siemens SMART CCD (2.**38** and 2.**59**), Enraf Nonius CAD4 (2.**47** $1/2C_6H_6$ and 2.**48**) and Enraf-Nonius MACH3 (2.**61**) diffractometers. All data was collected at 293K using MoKα (λ = 0.7107Å) radiation. Structure solution and refinement were done by standard techniques.[61] In 2.**38** the three carbons of the *t*-butyl group at C(6) are disordered with site occupancies of 0.621 and 0.379; only one of these positions is shown in the ORTEP drawing [Fig. 2.6]. H-atoms were fixed in 2.**38**, 2.**48** and 2.**61** by geometry using a riding model and not refined. For 2.**47**.$1/2C_6H_6$ all the H-atoms were refined isotropically. The unit cell of this molecule contains one molecule of benzene in addition to two molecules of 2.**47**. In compound 2.**48** all except H(1) and H(2) were fixed by geometry and were not refined; Atoms H(1) (connected to N(1)) and H(2) (connected to P(2)) were located by difference map and refined isotropically. Both the *t*-butyl groups in this molecule are severely disordered with three positions each for the methyl carbons at N(3) and two positions each for the methyl carbons at N(2). Further details are found in Table 2.11. Atomic coordinates are given in the Appendix.

Table 2.11 Crystal data for 2.**38**, 2.**47**.1/2C_6H_6, 2.**48**, 2.**59** and 2.**61**

Compd No	2.**38**	2.**47**.1/2C_6H_6	2.**48**	2.**59**	**2.61**
Emp. formula	$C_{24}H_{36}N_2O_2P_2$	$C_{34}H_{51}N_2O_2P_2$	$C_{29}H_{32}N_2O_2P_2$	$C_{14}H_{31}N_3OP_2$	$C_{31}H_{48}N_2O_2P_2Se_2$
F. wt. (Å)	446.49	581.73	502.51	319.36	700.57
Crystal System	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/C$	$P\bar{1}$	$P2_1$	C2/c	$P2_1/n$
a /Å	12.4190 (2)	9.764 (1)	11.387 (2)	18.6682 (3)	13.891 (2)
b /Å	10.9526 (2)	12.964 (1)	18.824 (4)	8.7440 (2)	16.502 (5)
c /Å	19.8033 (3)	14.323 (2)	13.428 (2)	24.2120 (3)	14.773 (2)
α /°	90.0	77.25 (8)	90.0	90.0	90.0
β /°	102.3010 (10)	74.15 (7)	111.18 (1)	109.248 (1)	99.27 (2)
γ /°	90.0	78.25 (6)	90.0	90.0	90.0
v	2631.73 (6)	1681.1 (8)	2683.8 (8)	3731.3 (1)	3342.0 (13)
Z	4	2	4	8	4
D calc/ gcm^{-3}	1.127	1.149	1.244	1.137	1.392
μ/ mm^{-1}	0.186	0.15	0.190	0.234	2.338
Cryst.size/ mm	0.50 x 0.40 x 0.35	0.4 x 0.5 x 0.8	0.4 x 0.3 x 0.2	0.30 x 0.25 x 0.18	0.6 x 0.5 x 0.2
Reflns.collected	15783	6280	5071	11399	5875

contd...

Table 2.11 contd...

Indep.reflns	6225 (Rint = 0.0262)	6280 (Rint = 0.0123)	4819 (Rint = 0.0475)	4537[e] (Rint = 0.0393)	5875 (Rint = 0.0000)
Data/ Parameters	6219/ 300	4892/ 565	4818/1 / 647	4537/ 162/237	5875/ 366
GooF	0.994	2.62	1.047	1.010	1.039
R1[(I>2σ (I)]	0.0517 [a,b]	0.045 [c]	0.0645 [b,d]	0.0512	0.0581 [f]
wR2 [I>2σ (I)]	0.1314	0 034	0.1222	0.1374	0.1467
Largest diff.peak and hole/ eÅ^{-3}	0.218/ -0.219	0.3/ -0.3	0.643/ -0.216	0.284/ -0.243	0.602/ -0.842

[a]Extinction coeff. 0.0008(6). [b]Refinement on F^2. [c]Refinement on F. [d]Extinction coeff. 0.0061(10); absolute structure parameter 0.2(2). [e]Absorption correction: SADABS (Sheldrick, 1996); max. and min. transmission 0.9661 and 0.5893. [f]Absorption correction: (DIFABS Statistical) [N.Walker and D.Stuart, *Acta Crystallogr.,Sect. A*. 1983, **39**, 159.]

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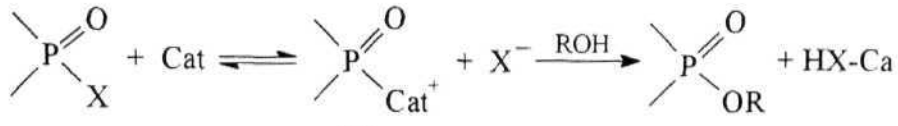
PART 3. REACTIONS OF CHLOROPHOSPHORUS(III) AND CHLOROPHOSPHORUS(V) COMPOUNDS WITH LEWIS ACIDS AND BASES

PART 3. REACTIONS OF CHLOROPHOSPHORUS(III) AND CHLOROPHOSPHORUS(V) COMPOUNDS WITH LEWIS ACIDS AND BASES

3.1 *Introduction*

Nucleophilic substitution reactions of chlorophosphates are most often carried out in the presence of a base. Since in the absence of the base this reaction will be slow, sometimes the activating base is called a nucleophilic catalyst (rather inappropriately). The mechanism of rate enhancement (nucleophilic catalysis) of the nucleophilic substitution at phosphorus is commonly interpreted by two consequtive $SN_2(P)$ reactions (Scheme 3.1).[1-3]

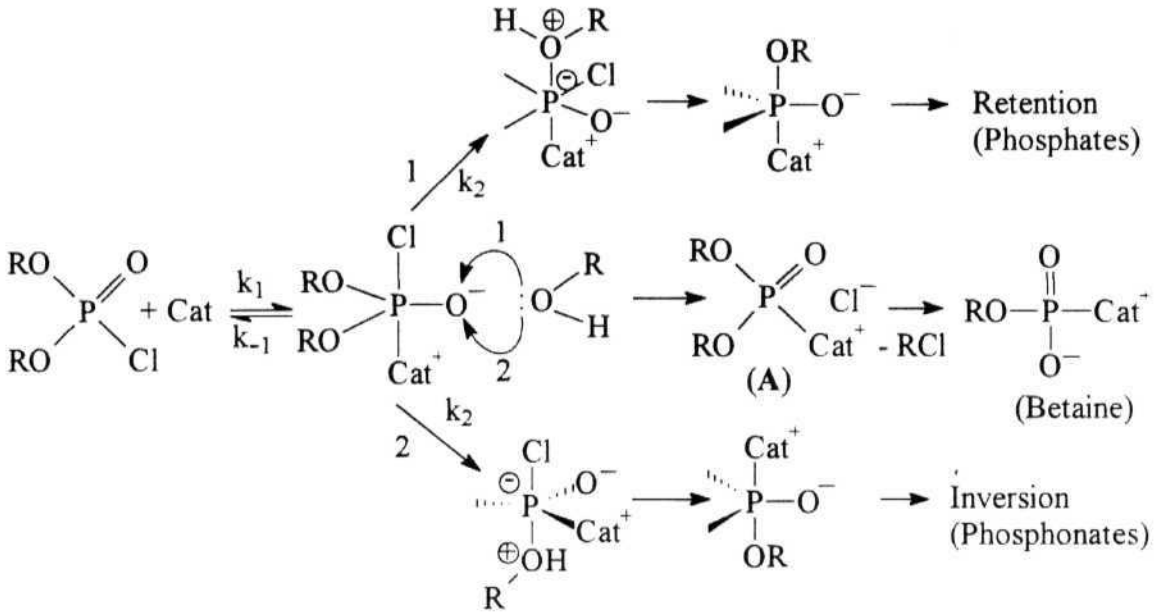
Scheme 3.1



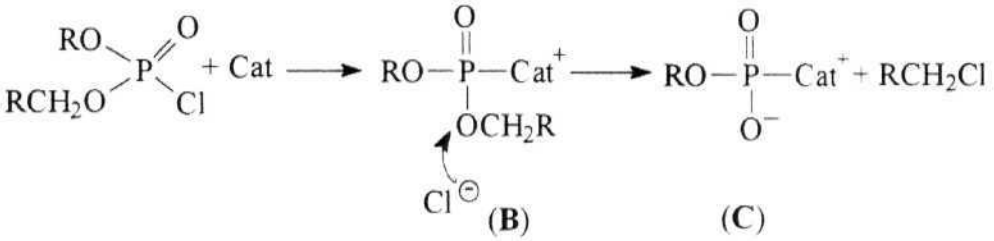
(**A**)

The leaving group X is substituted by the nucleopilic catalyst (Cat; can be imidazole, N-methyl imidazole, DBU etc) leading to a very reactive intermediate (**A**). The nucleophile then reacts with this intermediate giving the product (Scheme 3.1). The general mechanism proposed by Lanneau for the nucleophile assisted substitution is shown in Scheme 3.2.[4] Although a species of type **A** has never been detected when the mixture of alcohol and catalyst was added to the chlorophosphates, it is identified by NMR in the absence of alcohol. In the reaction of $(RO)(RCH_2O)P(O)Cl$ with the catalyst (Cat), formation of the betaines **C** is observed and is assumed to occur *via* the intermediate **B** (Scheme 3.3).[2] We have been interested in identifying/ isolating intermediates of types (**A**)- (**C**) and hence literature on such species is briefly reviewed here.

Scheme 3.2



Scheme 3.3



In the reaction of N-methylimidazole with diethylchlorophosphate, $(EtO)_2P(O)Cl$ (3.**1**) three products (3.**2**-3.**4**) are observed (Scheme 3.4). The percentage of these products varies with time and is shown below in Table 3.1.[2] Reactions such as the one shown in Scheme 3.4 may have relevance in the synthesis of biophosphate esters by the reaction of a chlorophosphate and an alcohol in the presence of a base.[5] Compounds analogous to 3.**2** have been isolated when 4-dimethylaminopyridine was allowed to react with methylphosphorodichloridate 3.**5** (Scheme 3.5);[6-8] presumably the pyridine nitrogen

displaces chlorine from the phosphorodichloridate to give the salt 3.**6** which then loses MeCl to give the betaine 3.7.[9]

Scheme 3.4

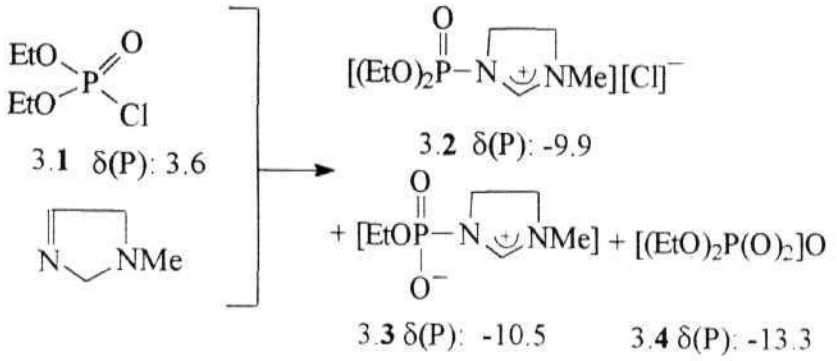
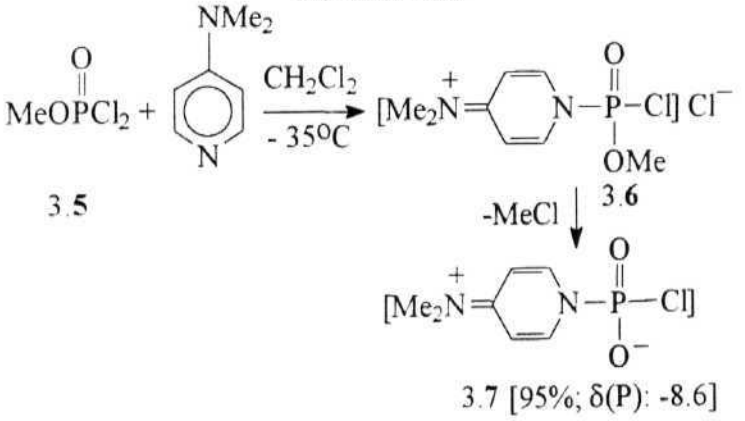


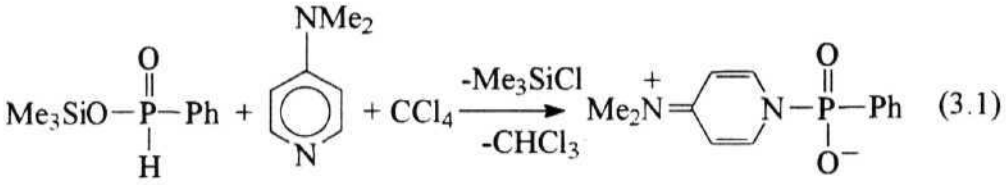
Table 3.1 Product distribution w.r.t. time in the reaction of 3.**1** with N-methylimidazole

Time	3.**1**	3.**2**	3.**3**	3.**4**
3 min	50%	28.6%	21.3%	0%
15 min	33%	12.7%	35.9%	18.4%
2 h	0%	0%	69%	31%

Scheme 3.5



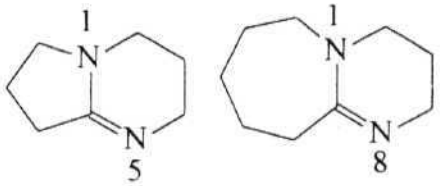
In a rather unique way, compound 3.**8** reacts with 4-dimethylaminopyridine or N-methylimidazole/ CCl_4 to give the betaine 3.**9** (eq 3.1).[10] However no other data is available to support the structure 3.**9** and the mechanism of its formations is unknown.



(3.1)

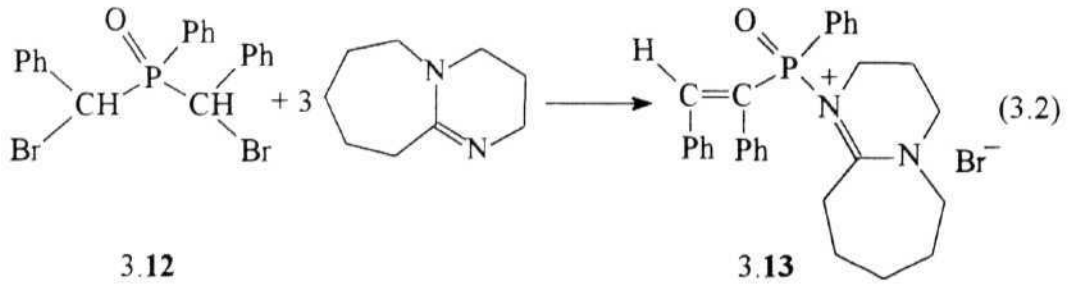
3.**8** 3.**9** [δ(P): 9.2]

1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU, 3.**10**)[11] and 1,5-Diazabicyclo(4.3.0) non-5-ene (DBN, 3.**11**) have one sp^2 hybridized nitrogen and should be analogous in their behaviour towards phosphorus reagents; both of these are known to be strong bases [pK_a values: DBU 11.5; Et_3N 10.87; N,N-dimethylaniline 5.15].



3.**10** 3**11**

In an interesting reaction, the phosphine oxide 3.**12** reacted with DBU to furnish an (*E*)-1,2-diphenylvinyl phosphorus derivative 3.**13** (eq 3.2).[12] Compound 3.**13** is a reactive salt analogous to 3.**2** or 3.**6**; solvolysis of 3.**13** in methanol replaces the P-N bond with P-OMe to give the methyl ester.

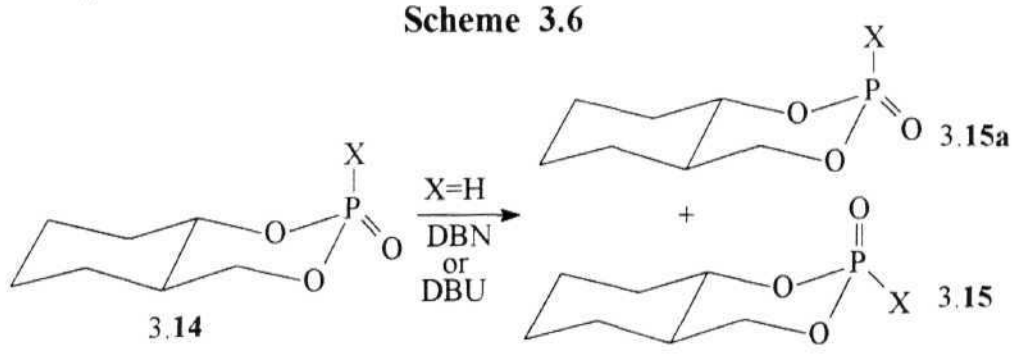


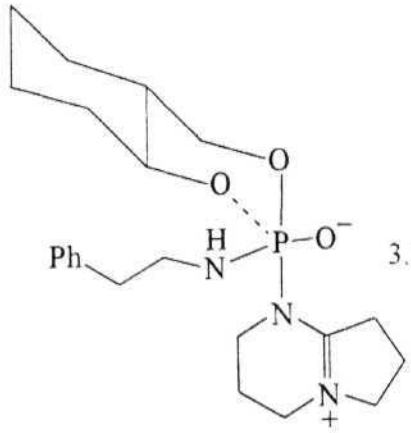
(3.2)

3.**12** 3.**13**

An article of interest in this connection is that reported by Merckling and Ruedi.[13] They reacted the axially substituted chloridate (±) 3.**14** with a series of O-, N- and S-nucleophiles under various conditions in an effort to isolate both P-epimers for further investigation. In order to enhance the reactivity, DBN or DBU was added as an auxiliary base. Surprisingly, an unexpected compound was the main product when using DBN as the auxiliary base in the reaction of (±) 3.**14** with 2-phenylethylamine. The structure 3.**16** is assigned to this compound based on CIMS [m/ z 420.4, $(M + H)^+$] as well as ^1H and ^{13}C NMR spectra.

Scheme 3.6





3.**16** [δ (P): 8.2]

In the reactions of chlorophosphorus(III) compounds with nucleophiles also, very often a base is used (eq 3.3). Now the question is about the role of the base in the reaction pathway. Whether a species such as 3.**17** is involved in any of these reactions involving a base such as NR_3 is a point to ponder.

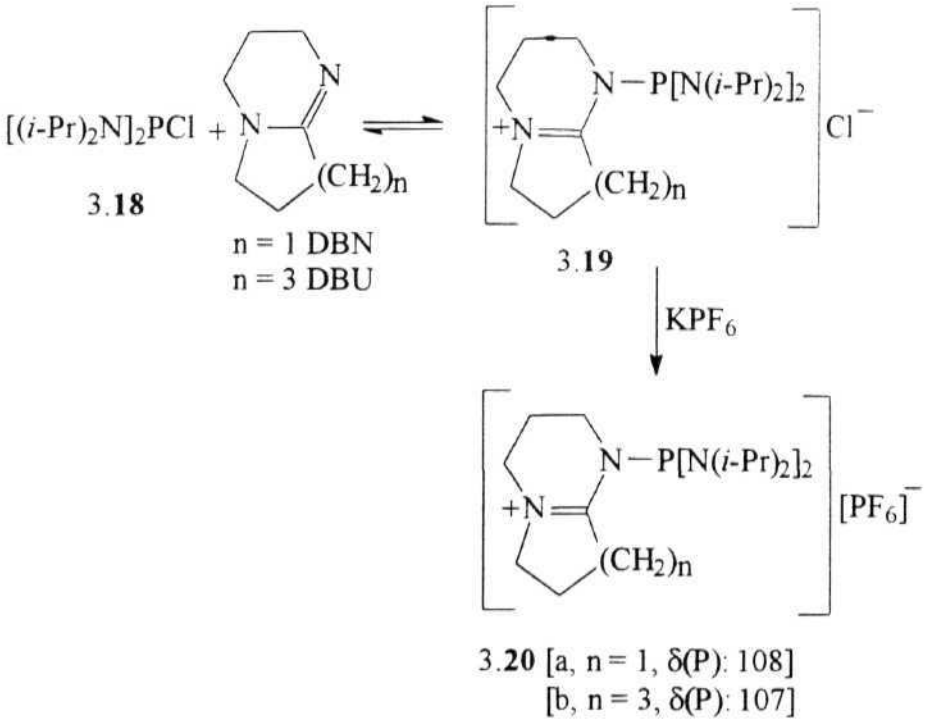
$$R_2PCl + ArOH \xrightarrow{Base} R_2POAr + Base.HCl \qquad (3.3)$$

$$[R_2P-\overset{+}{N}R_3]\,Cl^-$$

3.17

A case in point is the only report by Bertrand and coworkers on the reactions of chlorobis(diisopropylamino)phosphane (3.**18**) with DBN or DBU (Scheme 3.7).[14] In dichloromethane solution 3.**18** and DBN or DBU are in equilibrium with 3.**19**. This equilibrium is shifted towards the products in acetonitrile or by exchanging the chloride for hexafluorophosphate to yield 3.**20**. Compound 3.**20b** has been characterized in the solid state by X-ray crystallography, [Fig 3.1]. Although the P-N bond to the DBN moiety is pretty long (compared to the other two P-N bonds), this nitrogen is close to planarity. This is a point that would be of interest in understanding the nature of the P-N bond.[15]

Scheme 3.7



3.**20** [a, n = 1, δ(P): 108]
[b, n = 3, δ(P): 107]

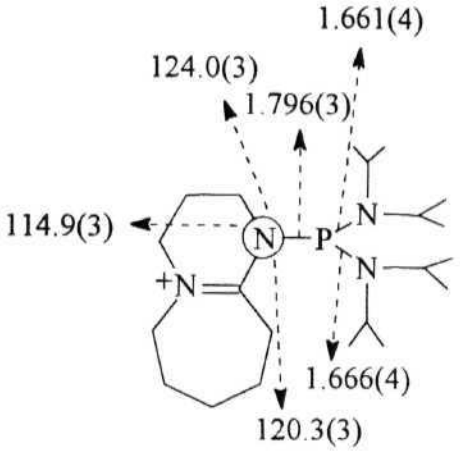
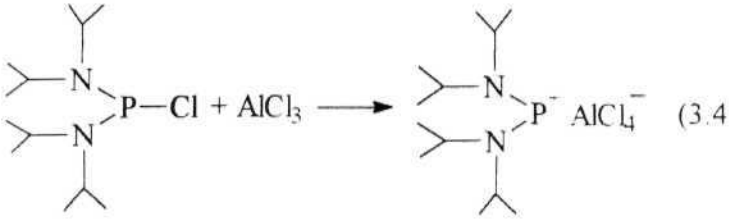


Fig. 3.1 Selected bond parameters in 3.**20(b)**

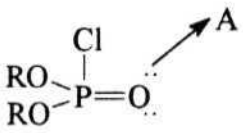
The reaction of a chlorophosphorus(III) compound with a halide acceptor can lead to another type of reactive species, the phosphenium cation. An example is shown in (eq. 3.4). It can be noted that the cation in 3.**21** is electronically equivalent to a carbene.[16] Although in the present study it was intended to study the synthesis and reactivity of various species like 3.**21,** the expected results were not obtained and hence the literature on this part is not further elaborated.



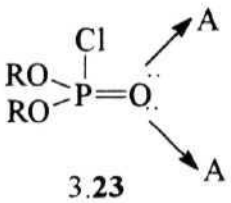
(3.4

3.**21**

Finally, the reaction of chlorophosphates $(RO)_2P(O)Cl$ with a Lewis acid may lead to acid-base adducts in which the lone pairs on the phosphoryl oxygen coordinate to the acid (3.**22** and 3.**23**).[17] The angle at the phosphoryl oxygen varies from 130 to 180° depending on the substitution and acid (or metal centre).[18] Although halide abstraction from the acid (eg. $AlCl_3$, $SbCl_5$) is possible, it is not observed.



3.**22**



3.**23**

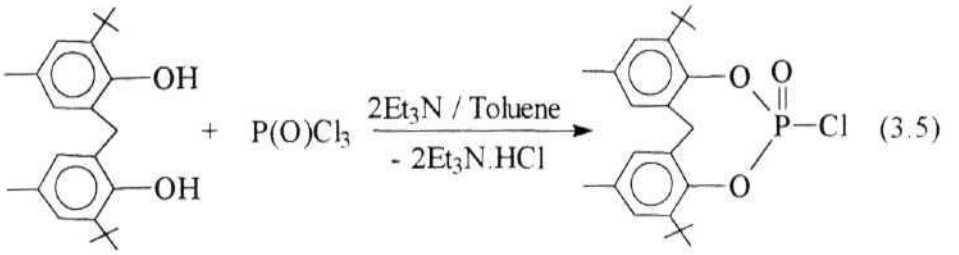
3.11 *OBJECTIVES OF THE PRESENT WORK*

The main objective of this part of the work is to study the reactions of chlorophosphorus(III) and chlorophosphorus(V) compounds with Lewis acids and bases, in particular with strong bases, in an effort to isolate phosphate-base complexes.

3.2 *Results and Discussion*

3.21 *Reactions of chlorophosphates with bases*

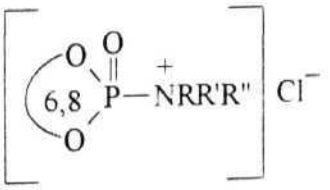
The cyclic chlorophosphates $[OCH_2CMe_2CH_2O]P(O)Cl$ (3.**24**), $CH_2[4,6\text{-}(t\text{-}Bu)_2\text{-}C_6H_2O]_2P(O)Cl$ (3.**25**) and $CH_2[4\text{-}Me\text{-}6\text{-}t\text{-}Bu\text{-}C_6H_2O]_2P(O)Cl$ (3.**26**) have been prepared by reacting phosphorus oxychloride with the diol in the presence of a base (*cf* eq. 3.5 for the synthesis fo 3.**26**). While 3.**24** is a known compound,[19] 3.**25** and 3.**26** are new. All these compounds are solids and stable under nitrogen atmosphere. The ^{31}P NMR chemical shifts vary from -2.4 to -3.4 ppm and are thus in the expected range.[20]



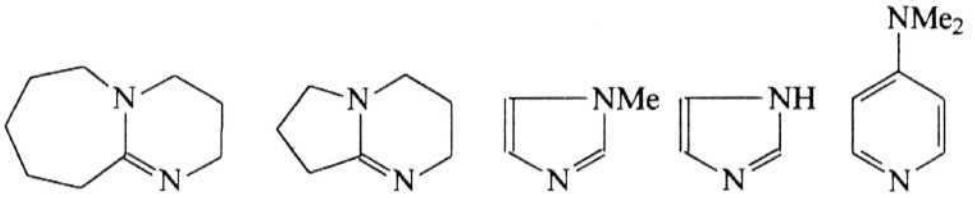
(3.5)

3.**26** [δ(P): -3.4]

As mentioned in the Introduction (Section 3.1), the main interest here has been to obtain salts such as (**D**), by reacting 3.**24**-3.**26** with the bases 1-8-diazabicyclo(5.4.0)undec-7-ene (DBU), 1,5-diazabicyclo(4.3.0)non-5-ene (DBN), N-methyl imidazole (NMI), imidazole (IM) and 4-dimethylaminopyridine (DMAP). All these have two nitrogens, one sp^2 hybridized and the second sp^3 hybridized.

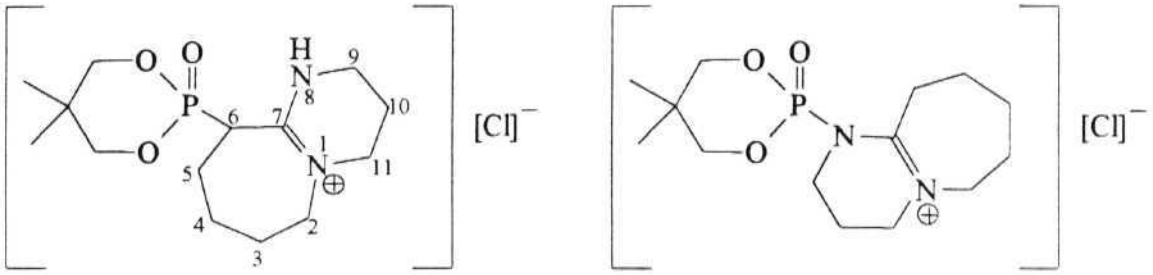


(**D**)



DBU DBN NMI IM DMAP

In the reaction of 3.**24** with DBU in toluene, we obtained the product 3.**27** rather than the expected compound 3.**28**; essentially pure 3.**27** (^{31}P NMR evidence) is immediately precipitated upon addition of DBU to 3.**24**.



3.**27** [δ(P): 10.7] 3.**28**

Although the ^{1}H NMR spectrum of 3.**27** [Fig 3.2(a)] is complex, the P-C*H* signal [δ ~3.05, ^{2}J(P-H) ~ 12Hz] can be readily identified. More characteristic is the ^{13}C NMR [Fig 3.2(b)] in which C(7) appears as a doublet [^{1}J(P-C) = 126.5Hz]. The ^{31}P NMR chemical shift value of 10.7 ppm is close to that of several other phosphonates (3.**29**) prepared in our laboratory.[21] This chemical shift value is a point of some interest because the compound 3.**16** (*vide supra*) reported by Merckling and Ruedi has a similar ^{31}P NMR chemical shift.[13]

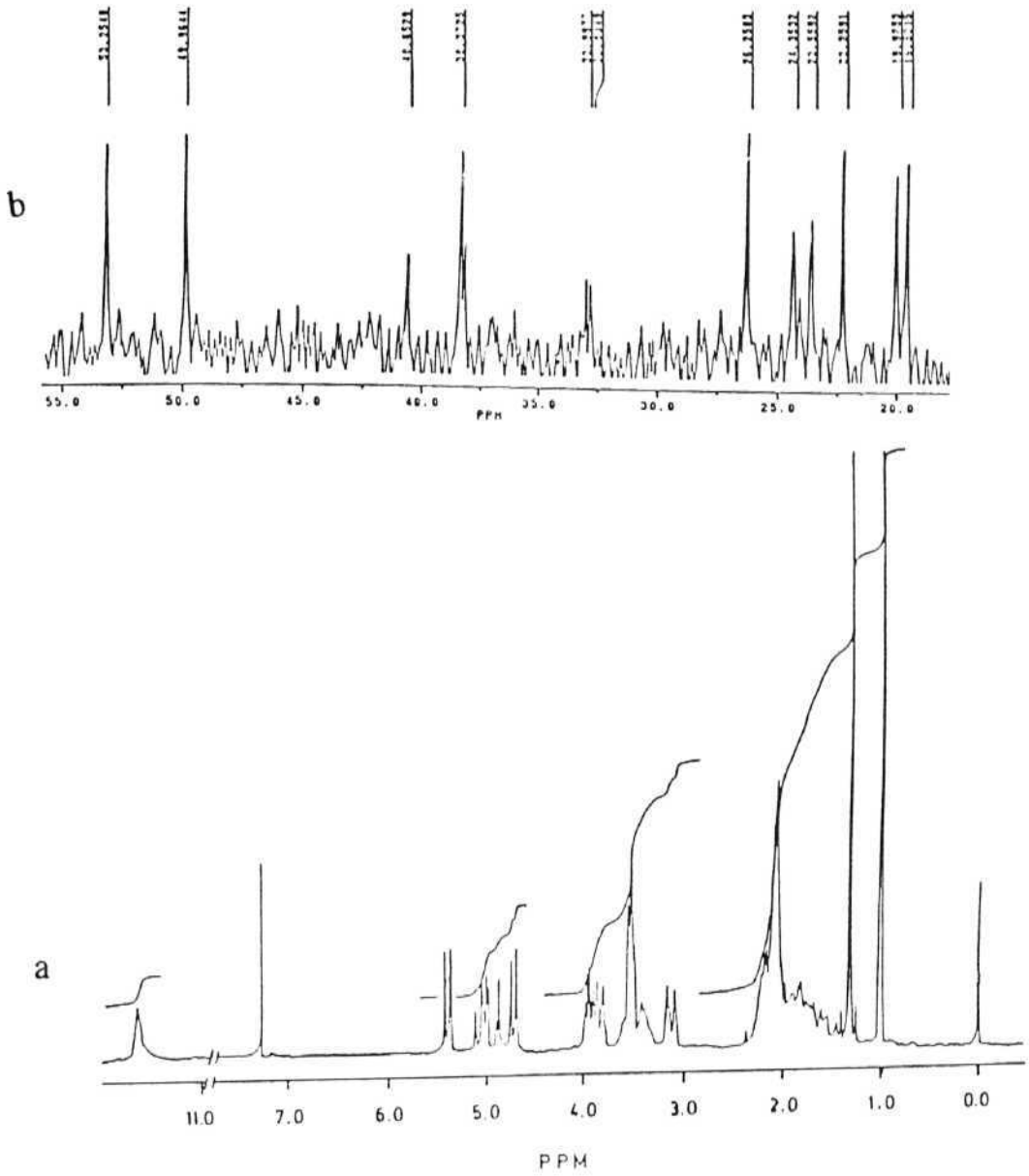
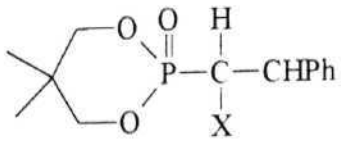


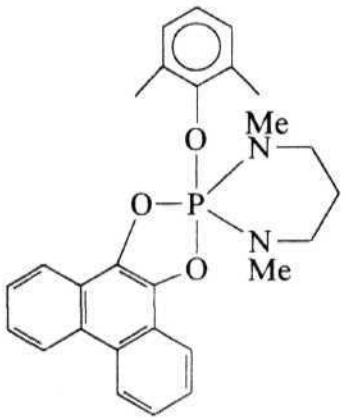
Fig 3.2 a) ^{1}H and b) ^{13}C NMR spectra of 3.**27**.

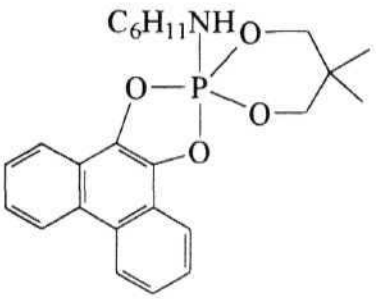


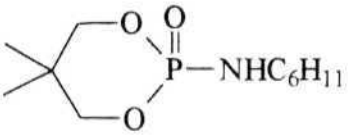
3.**29**

a) X = Cl [δ(P): 8.1]
b) X = OH [δ(P): 13.3]

Also of interest are the ^{31}P NMR chemical shift values of 3.**30**-3.**32**. This data in conjunction with that for our compound 3.**27** do not fit in well with the ^{31}P chemical shift reported for 3.**16**. Since we have an X-ray structure for 3.**27** as a hydrate (see Section 3.25), we believe that more studies on these systems will be needed to clarify this point.

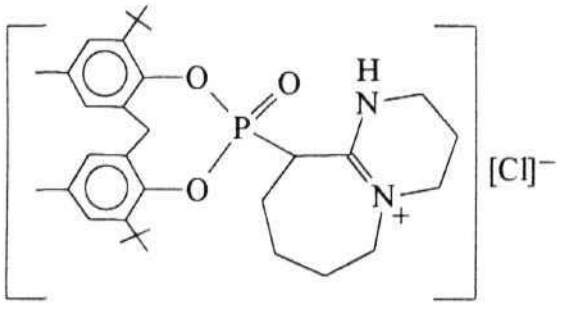


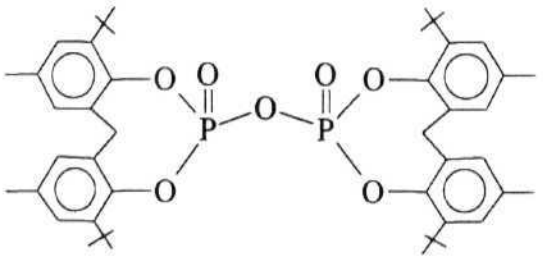




3.**30** [δ(P): -38.9; ref. 22] 3.**31** [δ(P): -46.2; ref. 23] 3.**32** [δ(P): 4.4; ref. 23]

In the reaction of 3.**26** with DBU, compound 3.**33** which is also a phosphonate salt, is obtained. In addition to the characteristic ^{31}P NMR chemical shift, this compound exhibits a $^{1}J(\underline{P}\text{-}\underline{C})$ of 126 Hz. In addition to 3.**33**, the pyrophosphate 3.**34** is also obtained in fair yields (33%, NMR, X-ray) from the same reaction.

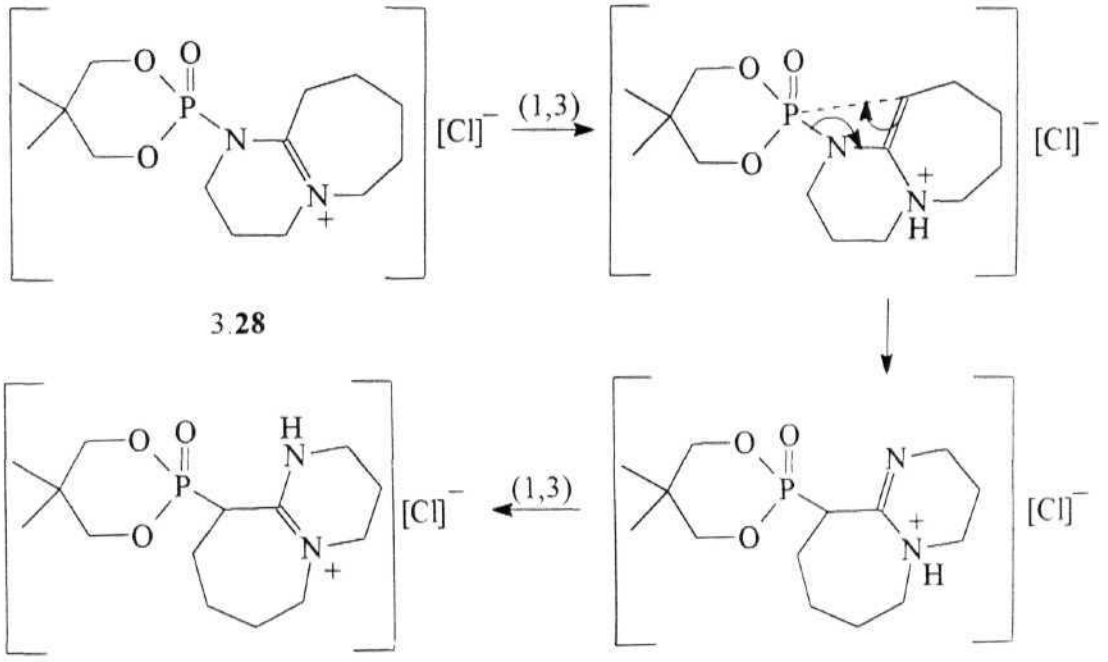




3.**33** [δ (P): 7.2] 3.**34** [δ (P): -28.6]

Isolation of phosphonates such as 3.**27** or 3.**33** while using DBU is rather unique and so far, to our knowledge, such a pathway has not been inferred. However, it is known that DBU can be lithiated at the C-6 position by n-butyllithium.[11] Formation of these phosphonates (Scheme 3.8) may involve the salt 3.**28** which undergoes 1,3-proton shift from C-6 to N-1 to give an enamine; this could reorganize to 3.**27** *via* a cyclic 4-membered transition state involving C-6, C-7, N-8 and P (Scheme 3.8).

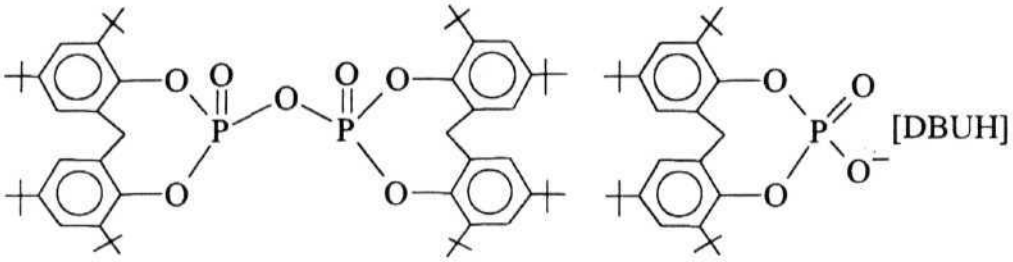
Scheme 3.8



3.**28**

3.**27**

In contrast to the above, in the reaction of 3.**25** with DBU, we were unable to detect the phosphonate salt. The products that could be identified were 3.**35** and 3.**36**; compound 3.**35** has been isolated from a different reaction independently (see below) and



3.**35** 3.**36** (X-ray)

compound 3.**36** has been obtained in crystalline form as a hydrate (see X-ray section). The main identification in solution is by ^{13}C NMR which shows the absence of a $^{1}J(P\text{-}C)$ doublet (expected for a phosphonate; *cf* compound 3.**27**); the position of the unsaturated carbon [δ(C): 166.0] is also different from that in 3.**25** [δ(C): 161.4] or 3.**27** [δ(C): 161.0]. We believe that the formation of 3.**36** occurs through an intermediate analogous to 3.**28**, which, instead of isomerizing to the phosphonate salt, undergoes facile hydrolysis to give the phosphate $[CH_2\{4,6\text{-}(t\text{-}Bu)_2C_6H_2O\}_2]P(O)OH$. The proton from the acid is picked up by DBU. The phosphate 3.**36** can also react with the chloro precursor 3.**25** to lead to the pyrophosphate ester 3.**35**. Since we have used 1:1 stoichiometry of 3.**25** and DBU, isolation of the phosphate salt 3.**36** [in addition to DBU.HCl] may also indicate facile hydrolysis of 3.**25** in the presence of even traces of moisture; another contributing factor in the ready isolation of 3.**36** probably rests with the similar sizes of the cation and anion which could lower its solubility.

Since for reactions at the phosphorus centre, 3.**25** and 3.**26** have same steric factors operating, formation of different products utilizing them may be due to electronic effects; more studies are required for a detailed explanation for this.

In order to check these reactions further, we also treated benzoyl chloride with DBU and observed immediate precipitation. However the NMR (^{1}H and ^{13}C) was too complicated; in addition to this, precipitate quickly turned into a semisolid and gave a complicated NMR. Therefore further analysis was not performed.

Although DBN is also a dinitrogen base similar to DBU, we did not observe a phosphonate salt in reactions utilizing the former. The reaction mixture (solid) obtained by treating 3.**24** with DBN initially showed two peaks in the ^{31}P NMR at -6.8 and -12.0 ppm. From this the product with the downfield shift [δ(P): -6.8] could be isolated as an air-sensitive solid. Since the product obtained by treating $(OCH_2CMe_2CH_2O)P(O)OH$[21] with DBN showed a ^{31}P NMR chemical shift of -4.2 ppm, this product is not the phosphate salt $(OCH_2CMe_2CH_2O)P(O)O^-(DBNH)^+$. In the ^1H NMR [Fig 3.3] there was no observable peak in the range 8.0-12.0 ppm assignable to NH^+ or H_3O^+ protons. In the $^{13}C\{^1H\}$ NMR [Fig 3.4(a)] doublets were observed at 43.8 [$^2J(\underline{P}\text{-}\underline{C}) = 15.0$ Hz] and 167.9 [$^2J(P\text{-}C) \approx 9$ Hz; for comparison the same carbon in $\{(i\text{-}Pr_2N)_2P(DBN)^+\}Cl^-$ appears at 165.5 ppm]. These two signals are attributable to C2 and C4 in structure 3.**37** [Note: The signals at 54.2 and 52.4 ppm do not form a part of the $^{31}\underline{P}\text{-}^{13}\underline{C}H$ doublet, as inferred from the coupled ^{13}C NMR spectrum, which clearly shows two triplets [Fig 3.4(b)]. We were

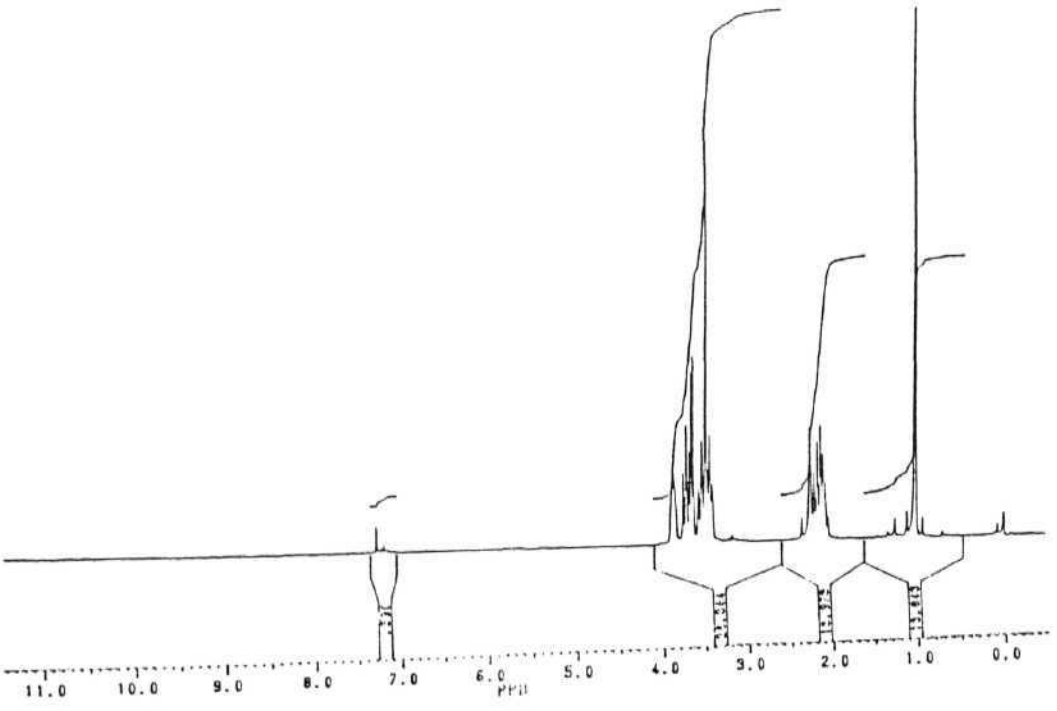
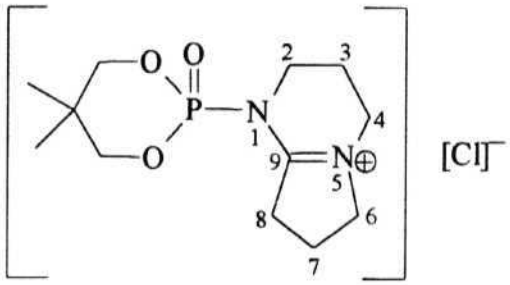


Fig 3.3 ^1H NMR spectrum of 3.**37**.



3.**37**

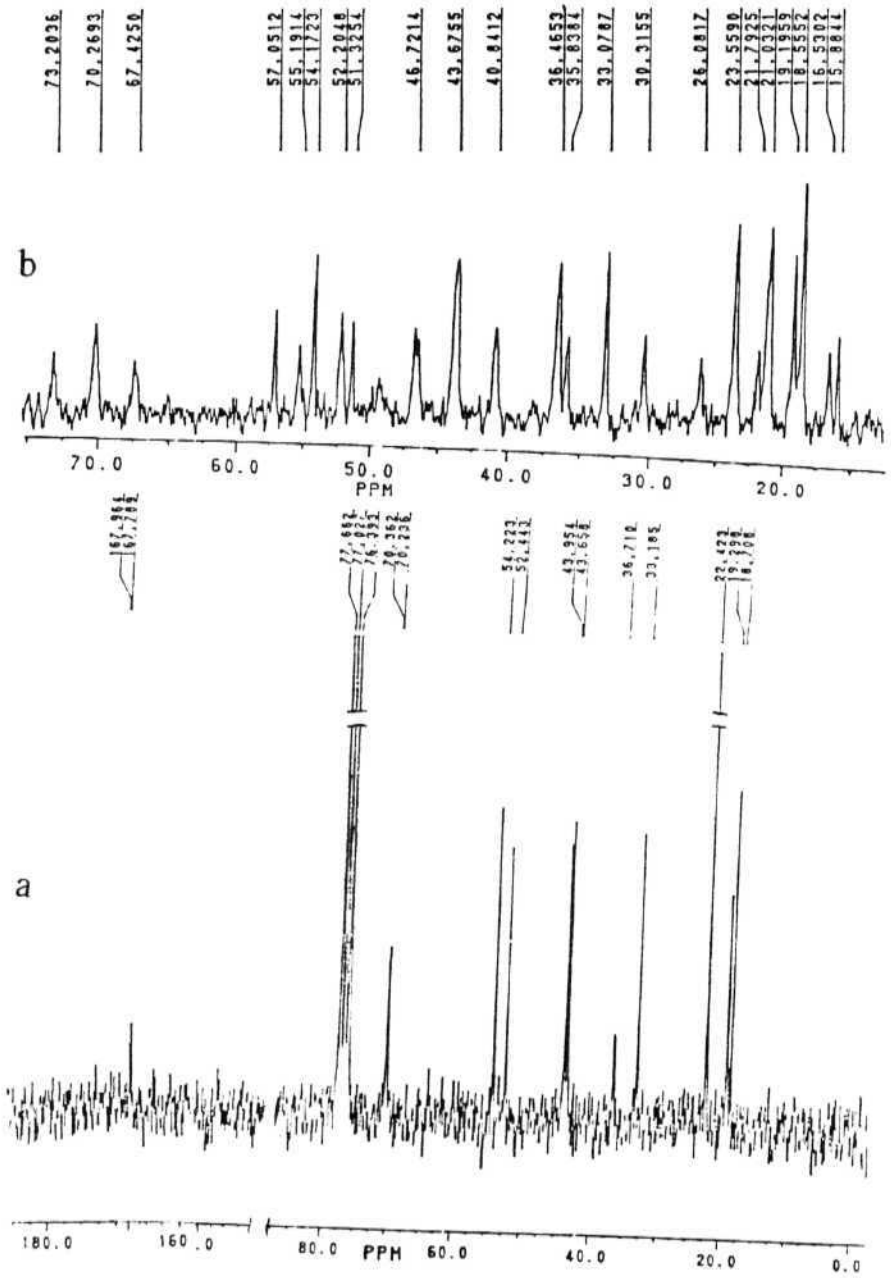


Fig. 3.4 a) ^{13}C and b) ^{1}H coupled ^{13}C NMR spectra of 3.**37**.

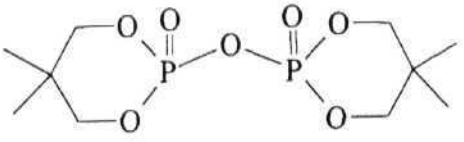
unable to obtain the elemental analysis because of the moisture sensitivity of this compound.

The results of other reactions are summarized in Table 3.2. The pyrophosphate 3.**38** is a major product in most of these reactions.

Table 3.2 Further details on the reaction of chlorophosphates with bases

Substrate	Base	^{31}P NMR	Remarks
3.**24**	NMI	-11.4 (90%) -21.9 (3.**38**)	Intensity of peak at -21.9 ppm increases with time
3.**24**	IM*	-14.3, -22.1 (3.**38**) ($CDCl_3$ + DMSO)	Intensity varies; 3.**38** isolated
3.**24**	DMAP	-7.1, -21.9 (3.**38**)	intensity varies; 3.**38** isolated
3.**25**	NMI, IM, DMAP	*ca* -11.0, -28.5 (3.**35**)	(i) intensity variable (ii) The peak around -11.0 ppm may be phosphate salt similar to 3.**36**. (iii) Compound 3.**35** isolated.

* Note: It is possible that one product could be the aminophosphate $(OCH_2CMe_2CH_2O)P(O)(NCH_2CH_2NCH)$.



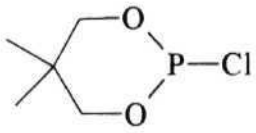
3.**38** [δ(P): -21.9; lit.: -21.9, ref. 24]

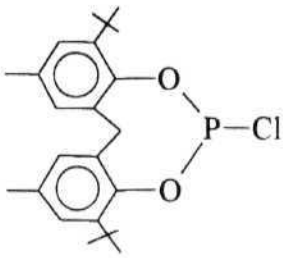
Since the product of $(OCCMe_2CH_2O)P(O)OH$ with these bases generally showed a signal in ^{31}P NMR at *ca* -4.5 ppm, the low field peak in the first three entries of Table 3.2 is most likely not the phosphate salt $\{(OCH_2CMe_2CH_2)P(O)O^-\}\{BaseH^+\}$ as pointed

out before. However since we could not isolate the products in a pure state, it is difficult to ascertain their nature.

3.22 *Reaction of chlorophosphorus(III) compounds with bases*

We have chosen the substrates 3.**39**[25] and 3.**40**[26] and followed Bertrand's procedure using acetonitrile as a solvent.[14] In the reaction of 3.**39** with DBU three peaks





3.**39** [δ (P): 120.8] 3.**40** [δ (P): 153.0]

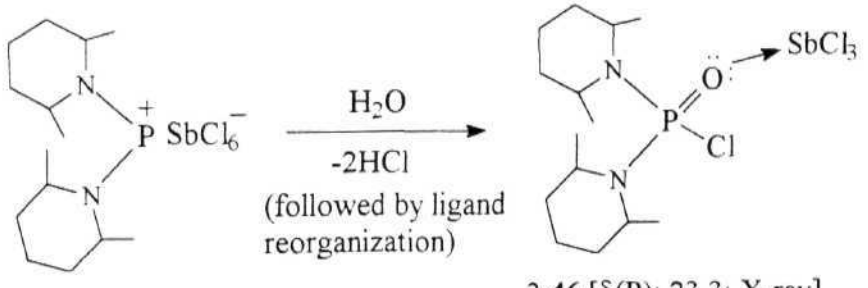
were observed in the ^{31}P NMR spectrum: δ 145.5(s), 108.2(s), 2.4(s). The peak at 2.4 ppm is due to the hydrolysed product $(OCH_2CMe_2CH_2O)P(O)H$ (3.**41**).[21,23] Since Bertrand's compound $[\{(i\text{-}Pr)_2N\}P\text{-}DBU]^+Cl^-$ has a δ(P) of 107 ppm,[14] we assign the peak at 108.2 ppm to the salt $[(OCH_2CMe_2CH_2O)P\text{-}DBU]^+Cl^-$ (3.**42**); the other peak at 145.5 ppm is unassigned. Similarly in the reaction of 3.**40** with DBU three peaks at δ(P) 170.1, 124.7 (major) and 0.1 ppm were observed; whereas the peak at 124.7 ppm is ascribable to $[CH_2\{(4\text{-}Me\text{-}6\text{-}t\text{-}Bu\text{-}C_6H_2O)_2\}P\text{-}(DBU)]^+[Cl]^-$ (3.**43**), the peak at 0.1 ppm is due to the hydrolysed product $[CH_2\text{-}\{4\text{-}Me\text{-}6\text{-}t\text{-}Bu\text{-}C_6H_2O)_2\}P(O)H$ (3.**44**).[27] The reaction mixture obtained by treating 3.**40** with 4-dimethylaminopyridine exhibited peaks at 124.6 and 0.1 ppm in the ^{31}P NMR; these peaks are ascribable to the salt and hydrolyzed product respectively.

We have not been successful in isolating a pure product from the above reactions, one possible reason is the smaller steric bulk in 3.**39** and 3.**40** compared to Bertrand's compounds $(R_2N)_2PCl$ [R = *i*-Pr, cyclohexyl]. We tried to stabilize the salts by adding

KPF_6 to the reaction mixture[14] but were not successful in isolating a pure product and hence did not pursue this aspect further.

3.23 *Reaction of P(III) compounds* $(OCH_2CMe_2CH_2O)PCl$ *(3.39) and* $(2,6\text{-}Me_2C_5H_8N)_2PCl$ *(3.45) with antimony pentachloride (a Lewis acid)*

As mentioned before, these reactions were aimed at obtaining the phosphenium cations with the $[SbCl_6]^-$ counterion. In the reaction using 3.**39** there was no product which could be identified clearly [^{31}P NMR of the reaction mixture: 145.6, 16.7 (15%), 2.3 ppm (15%, hydrolysed product 3.**41**)]. In the reaction using 3.**45**, we obtained the adduct $(2,6\text{-}Me_2C_5H_8N)_2PCl(O).SbCl_5$ (3.**46**), δ(P): 23.3, as the only isolable product, although the reaction mixture exhibited an additional peak at 43.8 ppm. It is possible that formation of 3.**46** took place by hydrolysis of the phosphenium salt; however, since compounds of the type 3.**46** did not form the theme of the present work, we did not proceed further.

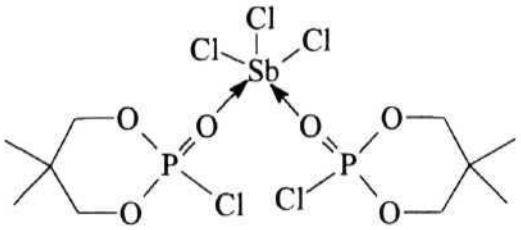


3.**46** [δ(P): 23.3; X-ray]

3.24 *Reaction of* $(OCH_2CMe_2CH_2O)P(O)Cl$ (3.**24**) *with antimony trichloride*

Antimony trichloride can also act as a Lewis acid[28] and form the $[SbCl_4]^-$ ion. In the reaction with 3.**24**, $SbCl_5$ can lead to $[(OCH_2CMe_2CH_2O)P(O)]^+[SbCl_4]^-$ (polymeric/ oligomeric) or utilize the lone pair on the phosphoryl oxygen to form a simple adduct. Thus a 1:1 reaction of 3.**24** with $SbCl_5$ was conducted; interestingly the hygroscopic

crystalline solid obtained from this reaction analysed as $[(OCH_2CMe_2CH_2O)P(O)Cl]_2.SbCl_3$ (3.**47**); however the crystals were not suitable for X-ray studies. The structure 3.**47** is assigned to this compound.



3.**47** [δ (P): -3.4]

Since no interaction with the P-Cl bond is inferred we did not pursue these studies with other chlorophosphate esters.

3.25 *X-ray structural studies*

X-ray structures for compounds 3.**27**·H_2O, 3.**34**, 3.**36**·1.5 H_2O and 3.**46** have been determined. These studies confirm the assigned structures. Selected atomic coordinates for compounds 3.**27**·H_2O, 3.**34**, 3.**36**·H_2O and 3.**46** are available in the Appendix. Some details are discussed below.

In the structure of 3.**27**·H_2O [Fig 3.5; Table 3.3 for bond lengths and bond angles], the 1,3,2-dioxaphosphorane ring has a *chair* conformation and the ring P-O bond lengths [mean: 1.562Å] are shorter than those observed in $(OCH_2CMe_2CH_2O)P(NHC_6H_{11})$ [mean: 1.633Å, molecule 1of the four molecules present in the asymmetric unit] or in $(OCH_2CMeCH_2O)P(1,2\text{-}O_2C_6Cl_4)(NHC_6H_{11})$ [mean: 1.608Å],[23] the reason for this is not apparent, but the +ve charge caused by the $(OCH_2CMe_2CH_2O)P(O)(DBU)]^+$ moiety may be one of the factors. There is some disorder at

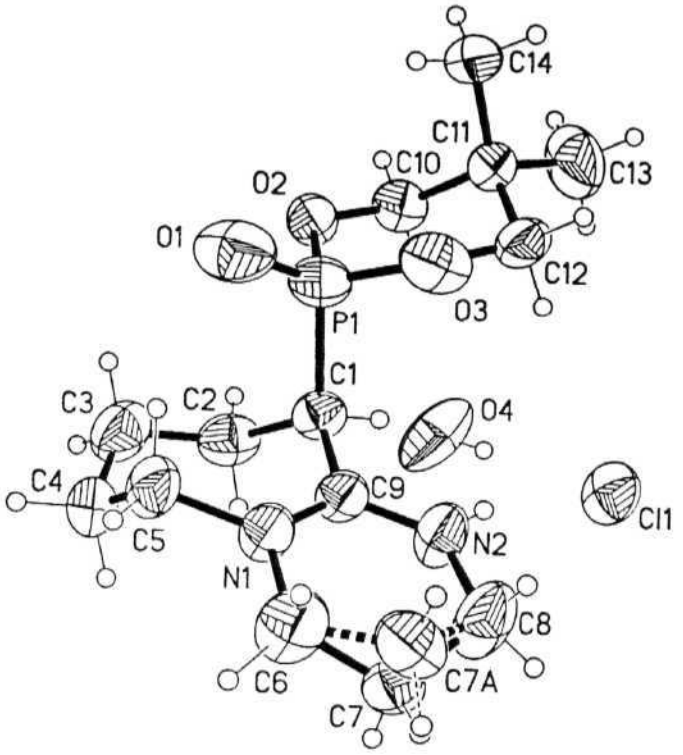


Fig 3.5 Molecular structure of 3.**27**·H_2O; only non-hydrogen atoms are shown for clarity.

C(7) as shown in Fig 3.5. The N(1)-C(9) and C(9)-N(2) distances are short and interestingly, are close to the analogous distances in $[(i\text{-}Pr_2N)_2P(DBU)]^+Cl^-$ [1.293(5) and 1.322(5)Å respectively].

There are some close contacts involving the chloride, water and NH^+ as shown in Fig 3.6; since their effect is mainly in the crystal packing, no further discussion is made here.

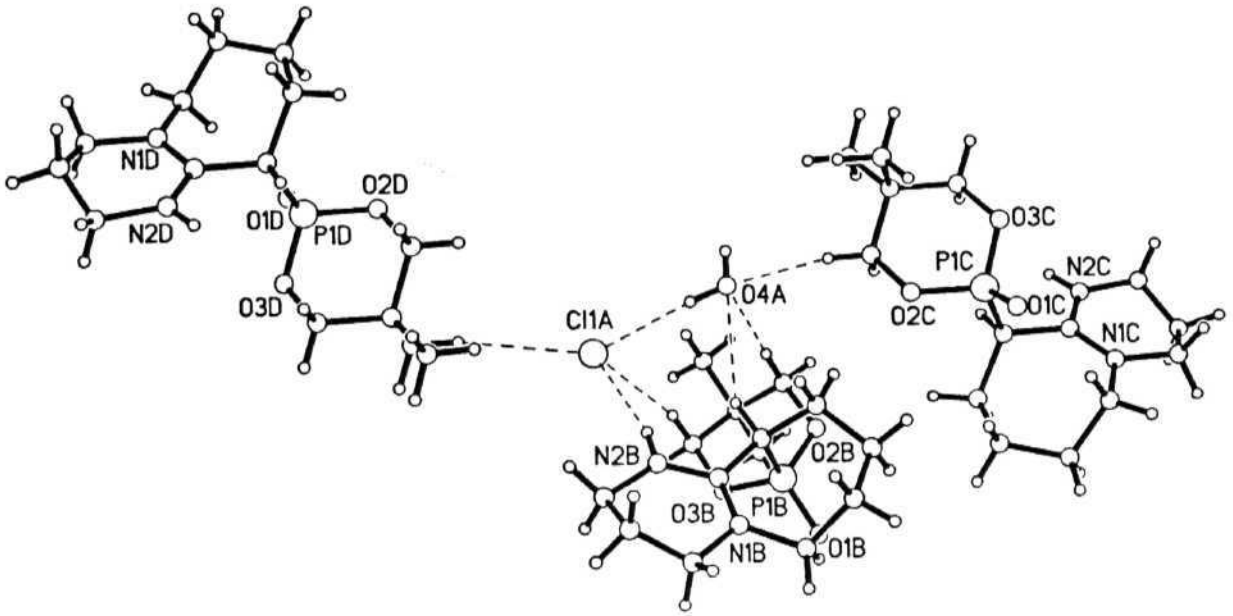


Fig 3.6 Molecular structure of 3.**27**·H_2O showing some close contacts involving the chloride, water and NH^+.

Table 3.3 Selected bond lengths [Å] and angles [°] for 3.**27**·H_2O·with esd's in parentheses

P (1) - O (1)	1.458 (2)	P (1) - O (3)	1.560 (2)
P (1) - O (2)	1.565 (1)	P (1) - C (1)	1.833 (2)
O (2) - C (10)	1.462 (2)	O (3) - C (12)	1.459 (3)
N (1) - C (9)	1.317 (2)	N (1) - C (6)	1.475 (3)
N (1) - C (5)	1.485 (3)	N (2) - C (9)	1.318 (2)
N (2) - C (8)	1.461 (3)	C (1) - C (9)	1.510 (2)
C (1) - C (2)	1.546 (3)	C (2) - C (3)	1.514 (4)
C (3) - C (4)	1.515 (4)	C (4) - C (5)	1.510 (4)
C (6) - C (7A)	1.419 (4)	C (6) - C (7)	1.443 (3)
C (7) - C (8)	1.427 (3)	C (7A) - C (8)	1.427 (4)
C (10) - C (11)	1.517 (3)	C (11) - C (14)	1.532 (3)
C (11) - C (12)	1.527 (3)	C (11) - C (13)	1.532 (4)

contd...

Table 3.3 contd..

O (1) - P (1) - O (3)	111.98 (11)	O (1) - P (1) - O (2)	112.09 (10)
O (3) - P (1) - O (2)	106.64 (8)	O (1) - P (1) - C (1)	115.30 (10)
O (3) - P (1) - C (1)	105.46 (9)	O (2) - P (1) - C (1)	104.67 (8)
C (10) - O (2) - P (1)	121.12 (12)	C (12) - O (3) - P (1)	122.36 (14)
C (9) - N (1) - C (6)	120.4 (2)	C (9) - N (1) - C (5)	124.5 (2)
C (6) - N (1) - C (5)	115.1 (2)	C (9) - N (2) - C (8)	124.7 (2)
C (9) - C (1) - C(2)	115.1 (2)	C (9) - C(1) - P (1)	113.05 (13)
C (2) - C (1) - P (1)	114.45 (13)	C (3) - C (2) - C (1)	117.8 (2)
C (2) - C (3) - C (4)	114.7 (2)	C (5) - C (4) - C (3)	112.7 (2)
N (1) - C (5) - C (4)	114.4 (2)	C (7A) - C (6) - N (1)	115.2 (3)
C (7) - C (6) - N (1)	113.5 (2)	C (8) - C (7) - C (6)	116.9 (2)
C (6) - C (7A) - C (8)	118.5 (4)	C (7A) - C (8) - N (2)	112.5 (3)
C (7) - C (8) - N (2)	109.6 (2)	N (1) - C (9) - N (2)	120.9 (2)
N (1) - C (9) - C (1)	123.0 (2)	N (2) - C (9) - C (1)	116.1 (2)
O (2) - C (10) - C (11)	111.8 (2)	C (10) - C (11) - C (14)	111.8 (2)
C (10) - C (11) - C (12)	108.4 (2)	C (14) - C (11) - C (12)	110.3 (2)
C (10) - C (11) - C (13)	107.5 (2)	C (14) - C (11) - C (13)	109.6 (2)
C (12) - C (11) - C (13)	109.0 (2)	O (3) - C (12) - C (11)	111.9 (2)

The structure of 3.**34** [Fig 3.7; selected bond distances in Table 3.4] is straightforward. The two halves of the molecule are symmetrically related through the bridging oxygen O(3). The ring P-O bond lengths are in the expected range [mean: 1.565Å] but again, as in the case of 3.**27**·H_2O, shorter than those in $(OCH_2CMe_2CH_2O)P(NHC_6H_{11})$ or in $(OCH_2CMe_2CH_2O)P(1,2\text{-}O_2C_6Cl_4)(NHC_6H_{11})$.[23] The phosphorus to bridging oxygen distance is however, longer [1.591(3)Å]. The 1,3,2-dioxaphosphocin ring has a "tub" conformation similar to that found in the pentacoordinated compound $[CH_2\{4,6\text{-}(t\text{-}Bu)_2\text{-}C_6H_2O)_2\}]P(1,2\text{-}O_2C_6Cl_4)(NHC_6H_{11})$.[23]

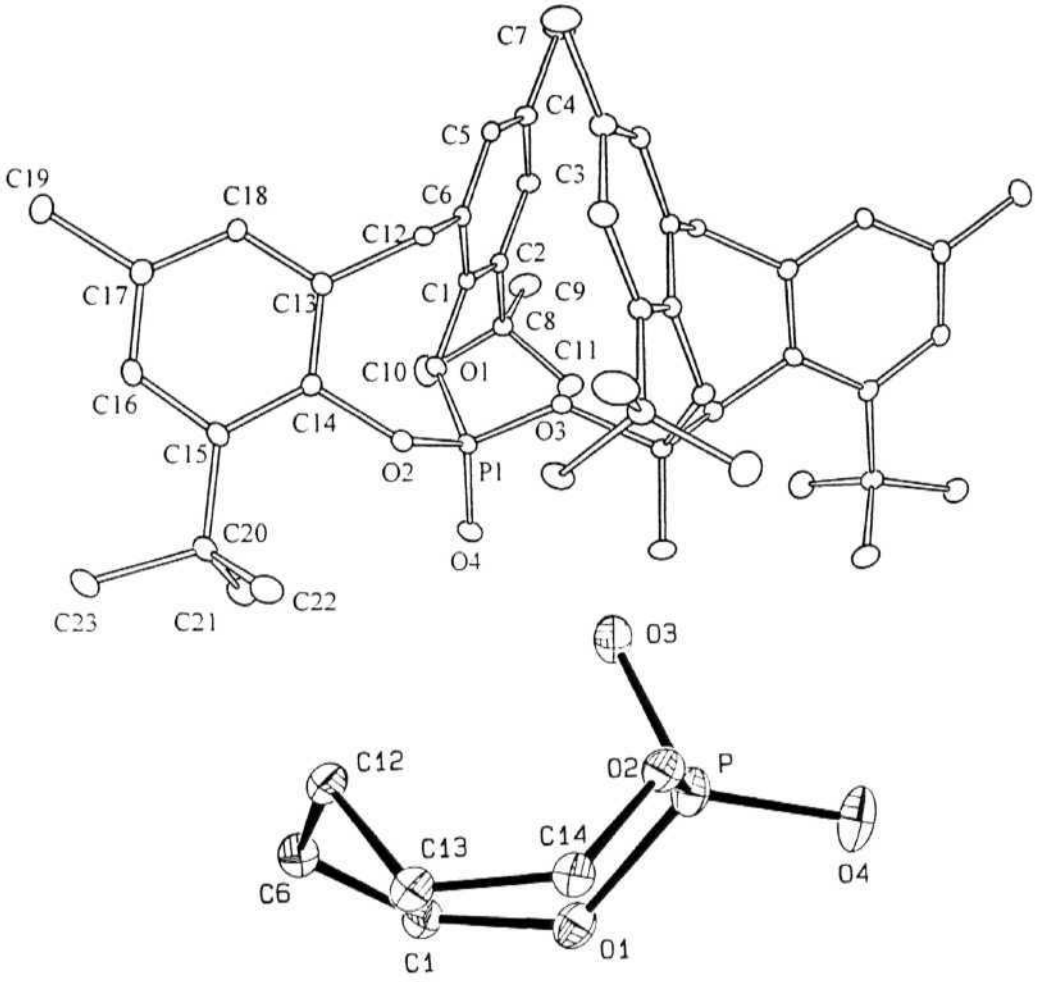


Fig 3.7 Molecular structure of 3.**34**; only non-hydrogen atoms are shown for clarity. Also shown at the bottom is the conformation of the eight membered 1,3,2-dioxaphosphocin ring.

In 3.**36**.1.5H_2O [Fig 3.8; selected distances in Table 3.5] the ring P-O distances [mean: 1.628Å] are longer than those found in 3.**34**; the other two P-O bonds are significantly shorter [mean 1.471Å] and are close to the phosphoryl bond distance.[29] The eight membered 1,3,2-dioxaphosphocin ring has a *boat-chair* conformation similar to several other structures containing this ring in which phosphorus is tricoordinated[23] or pentacoordinated (with diequatorial placement of the oxygens in the TBP geometry).[30]

Table 3.4 Selected bond lengths [Å] and angles [°] for 3.**34** with esd's in parentheses

P - O (4)	1.439 (6)	P - O (1)	1.566 (5)
P - O (2)	1.564 (5)	P - O (3)	1.591 (3)
O (3) - P# 1	1.591 (3)	O (2) - C (14)	1.431 (9)
O (1) - C (1)	1.405 (9)	C (1) - C (6)	1.382 (10)
C (6) - C (12)	1.553 (10)	C (12) - C (13)	1.525 (10)
C (13) - C (14)	1.393 (11)		

O (4) - P - O (1)	112.6 (4)	O (4) - P - O (2)	114.6 (3)
O (1) - P - O (2)	107.0 (3)	O (4) - P - O (3)	115.2 (4)
O (1) - P - O (3)	103.6 (3)	O (2) - P - O (3)	102.6 (2)
P - O (3) - P # 1	135.4 (5)	C (14) - O (2) - P	125.0 (4)
C (1) - O (1) - P	129.9 (5)	C (6) - C (1) - O (1)	119.1 (6)
C (1) - C (6) - C (12)	122.5 (6)	C (13) - C (12) - C(6)	114.8 (6)
C (14) - C (13) - C (12)	121.5 (7)	C (13) - C (14) - O (2)	116.9 (6)

The two N-C distances [N(1)-C(2): 1.306(13); N(2)-C(21): 1.337(14)Å] to the unsaturated carbon C(21) in the DBU part are short and similar to those in 3.**27**·H_2O.

Hydrogen bonding is present in 3.**36**·3/2H_2O [Fig 3.9] with one of the water molecules [at O(5) in special position] H-bonded to two phosphoryl oxygens that are symmetry related [O(5)-O(4,4A): 2.971Å]. There is also another water molecule [not shown in Fig 3.8] with its oxygen [O(6)] H-bonded to another oxygen [O(6A)] of the water molecule from a different asymmetric unit. Overall, in the asymmetric unit one full water molecule [corresponding to O(6)] and one half water molecule [corresponding to O(5)] are present.

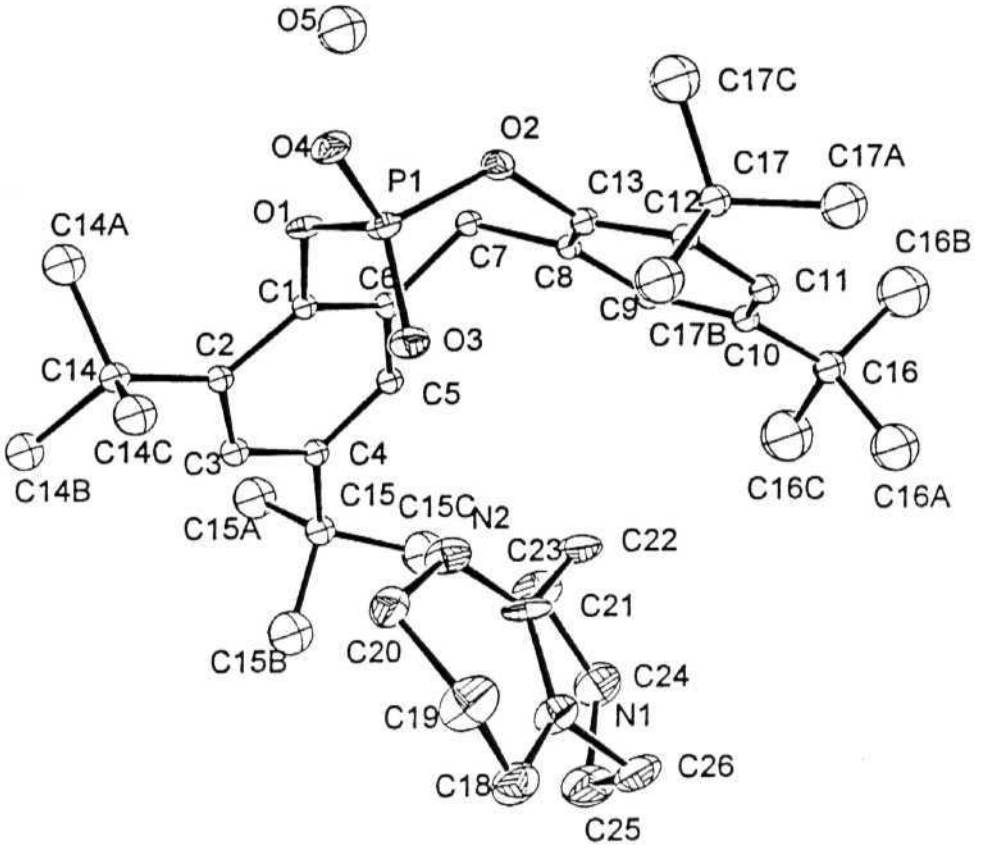


Fig 3.8 Molecular structure of 3.**36**·1.5H_2O; only non-hydrogen atoms are shown for clarity.

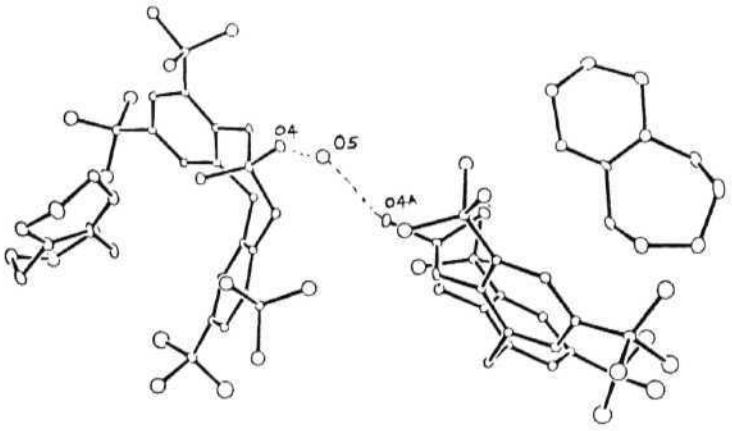


Fig 3.9 A diagram showing hydrogen bonding in 3.**36**.3/2H_2O showing one of the water molecules [at O(5) in special position] H-bonded to two phosphoryl oxygens that are symmetry related.

Table 3.5 Selected bond lengths [Å] and angles [°] for 3.**36**·1.5 H_2O with esd's in parentheses

P (1) - O (4)	1.466 (7)	P (1) - O (3)	1.476 (7)
P (1) - O (1)	1.627 (7)	P (1) - O (2)	1.630 (7)
O (1) - C (1)	1.395 (11)	O (2) - C (13)	1.401 (11)
N (1) - C (18)	1.491 (15)	N (1) - C (26)	1.542 (17)
N (2) - C (21)	1.337 (14)	N (2) - C (20)	1.443 (13)
C (18) - C (19)	1.450 (18)	C (19) - C (20)	1.503 (17)
C (21) - C (22)	1.508 (16)	C (22) - C (23)	1.438 (18)
C (23) - C (24)	1.532 (17)	C (24) - C (25)	1.56 (2)
C (25) - C (26)	1.45 (2)	C (1) - C (6)	1.394 (13)
C (6) - C (7)	1.513 (13)	C (7) - C(8)	1.508 (13)
C (8) - C (13)	1.401 (13)		

O (4) - P (1) - O (3)	122.1 (5)	O (4) - P (1) - O (1)	106.5 (4)
O (3) - P (1) - O (1)	107.8 (4)	O (4) - P (1) - O (2)	105.4 (4)
O (3) - P (1) - O (2)	109.5 (4)	O (1) - P (1) - O (2)	104.3 (4)
C (1) - O (1) - P (1)	124.3 (6)	C (13) - O (2) - P (1)	122.8 (6)
C (21) - N (1) - C (18)	123.1 (11)	C (21) - N (1) - C (26)	119.9 (11)
C (18) - N (1) - C (26)	116.9 (10)	C (21) - N (2) - C (20)	123.2 (9)
C (19) - C (18) - N (1)	110.0 (11)	C (18) - C (19) - C (20)	115.0 (12)
N (2) - C (20) - C (19)	109.2 (10)	N (2) - C(21) - N (1)	120.9 (11)
N (2) - C (21) - C (22)	118.4 (9)	N (1) - C (21) - C (22)	120.6 (12)
C (23) - C (22) - C (21)	110.6 (12)	C (22) - C (23) - C (24)	114.0 (13)
C (23) - C (24) - C (25)	111.1 (12)	C (26) - C (25) - C (24)	114.3 (13)
C (25) - C (26) - N (1)	112.5 (12)		

An ORTEP drawing of molecule 3.**46** is shown in Fig 3.10 [selected distances in Table 3.6]. The Sb-O distance of 2.396(4)Å in 3.**46** suggests only a moderate interaction of the Sb atom with the phosphoryl O atom; this distance is much longer than that in $Cl_3P{=}OSbCl_5$ [2.17(2),[31] reflecting the lower acidity of $SbCl_3$ as compared to $SbCl_5$ and thus leading to a weaker Sb-O bond in the former. The Sb-Cl distances are in the normal

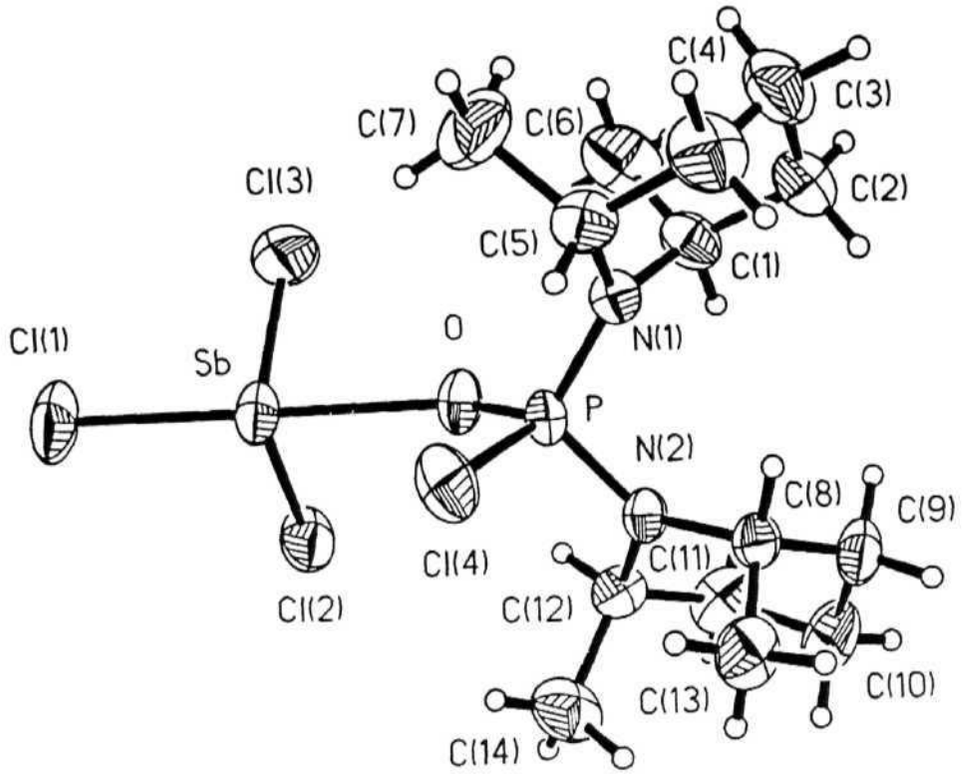


Fig. 3.10 An ORTEP drawing of compound 3.**46**.

Table 3.6 Selected bond lengths [Å] and angles [°] for 3.**46** with esd's in parentheses

Sb - Cl (1)	2.460 (3)	P - O	1.492 (3)
Sb - Cl (2)	2.345 (3)	P - N (1)	1.621 (4)
Sb - Cl (3)	2.348 (3)	P - N (2)	1.613 (4)
Sb - O	2.396 (4)	P Cl (4)	2.037 (3)
Cl (2) - Sb - Cl (3)	95.85 (10)	O - P - N (1)	117.4 (2)
Cl (2) - Sb - O	83.78 (12)	O - P - Cl (4)	106.3 (2)
Cl (3) - Sb - O	83.89 (13)	N (2) - P - Cl (4)	108.9 (2)
Cl (2) - Sb - Cl (1)	92.42 (11)	N (2) - P - N (1)	108.8 (2)
Cl (3) - Sb - Cl (1)	92.10 (12)	N (1) - P - Cl (4)	104.6 (2)
Cl (1) - Sb - O	174.15 (7)	P - O - Sb	133.4 (2)
O - P - N (2)	110.4 (2)		

range.[18] The P=O distance [1.492(3)Å] as well as the P-O-Sb angle [133.4(2)°] are also consistent with mainly σ-donation and moderate or a low π-interaction for the Sb-O bond.

The geometry around antimony, including the lone pair, is distorted trigonal bipyramidal (TBP) [valence shell electron pair repulsion (VSEPR) theory] with the O and Cl(1) atoms *trans* to one another; the deviation from TBP to a square pyramidal structure based on the angles between the planes containing Cl(1), Cl(2), Cl(3) and Cl(2), Cl(3), Cl(4) is *ca* 15%. The Sb-Cl distance [2.460(3)] *trans* to the Sb-O bond is more than the other two Sb-Cl distances [mean; 2.347Å], as expected in the TBP geometry.

3.26 *Conclusions*

The reaction of chlorophosphates with DBU leads to a *phosphonate* salt rather than a *phosphoramidate* salt. This result contrasts with the previously assumed formation of only phosphoramidate salts. In the reactions with other bases like DBN, NMI etc, *pyrophosphates* are the isolable products formed *via* the phosphoramidate salt.

The attempted synthesis of phosphenium salts of type $[(2,6\text{-}Me_2C_5H_8N)_2P]^+[SbCl_6]^-$ by reacting $(2,6\text{-}Me_2C_5H_8N)_2PCl$ with $SbCl_5$ led to the isolation of the adduct $(2,6\text{-}Me_2C_5H_8N)_2PCl(O).SbCl_3$ probably formed by hydrolysis of the phosphenium salt.

3.3 *Experimental*

General description of the experimental methods has already been given in Part 1 (Section 1.3). The compounds $\{CH_2[(t\text{-}Bu)_2C_6H_2OH]_2\}$ (m.p. 147-149°C),[32] $\{CH_2[C_{10}H_6OH]_2\}$ (m.p. 200°C),[33] $(OCH_2CMe_2CH_2O)PCl$ (3.**39**; b.p: 32°C/ 1 mm, δ(P): 120.8)[25] and $(OCH_2CMe_2CH_2O)P(O)(OH)$ (3.**48**, m.p. 174-176°C; δ(P): -4.0)[25] were prepared by literature methods. Other syntheses/ reactions are discussed below.

(i) Preparation of $(OCH_2CMe_2CH_2O)P(O)Cl$ (3.**24**)

2,2-Dimethylpropane-1,3-diol (8.5 g, 82 mmol) in warm benzene (40 cm^3) was added dropwise to a mixture of freshly distilled phosphorus oxychloride (12.5 g, 82 mmol) and pyridine (12.9 g, 160 mmol) in benzene (20 cm^3) at 40-50°C with continous stirring. The mixture was stirred further for 5 h, poured into cold water and the benzene layer was washed with 2N HCl (2 x 25 cm^3) followed by water (2 x 25 cm^3) and dried over anhydrous Na_2SO_4. Solvent was removed *in vacuo* and the residue crystallized from 1,2-dichloroethane to afford 3.**24**.

Yield: 10.2 g, (68%).

M.p. 102-103°C (lit[19]. m.p: 102-103°C)

^1H NMR: 0.87 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 3.80-4.30 (m, 4H, OCH_2)

^{31}P NMR: -3.4 (lit[19]: -3.4).

(ii) Preparation of $CH_2[4,6\text{-}(t\text{-}Bu)_2C_6H_2O]_2P(O)Cl$ (3.**25**)

A mixture of 2,2'-methylene-bis(4,6-di-*t*-butylphenol) (3.0 g, 7 mmol) and triethyl amine (1.43 g, 14 mmol) in benzene (20 cm^3) was added dropwise (10 min.) to phosphorus oxychloride (1.08 g, 7 mmol) at room temperature with continuous stirring. The mixture, after stirring overnight, was filtered and the solvent removed. The residue was crystallized from ether (10 cm^3) to give 3.**25**.

Yield: 3.2 g (83%).

M.p. 207°C.

^{1}H NMR: 1.32 (s, 18H, *t*-Bu-*H*), 1.46 (s, 18H, *t*-Bu-*H*), 4.07 (br, 2H, CH_2), 7.20, 7.30 (s each, 4H, Ar-*H*).

^{31}P NMR: -2.5.

M.S.: 490, 488 [10%, $(M\text{-}CH_3 + H)^+$], 468 [80%, (M-HCl)], 453 [100%, $(M\text{-}HCl\text{-}CH_3)^+$].

Found: C, 68.96; H, 8.38. $C_{29}H_{42}ClO_3P$ requires C, 68.99; H, 8.33 %.

(iii) Preparation of CH_2[4-Me-6-*t*-Bu-C_6H_2O]$_2$P(O)Cl (3.26)

A solution 2,2'-methylene-bis(4-methyl-6-*t*-butyl-phenol) (5.0 g, 14 mmol) and triethylamine (3 g, 30 mmol) in toluene (30 cm^3) was added to phosphoryl chloride (2.14 g, 14 mmol) in toluene (15 cm^3) over a period 30 min at room temperature and the mixture stirred overnight. Filtration followed by concentration afforded 3.**26** (^{1}H and ^{31}P NMR in Fig. 3.11) as a crystalline solid which was recrystallized from toluene.

Yield: 5.3 g (85%).

M.p. 162 - 164°C.

^{1}H NMR: 1.44 (s, 18H, *t*-Bu-*H*), 2.31 (s, 6H, CH_3), 3.85-4.20 (AB qrt., 2H, Ar-CH_2), 7.07, 7.10 (s each, 4H, Ar-*H*).

^{31}P NMR: -3.4.

Found: C, 65.64, H, 7.13. $C_{23}H_{30}ClO_3P$ requires C, 65.80; H, 7.40%.

(iv) Preparation of $[(OCH_2CMe_2CH_2O)P(O)(DBU)]^+Cl^-$ (3.27)

To a solution of 3.**24** (0.77 g, 4.21 mmol) in toluene (10 cm^3) a solution of DBU (0.64 g, 4.21 mmol) in toluene (10 cm^3) was added over a period of 10 min. at 25°C and the mixture stirred overnight. The powder obtained (^{31}P NMR: single peak at 10.7 ppm)

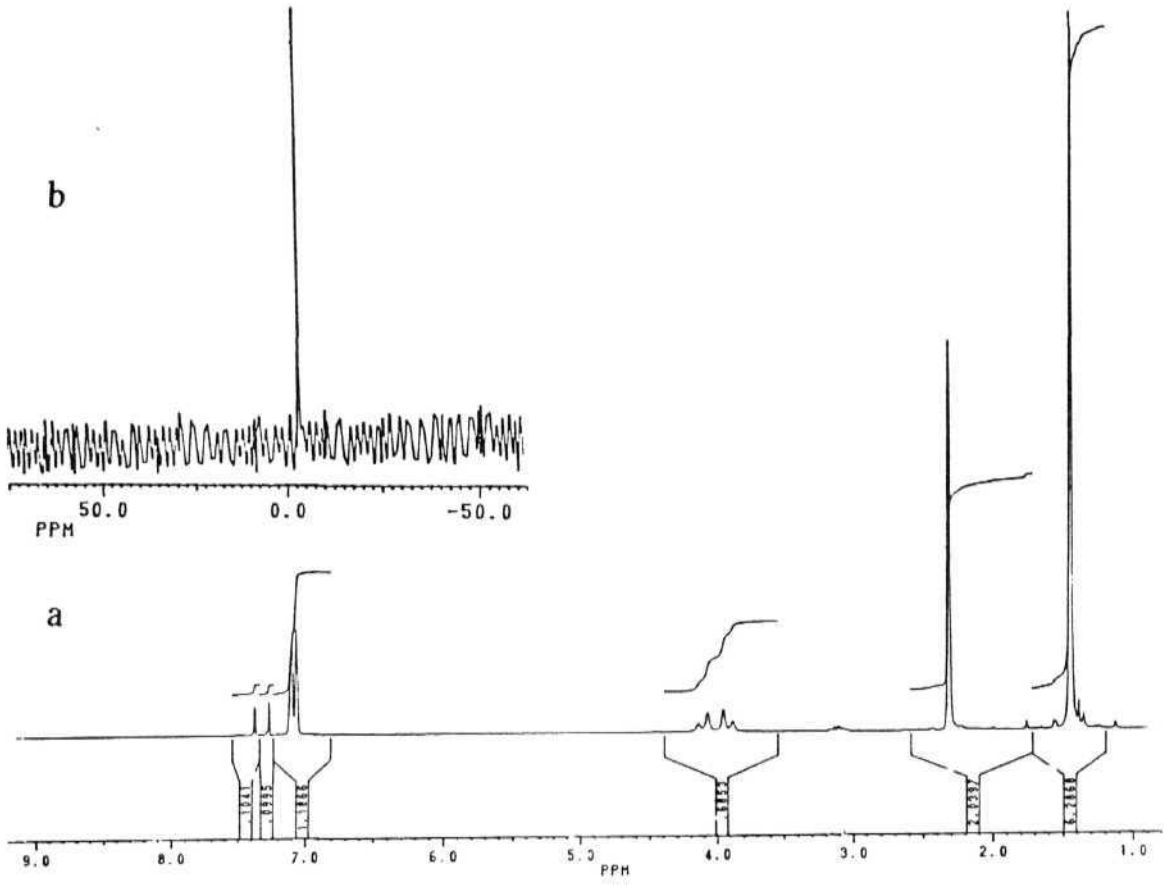


Fig 3.11 a) ^{1}H and b) ^{31}P spectra of 3.**26**.

was filtered and washed with cold toluene (2 x 5 cm^3). Recrystallization was done from hot toluene to obtain 3.**27**·H_2O. The ^{1}H NMR spectrum of the powder (3.**27**) was nearly identical to that of the hydrate (3.**27**·H_2O).

Yield: 1.21 g (84%).

M.p. 184°C.

^{1}H NMR: 0.95 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.64-2.17 (m, 8H, CH_2), 3.00-3.10 (d, $^{2}J \approx 12$ Hz, PC*H*), 3.41-3.92 (m, 6H, NCH_2), 4.67 (d, $^{2}J = 11.1$ Hz, OCH_AH_B), 4.78-4.97 (m, 2H, OCH_2), 5.34 (d, $^{2}J = 11.1$ Hz, OCH_ACH_B), 11.48 (br s, 1H NH^+).

^{13}C NMR: 19.5, 20.0, 22.3, 23.6, 23.6, 24.4, 26.3, 32.8, 33.0, 38.4, 39.4 [^{1}J(P-*C*) = 126.5 Hz], 50.0, 53.3, 78.6, 161.4.

^{31}P NMR: 10.7.

Found: C, 47.88; H, 8.09; N, 8.60. $C_{14}H_{30}ClN_2O_4P$ (with one molecule of water that probably entered during the process of crystallization) requires C, 47.13; H, 8.41; N, 7.85%.

The filtrate showed a small quantity of the pyrophosphate [($OCH_2CMe_2CH_2O$)P(O)]$_2$O (3.**38**, see later).

(v) Preparation of {CH_2[4-Me-6-*t*-Bu-C_6H_2O]$_2$P(O)(DBU)}$^+$Cl$^-$ (3.33) and {CH_2[4-Me-6-*t*-Bu-C_6H_2O]$_2$P(O)}$_2$O (3.34)

To a solution of 3.**26** (0.328 g, 0.78 mmol) in toluene (10 cm^3), a solution of DBU (0.118 g, 0.78 mmol) in toluene (10 cm^3) was added dropwise at 25°C and the mixture was stirred overnight. Upon concentration to *ca* 10 cm^3, compound 3.**33** came out as a solid.

Yield: 0.2 g, (45%).

M.p. 220°C.

^{1}H NMR (Fig. 3.12): 1.38, (s, 9H, *t*-Bu-*H*), 1.42, (s, 9H, *t*-Bu-*H*). 1.80-2.30 (m, 8H, CH_2), 3.20 (br, 2H, CH_2), 3.45-3.60 (m, 6H, NCH_2), 4.90 (d, 1H, Ar-C$H_A$$H_B$), 5.50 (d, 1H, Ar-C$H_A$$H_B$), 7.00-7.25 (m, 4H, Ar-*H*). 11.48 (br, 1H, NH^+). An additional peak of low intensity at 12.00 ppm was also observed.

^{13}C NMR (Fig 3.12): 19.2, 19.6, 20.8, 21.3, 23.3, 24.0, 24.4, 25.3, 26.8, 28.9, 31.0, 31.3, 32.1, 34.6, 34.8, 34.9, 39.1, [^{1}J(P-*C*) = 126.0 Hz], 43.1, 48.8, 49.3, 52.6, 54.4, 125.3, 127.3, 127.4, 128.2, 129.0, 129.2, 134.1, 134.4, 135.3, 137.8, 140.2, 140.6, 144.7, 161.0. A detailed analysis was not possible.

^{31}P NMR: 7.2.

Found: C, 66.56; H, 7.99; N, 4.31. $C_{31}H_{42}N_2O_3PCl$ requires C, 66.81; H, 7.59; N, 5.05%.

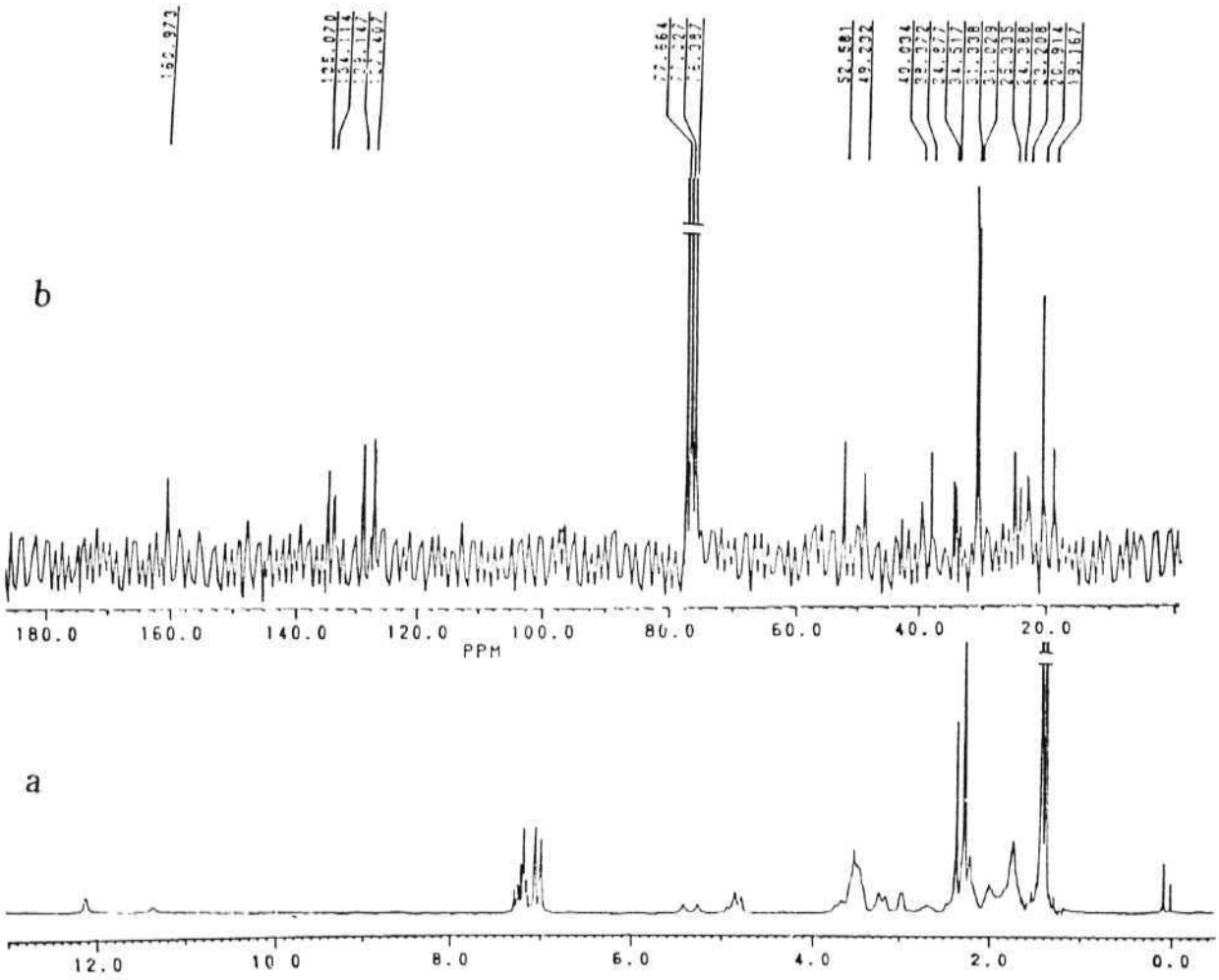


Fig 3.12 a) ^{1}H and b) ^{13}C NMR spectra of 3.**33**.

The residue showed two peaks in ^{31}P NMR (-12.6, -28.6), with the one at -28.6 as the major component. Further concentration of the mother liquor afforded the latter component (pyrophosphate 3.**34**) as a crystalline solid.

Yield: 0.15 g, (33%).

Mp. 276°C.

^{1}H NMR (Fig. 3.13): 1.44 (s, 18H, *t*-Bu-*H*), 2.31 (s, 6H, CH_3), 3.70 (d, ^{2}J = 15 Hz, Ar-CH_AH_B), 4.31 (d, ^{2}J = 15 Hz 1H, Ar-CH_AH_B), 7.21-7.24 (m, 4H, Ar-*H*).

^{13}C NMR (Fig. 3.12): 20.9, 30.9, 34.6, 35.0, 127.7, 129.4, 131.4, 135.2, 141.3, 146.0.

^{31}P NMR: -28.6.

Found: C, 70.43; H, 7.81. $C_{46}H_{60}O_7P_2$ requires C, 70.23; H, 7.63%.

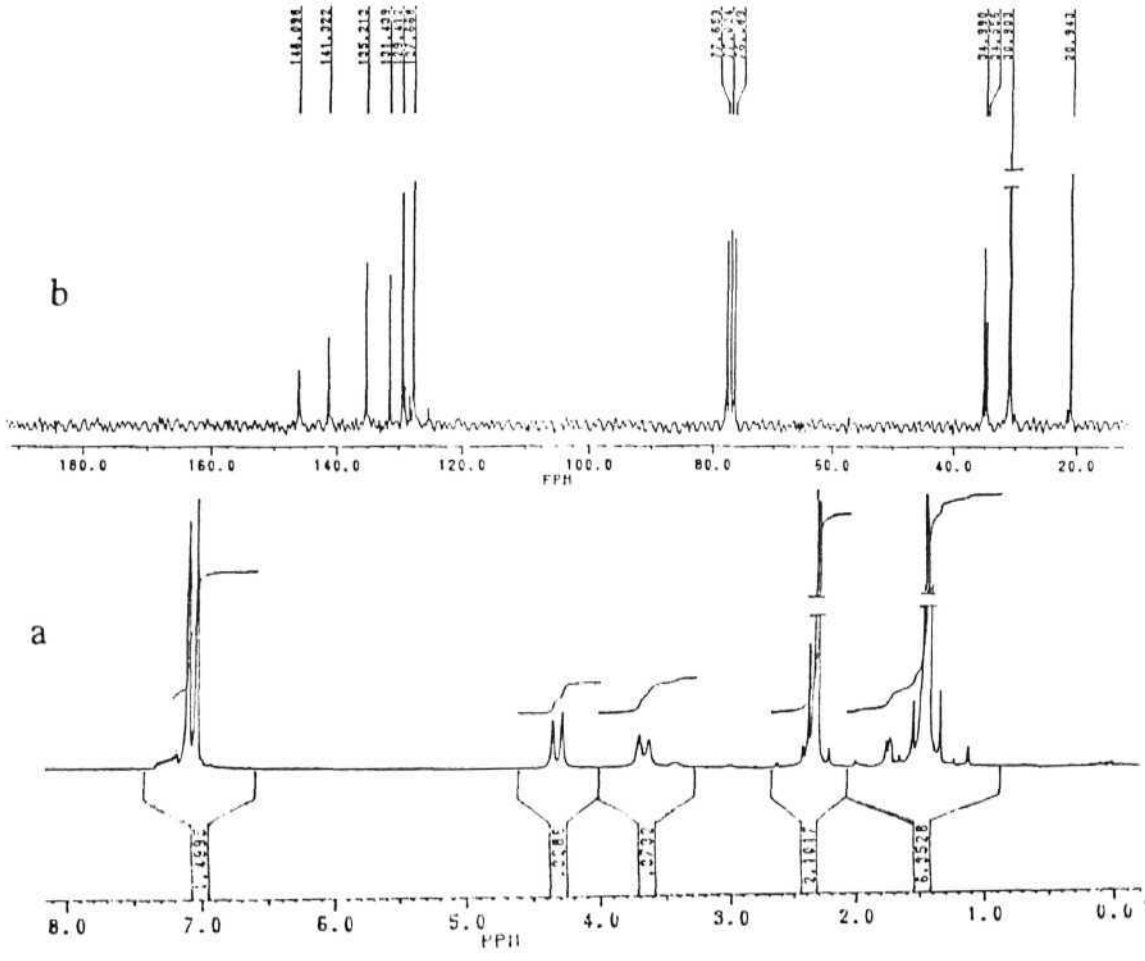


Fig 3.13 a) ^{1}H and b) ^{13}C NMR spectra of 3.**34**.

(vi) Reaction of $(OCH_2CMe_2CH_2O)P(O)Cl$ (3.24) with other bases [DBN, N-methylimidazole, imidazole and 4-dimethylaminopyridine]. Synthesis of $[(OCH_2CMe_2CH_2O)P(O)(DBN)]^+Cl^-$ (3.37) and $[(OCH_2CMe_2CH_2O)P(O)]_2O$ (3.38)

These reactions were conducted in a manner analogous to that given in **(iv)**. A phosphonate salt analogous to 3.**27** was not detected. The pyrophosphate $[(OCH_2CMe_2CH_2O)P(O)]_2O$ (3.**38**) was obtained as the end product in all the reactions except in the case of DBN. It was isolated in several instances in yields of *ca* 50%, after removing the less soluble portions.

M.p. 193-195°C (lit.[24] m.p: 194-196°C).

^{1}H NMR: 0.90 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 3.80-4.20 (m, 2H, OCH_2), 4.45 (d, ^{3}J(P-H) ≈ 10Hz, 2H, OCH_2).

^{13}C NMR: 19.9, 21.8 (both CH_3), 32.1 (CMe_2), 79.0 (OCH_2).

^{31}P NMR: -21.9 (lit.[24] -21.9).

a) In the reaction of 3.**24** with DBN, the reaction mixture initially showed two peaks in the ^{31}P NMR at -6.8 and -12.0 ppm; the compound 3.**37** corresponding to the former was isolated as a crystalline solid.

Yield: 0.35 g, (53%).

M.p. 134°C.

^{1}H NMR: 1.00 (s, 6H, CH_3), 2.00-2.20 (m, 6H, CH_2), 3.20-3.80 (m, 10H, NCH_2, OCH_2).

^{13}C NMR: 18.7, 19.3, 22.4 (s each, two CH_3 and a CH_2), 33.2 (CH_2), 36.7 (CMe_2), 43.8 [^{2}J (P-C) = 18.0 Hz, NCH_2], 52.4 (NCH_2), 54.2 (NCH_2), 70.3 (d, J = 6.5 Hz, OCH_2), 167.9 (J = 9.0 Hz, N=C).

^{31}P NMR: -6.8.

Elemental analysis could not be obtained due to moisture sensitivity.

(b) In the reaction of 3.**24** with N-methylimidazole in toluene, the solid which precipitated out showed peaks at -11.4 (>90%) and -21.9 (3.**38**, *ca* 10%) in the ^{31}P NMR. the intensity of the peak at -21.9 increased with time and over a period of 9 days, was found to be the major product (>50%).

(c) The precipitate obtained in the reaction of 3.**24** with imidazole showed two peaks at -14.3 and -22.1 ppm (3.**38**) (solvent $CDCl_3$ + DMSO-d_6). Compound 3.**38** could be isolated (see above for details).

(d) The solid obtained by reacting 3.**24** with 4-dimethylaminopyridine showed mainly two peaks at -7.1 ppm (unassigned) and -21.9 ppm (3.**38**); only 3.**38** could be isolated (see above for spectral data).

(vii) Reaction of {[CH_2(4,6-(*t*-Bu)$_2$-C_6H_2O)$_2$]P(O)Cl (3.25) with bases (DBU, DBN, N-methylimidazole and 4-dimethylaminopyridine)

As in the case of the reactions given in (**vi**), the pyrophosphate {[CH_2(4,6-(*t*-Bu)$_2$-C_6H_2O)$_2$]$_2$P(O)}$_2$O (3.**35**) was a product that could be readily identified; in the reaction with 4-dimethylaminopyridine it could be isolated readily (yield ≈ 40%).

M.p.. 220°C.

^{1}H NMR: 1.30 (s, 18H, *t*-Bu-*H*), 1.45 (s, 18H, *t*-Bu-*H*), 3.75 (d, ^{2}J = 11.9 Hz Ar-C$H_A$$H_B$), 4.41 (d, ^{2}J = 11.9 Hz, Ar-CH_ACH_B), 7.20, 7.30 (s each, 4H, Ar-*H*).

^{31}P NMR: -28.5.

Found: C, 72.90; H, 8.86. $C_{55}H_{84}O_7P_2$ requires C, 72.77; H, 9.36%

In the reaction of 3.**25** with DBU, DBN and N-methylimidazole, the other major product showed a ^{31}P NMR peak at *ca* -11 ppm; in the case of the DBU reaction the compound isolated was found to be {[CH_2(4,6-(*t*-Bu)$_2$$C_6H_2O$)$_2$]$PO_2^-$}[DBU.H]$^+$·1.5$H_2O$ (3.**36**·1.5H_2O). An X-ray structure is available for this compound.

M.p. 200°C (dec.).

^{1}H NMR (Fig. 3.14): 1.29 (s, 18H, *t*-Bu-*H*), 1.48 (s, 18H *t*-Bu-*H*), 1.55-2.10 (m, 6H, CH_2), 2.70-2.80 (m, 2H, CH_2), 3.15-3.50 (m, 6H, NCH_2), 4.08 (br, 2H, Ar-CH_2), 7.20 (s, 4H, Ar-*H*).

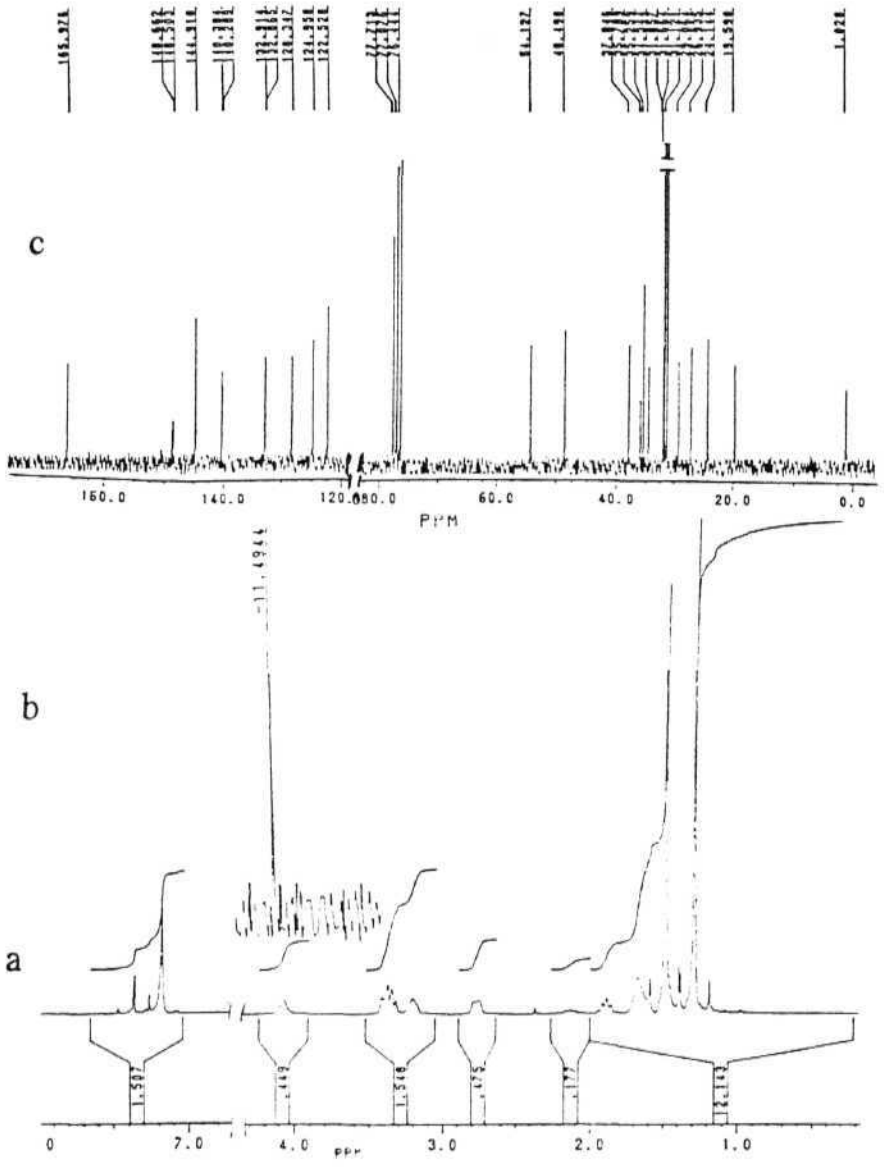


Fig 3.14 a) ^{1}H, b) ^{31}P and c) ^{13}C NMR spectra of 3.**36**.

^{13}C NMR (Fig. 3.14): 19.6, 24.1, 26.9, 29.1, 31.1, 31.7, 31.9, 34.3, 35.3, 35.8, 37.8, 48.5, 54.1, 122.5, 125.0, 128.3, 132.9 (d, J ≈ 3 Hz), 140.3(d, J ≈ 5 Hz), 144.9, 148.6 (d, J = 7.0 Hz), 166.0 (N=*C*).

^{31}P NMR(Fig. 3.14): -11.4.

(viii) Reaction of the phosphate ($OCH_2CMe_2CH_2O$)P(O)(OH) (3.48) with bases

The phosphate and the bases (DBU, NMI, DBN, IM or DMAP) were mixed in 1:1 stoichometry in dichloromethane. Slow evaporation of the solvent afforded an oil or solid which were checked by ^{31}P NMR. No clearcut changes that could be used for further analysis were observed in the ^{1}H NMR spectra; the N^+H proton was probably too broad to be located clearly.

(3.**48** + DBU) product: oil, ^{31}P NMR: -4.4.

(3.**48** + NMI) product: m.p. 82°C; ^{31}P NMR: -4.7.

(3.**48** + DBN) product: oil, ^{31}P NMR: -4.2.

(3.**48** + IM) product: oil, ^{31}P NMR: -4.6.

(3.**48** + DMAP) product: M.p. 116°C; ^{31}P NMR: -3.5.

(ix) Reaction of benzoylchloride with DBU

Using the same procedure as in (iv) above, benzoylchloride was treated with DBU [^{1}H NMR: 1.30 - 1.50 (br, 6H, CH_2), 1.60 (qrt, 2H, CH_2), 2.35 (br m, 2H, C=CH_2), 3.00 - 3.20 (m, 6H, NCH_2). ^{13}C NMR: 22.3, 25.6, 28.4, 29.6, 37.0, 43.9, 48.3, 52.8, 161.4]. A precipitate was formed immediately ^{1}H NMR: 1.60 - 4.30 (br, many peaks, 16H, 8CH_2), 7.10 - 8.30 (m, 5H, Ar-*H*), 12.0 (br s,*ca* N*H*$^+$?). ^{13}C NMR: 19.5, 24.0, 25.5, 26.1, 28.1, 28.8, 28.9, 32.1, 37.9, 48.1, 48.8, 53.9, 54.4, 67.8, 119.9, 128.4, 128.8, 129.8, 130.6, 134.1, 160.7, 164.7, 166.3. See Results and Discussion for comments.

This precipitate slowly became a semisolid over a period of 6 h and was not analysed further.

(x) Synthesis of $[C_5H_8(Me)_2N]_2PCl$ (3.45)

A mixture of *cis*-2,6-dimethyl piperidine (8.2 g, 72 mmol) and triethylamine (7.3 g, 72 mmol) in hexane (50 cm^3) was added dropwise to a solution of phosphorus trichloride (4.98 g, 36 mmol) in hexane (100 cm^3) at 25°C with continuous stirring. The reaction mixture was heated under reflux for 48 h and filtered. Evaporation of the solvent followed by vacuum distillation afforded 3.**45** as a liquid.

Yield: 6.86 g (65%).

B.p. 100°C/ 3mm.

^{1}H NMR: 1.22 (s, 6H, C*H*$_3$), 1.24 (s, 6H, C*H*$_3$), 1.25 - 1.80 (m, 12H, C*H*$_2$), 3.70 - 3.90 (br, 4H, NC*H*).

^{31}P NMR: 156.5.

The compound was too air sensitive in our hands to obtain CHN analysis.

(xi) Reaction of chlorophosphorus(III) compounds with bases

These reactions were conducted in methyl cyanide following the procedure of Bertrand and coworkers,[14] using 1:1 stoichiometry of the reactants; no product was isolated. Some details are given below.

(a) Compound 3.**39** + DBU: ^{31}P NMR (reaction mixture): 145.5 (s), 108.2 (s), 2.4 [s, assigned to $(OCH_2CMe_2CH_2O)P(O)H$ (3.**41**).[25]].

(b) Compound $[CH_2(4\text{-Me-6-}t\text{-Bu-}C_6H_2O)]PCl$ (3.**40**) δ(P): 153.0 ppm + DBU: ^{31}P NMR (reaction mixture): 170.1, 124.7 (major), 0.1 $\{[CH_2(4\text{-Me-6-}t\text{-Bu-}C_6H_2O)_2]P(O)H\}$ (3.**44**).[25]

(c) Compounds 3.**40** + DMAP: ^{31}P NMR (reaction mixture): 124.6, 0.1 {[CH_2(4-Me-6-*t*-Bu-$C_6H_2O)_2$]P(O)H} (3.**44**).

(xii) Reaction of chlorophosphorus(III) compounds 3.39 and 3.45 with antimony pentachloride (a Lewis acid)

(a) Preparation of $[C_5H_8Me)_2N]_2PCl(O).SbCl_3$ (3.**46**)

A solution of antimony pentachloride (prepared by reacting the trichloride with excess of chlorine) (0.52 g, 1.75 mmol) in dichloromethane (10 cm^3) was added dropwise with continuous stirring to a solution of 3.**45** (0.50 g, 1.75 mmol) in dichloromethane (10 cm^3) maintained at -78°C. After stirring for a further 2 h, the solvent was completely removed to give an oil [^{31}PNMR, 43.8, 24.6]. Attempted crystallization from acetonitrile-hexane (1:10) afforded a small quantity of 3.**46**.

Yield: 0.1g (10%).

M.p.: 146-148°C.

^{1}H NMR: 1.31 (s, 6H, C*H*$_3$), 1.42 (s, 6H, C*H*$_3$), 1.45 - 2.10 (m, 12H, C*H*$_2$), 3.85 - 4.10 (m, 4H, C*H*N*H*).

^{31}PNMR: 23.3. [The slight difference in the chemical shift from the reaction mixture is probably due to the influence of solvent or other products].

Found: C, 31.08; H, 5.30; N, 4.90. $C_{14}H_{28}Cl_4N_2OPSb$ requires C, 31.40; H, 5.20; N, 5.20%.

(b) Reaction of $(OCH_2CMe_2CH_2O)PCl$ (3.**39**) *with* $SbCl_5$

From this reaction no clearcut product could be isolated. ^{31}PNMR: [reaction mixture, 145.6, 16.7, (15%) 2.3 [15%, $(OCH_2CMe_2CH_2O)P(O)H$, 3.**41**].

(xiii) Reaction of 3.24 with $SbCl_3$: Isolation of the adduct $[(OCH_2CMe_2CH_2O)P(O)Cl]_2.SbCl_3$ (3.47)

Compound 3.**24** (0.46 g, 2.02 mmol), was reacted with antimony trichloride (0.46 g, 2.02 mmol) in ether (10 + 10 cm^3) for 24 h. Slow removal of solvent afforded 3.**47** as a hygroscopic crystalline solid.

Yield: 0.49 g (65%).

M.p. 60°C.

^{1}H NMR: 0.95 (s, 3H, C*H*$_3$), 1.35 (s, 3H, C*H*$_3$), 3.90 - 4.36 (m, 4H, OC*H*$_2$).

^{31}P NMR: -3.4.

Found: C, 19.70; H, 3.25. $C_{10}H_{20}Cl_5O_6P_2Sb$ requires C, 19.57; H, 3.26%.

X-ray Crystallography

X-ray data were collected after a) mounting the crystal at the end of the glass fibre (3.**27**·H_2O and 3.**34**) or b) inserting the crystal inside a Lindemann capillary (3.**36**·1.5H_2O and 3.**46**). All data were collected using MoKα (λ = 0.7107Å) radiation at 293(2)K. The structures were solved and refined by using standard methods [SHELXTL for 3.**27**·H_2O; SHELX86 and SHELXL93 for 3.**34** and 3.**46**; SHELX97 for 3.**36**·1.5H_2O].

For 3.**27**·H_2O all nonhydrogen atoms were refined anisotropically; some of the H atoms were located successfully. The positional and common isotropic thermal parameters of the H atoms attached to O(4) were refined and a riding model was used to place the rest of the hydrogen atoms in their idealized positions. Two orientations were found for C(7) [see.Fig 3.5 in Results and Discussion]. For 3.**34** all non-hydrogen atoms were refined anisotropically. H atoms were fixed by geometry using a riding model and not refined.

For 3.**36**·1.5H_20, the number of observed data was not sufficient to make all the non-hydrogen atoms anisotropic and hence only phosphorus, the four oxygens connected to phosphorus and the C atoms of the DBU ring were refined anisotropically. Two

oxygen atoms [O(5) and O(6)] were located in the Difference Fourier map, with one of them O(5) having half occupancy. Thus the asymmetric unit was assumed to contain $1.5 \cdot H_2O$ per molecule. While the O(6) was found related to another O(6) from a different asymmetric unit [O(6) - O(6A) 2.388Å], O(5) was symmetrically H bonded to O(4) [O(5) - O(4) 2.971Å]. The quality and amount of the data as well as high thermal parameters for some of the *t*-butyl carbons [at C(15) and C(16)] and the water molecules resulted in a rather high R value for this structure.

For 3.**46** all non-hydrogen atoms were refined anisotropically. H atoms were fixed by geometry using a riding model and not refined.

Further details on these compounds are given in Table 3.7.

Table 3.7 Crystal data for compounds 3.**27**·H_2O, 3.**34**, 3.**36**·1.5H_2O and 3.**46**

Compound no.	3.**27**·H_2O	3.**34**	3.**36**·1.5H_2O	3.**46**
Emp. formula	$C_{14}H_{28}ClN_2O_4P$	$C_{23}H_{30}O_{3.5}P$	$C_{38}H_{62}N_2O_{5.5}P$	$C_{14}H_{28}ClN_2OP{\cdot}SbCl_3$
Formula wt.	354.8	393.44	665.87	534.9
Diffractometer used	Siemens SMART CCD	Enraf Nonius MACH3	Enraf Nonius MACH3	Siemens-Stoe AED2
Crystal system	Monoclinic	Tetragonal	Orthorhombic	Triclinic
Space group	C2/c	P4	P*cca* (No. 54)	$P\bar{1}$
a/ Å	20.7477(3)	15.996(2)	38.3710(11)	10.092(11)
b/ Å	9.6620(1)	15.996(2)	18.3548(10)	10.514(11)
c/ Å	18.1810(3)	9.3227(7)	11.408(2)	12.415(14)
α/ °	90.0	90.0	90.0	70.53(8)
β/ °	95.733(1)	90.0	90.0	71.81(8)
γ/ °	90.0	90.0	90.0	61.85(7)
V/ $Å^3$	3626.41(8)	2385.4(5)	8034.9(16)	1076(2)
Z	8	4	8	2
Crystal size	0.32 x 0.28 x 0.27	0.4 x 0.3 x 0.3	0.5 x 0.4 x 0.4	0.3 x 0.2 x 0.2
D calc/ mgm^{-3}	1.300	1.096	1.101	1.651
μ / mm^{-1}	0.317	0.135	0.110	1.857

contd....

Table 3.7 contd...

Indep. refl.	4347 (Rint = 0.0189)	1680 (Rint = 0.0569)	5148 (Rint = 0.000)	2820 (Rint = 0.000)
Data/ restraints parameters	4347/ 6/ 220	1680/ 0/ 249	5148/ 0/ 279	2820/ 0/ 208
GOOF on F^2	1.032	1.573	1.233	1.147
R1[$I > 2\sigma(I)$]	0.0483[a] (3472 refl)	0.0698	0.1159[b] (obsd data 1823)	0.0322
wR2	0.1173	0.1811	0.3112	0.0853
Largest diff. peak and hole $eÅ^{-3}$	0.31/ -0.33	0.751/ -0.233	0.846/ -0.4	0.966/ -1.289
θ range	1.97-29.19	2.18-22.52	2.12-22.47	1.5-22.5

[a]An absorption correction {SADABS(Sheldrick, 1996) was applied. Max. and Min. transmission 0.945 and 0.830. Also an extinction correction of 0.0002(2) was applied.

[b]Two reflections omitted because they were found to be totally inconsistent with the data.

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APPENDIX

Selected atomic coordinates for compounds 1.**99**.1/2$C_4H_8Cl_2$, 1.**100**, 1.**101**, 1.**102**, 1.**103**, 2.**38**, 2.**47**.1/2C_6H_6, 2.**48**, 2.**59**, 2.**61**, 3.**27**.H_2O, 3.**34**, 3.**36**.1.5H_2O and 3.**46**. Except for 1.**99**, 1.**100**, 2.**47** and 3.**46** the coordinates are multiplied by 10^4 and isotropic thermal parameters are multiplied by 10^3.

Compound 1.**99**.1/2$C_4H_8Cl_2$

	x	y	z	Uiso
P2	1.18479	.47507	.63626	.04529
P4	1.37354	.62997	.76728	.05998
P6	1.24306	.61028	.88427	.03952
P8	1.03999	.46327	.75264	.03320
CL21	1.20252	.31779	.56212	.07814
CL22	1.14388	.57404	.56057	.10426
CL41	1.39381	.76700	.72743	.12464
CL42	1.54768	.59514	.80839	.10905
CL61	1.17664	.73817	.96091	.06770
CL62	1.36238	.54665	.96308	.07098
CL01	.51043	.24863	.49045	.13319
O1	.91919	.53384	.75296	.03392
O2	.99854	.33271	.74459	.03827
N1	1.07346	.46615	.67181	.04415
N3	1.31726	.51678	.69516	.05137
N5	1.31303	.67698	.84105	.04881
N7	1.14072	.50587	.83573	.03579
C1	.88554	.61195	.82262	.02722
C2	.85868	.72420	.82069	.03937
C3	.82548	.79807	.88898	.04608
C4	.81884	.75452	.95405	.03814
C5	.84208	.64028	.95251	.02990
C6	.87500	.56325	.88538	.02497
C7	.90218	.43851	.88498	.03125
C8	.87895	.28758	.74352	.03939
C9	.81731	.19145	.67679	.03600
C10	.70158	.15266	.67970	.03797
C11	.64895	.20293	.74291	.04015
C12	.71420	.29491	.80988	.04391
C13	.83288	.34174	.81076	.03619
C211	.86028	.77145	.74888	.06320
C41	.78790	.83783	1.02804	.07738
C91	.87149	.12852	.60421	.04107
C111	.52229	.15388	.74789	.05376
C14	.99239	.77942	.73757	.08964
C15	.78034	.69552	.66860	.09007
C16	.81714	.89363	.75718	.12586
C17	1.00206	.08972	.63767	.06629
C18	.87740	.21212	.55286	.06005
C19	.79073	.01701	.54768	.06439
C20	.66887	.86523	1.01148	.35991
C21	.80605	.80053	1.10018	.26231
C22	.84986	.94614	1.05651	.45244
C23	.44546	.25909	.76424	.12780
C24	.53823	.10238	.81612	.09713
C25	.46134	.06138	.66978	.11777
C026	.47917	.48997	.53281	.14061
C027	.54828	.38995	.56574	.12092

Compound 1.**100**

	x	y	z	U_iso
P2	.26496	.44074	.88565	.03328
P4	.32880	.36563	.70767	.03833
P6	.06750	.34138	.59292	.03397
P8	.01192	.37299	.80754	.03315
CL21	.38035	.45200	1.04720	.05400
CL22	.26343	.55161	.82801	.06989
CL41	.44836	.43192	.66359	.07863
CL42	.40746	.25964	.71980	.08393
CL61	.04744	.22916	.54216	.07451
CL62	-.04737	.39520	.45263	.05977
N1	.13383	.41913	.88377	.04176
N3	.33897	.38622	.83110	.04836
N5	.20287	.36897	.60509	.04593
N7	.01822	.35083	.68837	.05820
N11	-.00570	.29331	.87263	.05270
N31	-.11370	.42534	.78727	.04126
C41	-.19806	.41144	.84678	.10001
C51	-.20821	.33335	.88226	.09905
C61	-.10361	.28065	.91213	.20236
C1	.09923	.23592	.90371	.06487
C2	.05788	.15537	.85561	.08900
C3	.17088	.23325	1.03207	.0845
C4	-.12412	.50128	.72684	.05134
C5	-.24525	.50758	.62872	.07350
C6	-.09999	.57126	.80789	.08604

Compound 1.**101**

	x	y	z	U(eq)
P(2)	-81(1)	5723(1)	1964(1)	37(1)
P(4)	2490(1)	6316(1)	1610(1)	34(1)
P(6)	2086(1)	5268(1)	328(1)	37(1)
P(8)	203(1)	4247(1)	1042(1)	34(1)
Cl(21)	-1384(2)	6410(1)	1386(2)	103(1)
Cl(22)	-984(3)	5694(1)	2953(1)	110(1)
Cl(61)	1329(3)	6113(1)	-341(1)	101(1)
Cl(62)	3523(2)	4866(2)	-342(1)	89(1)
N(3)	1171(4)	6223(3)	2088(2)	39(1)
N(5)	2789(4)	5631(3)	1013(2)	44(1)
N(7)	1058(6)	4597(4)	392(3)	71(2)
N(1)	-122(5)	4880(3)	1663(3)	52(1)
N(11)	2532(5)	7182(3)	1187(3)	49(1)
N(31)	3747(4)	6342(3)	2190(2)	47(1)
N(12)	-1165(5)	3873(3)	714(3)	51(1)
N(32)	928(5)	3482(3)	1426(3)	54(1)
C(61)	3834(6)	7351(4)	854(4)	60(2)
C(51)	4942(7)	7325(5)	1422(4)	71(2)
C(41)	5021(6)	6546(5)	1844(4)	64(2)
C(1)	1680(7)	7855(3)	1409(4)	61(2)
C(2)	1182(12)	8250(5)	705(6)	112(4)
C(3)	2307(11)	8438(5)	1925(6)	102(3)
C(4)	3821(6)	5815(4)	2845(3)	57(2)
C(5)	4710(8)	5106(5)	2737(5)	88(3)
C(6)	4201(9)	6299(5)	3511(4)	83(2)
C(42)	427(15)	2710(5)	1380(9)	178(8)
C(52)	-556(12)	2500(4)	917(7)	126(4)
C(62)	-1267(11)	3055(4)	481(6)	113(4)
C(10)	2140(6)	3620(4)	1847(4)	60(2)
C(11)	1967(10)	3488(7)	2655(5)	102(3)
C(12)	3275(9)	3156(7)	1536(7)	117(4)
C(7)	-2220(6)	4414(4)	481(4)	69(2)
C(8)	-2478(9)	4419(6)	-326(5)	93(3)
C(9)	-3497(10)	4206(12)	895(6)	187(8)

Compound 1.**102**

	x	y	z	U(eq)
P(6)	3266(1)	1574(1)	5804(1)	45(1)
P(4)	1722(1)	3035(1)	4942(1)	53(1)
P(2)	2545(1)	1354(1)	3810(1)	56(1)
Cl(41)	214(1)	3101(2)	5443(1)	90(1)
Cl(21)	1798(2)	-8(2)	3243(2)	107(1)
Cl(22)	3471(2)	1768(2)	2637(1)	102(1)
Cl(42)	1938(2)	4683(1)	4608(1)	93(1)
N(5)	2512(3)	2697(3)	5796(3)	52(1)
N(3)	1683(3)	2325(4)	3933(3)	72(1)
N(1)	3255(3)	973(3)	4705(3)	53(1)
N(11)	2857(3)	706(4)	6664(3)	61(1)
N(31)	4493(3)	1899(3)	6115(3)	52(1)
C(61)	3574(5)	152(6)	7385(5)	88(2)
C(51)	4461(6)	834(7)	7691(5)	99(2)
C(41)	5074(5)	1403(7)	6947(5)	96(2)
C(1)	1709(4)	405(5)	6676(4)	66(1)
C(2)	1524(5)	-871(6)	6598(5)	93(2)
C(3)	1166(6)	933(7)	7586(6)	111(2)
C(4)	5105(4)	2603(5)	5413(4)	64(1)
C(5)	5425(8)	3718(6)	5859(7)	131(3)
C(6)	6043(7)	2007(7)	4981(7)	140(4)

Compound 1.**103**

	x	y	z	U(eq)
P(1)	288(1)	2485(1)	1589(1)	46(1)
P(2)	524(1)	1039(1)	1082(1)	35(1)
Cl(1)	1567(1)	2155(1)	2081(1)	81(1)
Cl(2)	-1151(1)	2522(1)	2040(1)	87(1)
Cl(3)	-517(1)	513(1)	592(1)	48(1)
O(1)	545(3)	3222(2)	1392(2)	87(1)
O(2)	582(2)	525(1)	1561(1)	40(1)
O(3)	1779(2)	1104(1)	831(1)	35(1)
N(1)	55(3)	1823(2)	1212(1)	44(1)
C(1)	486(3)	-280(2)	1573(1)	39(1)
C(2)	-509(4)	-595(2)	1816(1)	43(1)
C(3)	-544(4)	-1378(2)	1792(2)	50(1)
C(4)	320(4)	-1818(2)	1563(1)	47(1)
C(5)	1319(4)	-1464(2)	1364(1)	47(1)
C(6)	1432(3)	-682(2)	1367(1)	40(1)
C(7)	-1442(4)	-134(2)	2108(2)	51(1)
C(8)	-2150(4)	388(3)	1762(2)	68(1)
C(9)	-823(5)	324(3)	2524(2)	68(1)
C(10)	-2355(5)	-652(3)	2366(2)	78(2)
C(11)	2350(3)	608(2)	477(1)	32(1)
C(12)	2594(3)	886(2)	-5(1)	35(1)
C(13)	3184(3)	373(2)	-320(1)	40(1)
C(14)	3516(3)	-346(2)	-171(2)	41(1)
C(15)	3293(3)	-568(2)	321(1)	41(1)
C(16)	2721(3)	-92(2)	657(1)	35(1)
C(17)	2312(3)	1688(2)	-184(1)	43(1)
C(18)	2787(5)	1839(3)	-717(2)	72(2)
C(19)	2872(5)	2271(2)	171(2)	67(1)
C(20)	953(4)	1822(3)	-211(2)	62(1)
C(21)	2583(3)	-304(2)	1209(1)	42(1)
C(22)	205(5)	-2670(2)	1541(2)	66(1)
C(23)	4154(4)	-862(2)	-542(2)	57(1)

Compound 2.**38**

	x	y	z	U(eq)
P(1)	2470(1)	6846(1)	1825(1)	48(1)
P(2)	1675(1)	6938(1)	2917(1)	50(1)
O(1)	3133(1)	5534(1)	1791(1)	50(1)
O(2)	1735(1)	5574(1)	3293(1)	56(1)
N(1)	1276(1)	6466(2)	2082(1)	51(1)
N(2)	2917(1)	7128(2)	2683(1)	51(1)
C(1)	141(2)	6520(2)	1640(1)	60(1)
C(2)	-619(2)	5827(4)	2001(2)	109(1)
C(3)	175(2)	5934(3)	946(1)	95(1)
C(4)	-237(2)	7836(3)	1518(2)	94(1)
C(5)	3851(2)	7927(2)	3008(1)	63(1)
C(6)	3426(11)	9277(9)	2877(8)	123(4)
C(7)	4803(8)	7771(13)	2669(6)	110(4)
C(8)	4148(10)	7697(11)	3818(6)	87(3)
C(6')	3881(21)	9120(22)	2754(15)	158(12)
C(7')	4877(13)	7136(26)	2891(15)	156(10)
C(8')	3972(22)	7896(26)	3687(11)	146(11)
C(11)	3041(2)	4909(2)	1165(1)	48(1)
C(12)	2515(2)	3780(2)	1115(1)	58(1)
C(13)	2451(2)	3125(2)	504(2)	73(1)
C(14)	2897(2)	3573(3)	-21(1)	79(1)
C(15)	3430(2)	4676(2)	46(1)	68(1)
C(16)	3525(2)	5374(2)	644(1)	54(1)
C(17)	2066(2)	3272(2)	1706(2)	79(1)
C(18)	4164(2)	6557(2)	726(1)	72(1)
C(21)	2143(2)	5434(2)	4003(1)	52(1)
C(22)	3113(2)	4767(2)	4202(1)	61(1)
C(23)	3543(2)	4612(2)	4903(1)	77(1)
C(24)	3025(3)	5083(3)	5388(1)	85(1)
C(25)	2049(3)	5700(3)	5183(1)	83(1)
C(26)	1572(2)	5881(2)	4484(1)	66(1)
C(27)	3668(2)	4206(3)	3670(2)	85(1)
C(28)	469(3)	6500(3)	4266(2)	101(1)

Compound 2.47.1/2C_6H_6

	x	y	z	U_{iso}
	U_{11}	U_{22}	U_{33}	U_{12}
ATOM P2	.46741	.78889	.80012	.03998
UIJ P2	.03205	.03897	.04892	-.00302
ATOM P4	.58810	.59483	.84072	.03811
UIJ P4	.03202	.03945	.04286	-.00435
ATOM O1	.53147	.86706	.69452	.04191
UIJ O1	.03359	.03775	.05441	-.00462
ATOM O2	.73090	.54001	.76821	.04385
UIJ O2	.03235	.03910	.06008	.00158
ATOM N1	.47496	.66763	.76931	.03794
UIJ N1	.02754	.03783	.04844	-.00335
ATOM N3	.61131	.72080	.84656	.04016
UIJ N3	.03611	.04061	.04378	-.00542
ATOM C1	.66487	.90318	.66786	.03775
UIJ C1	.03745	.03701	.03879	-.00779
ATOM C2	.66813	1.01052	.66846	.04201
UIJ C2	.04646	.03707	.04250	-.00494
ATOM C3	.80470	1.03787	.65392	.04827
UIJ C3	.05489	.03441	.05549	-.01349
ATOM C4	.93043	.96523	.63676	.04670
UIJ C4	.04534	.04501	.04974	-.01348
ATOM C5	.92067	.86419	.62656	.04374
UIJ C5	.03579	.04429	.05116	-.00427
ATOM C6	.78896	.83137	.63945	.03723
UIJ C6	.03844	.03497	.03828	-.00600
ATOM C7	.77632	.72751	.61177	.03931
UIJ C7	.03646	.03960	.04186	-.00596
ATOM C8	.86532	.54633	.70370	.03643
UIJ C8	.02727	.03969	.04233	-.00290
ATOM C9	.96953	.45440	.71461	.04028
UIJ C9	.03141	.03930	.05013	-.00199
ATOM C10	1.09850	.45465	.64313	.04449
UIJ C10	.03229	.04135	.05984	.00452
ATOM C11	1.12690	.53667	.56487	.04455
UIJ C11	.03456	.04882	.05027	-.00630
ATOM C12	1.02206	.62447	.55867	.04389
UIJ C12	.04486	.04350	.04331	-.01190
ATOM C13	.88959	.63213	.62788	.03758
UIJ C13	.03409	.03772	.04095	-.00442
ATOM C14	.35966	.63037	.74193	.04640
UIJ C14	.02970	.04936	.06016	-.00601
ATOM C15	.66106	.74509	.92819	.05384
UIJ C15	.05758	.05480	.04915	-.01262
ATOM C16	.41141	.51688	.72418	.06468
UIJ C16	.05920	.05547	.07936	-.01378
ATOM C17	.22471	.63098	.82389	.13150
UIJ C17	.04268	.17886	.17296	-.04475
ATOM C18	.33724	.70280	.64722	.12578
UIJ C18	.15081	.06701	.15953	-.02905
ATOM C19	.81877	.70030	.91196	.15605
UIJ C19	.08605	.20188	.18021	.04616
ATOM C20	.56972	.70160	1.02656	.12604
UIJ C20	.19971	.13644	.04196	-.09885
ATOM C21	.64307	.86514	.92012	.09591
UIJ C21	.13990	.06975	.07808	-.03731
ATOM C22	1.07795	.27120	.79396	.07104
UIJ C22	.05716	.05289	.10306	.01090
ATOM C23	.89678	.38411	.89919	.07335
UIJ C23	.09555	.06785	.05665	.01190
ATOM C24	.82658	.30313	.77785	.06732
UIJ C24	.06013	.04680	.09502	-.01375
ATOM C25	.43590	1.07854	.78345	.07088
UIJ C25	.06974	.06012	.08279	.01792
ATOM C26	.44807	1.09367	.60417	.07775
UIJ C26	.07492	.05303	.10529	.01134
ATOM C27	.57063	1.20901	.65810	.08197
UIJ C27	.07999	.04168	.12424	.00083
ATOM C41	1.07456	.99867	.62655	.06768
UIJ C41	.05096	.06900	.08308	-.02733
ATOM C111	1.26653	.52780	.48714	.06047
UIJ C111	.04372	.07439	.06329	-.00867
ATOM C211	.53217	1.09571	.67976	.05111
UIJ C211	.05123	.03548	.06662	.00033
ATOM C91	.94168	.35584	.79600	.04760
UIJ C91	.04067	.04169	.06044	.00414
ATOM C01	1.08331	.94892	.92645	.09447
UIJ C01	.08679	.08617	.11045	-.01535
ATOM C02	.94600	.99442	.92463	.11448
UIJ C02	.11178	.14473	.08695	-.07635
ATOM C03	1.13705	.95500	1.00070	.09634
UIJ C03	.05808	.10755	.12340	-.00577
ATOM H3	.81206	1.10973	.65319	.03882
ATOM H5	1.00623	.81612	.60875	.04094
ATOM H10	1.16617	.39213	.64487	.04599
ATOM H12	1.03774	.68028	.50562	.03545
ATOM H71	.68416	.71127	.64331	.03583
ATOM H72	.78349	.74187	.54085	.04120
ATOM H01	1.15440	.91717	.86490	.18570
ATOM H02	.91142	.99363	.87486	.14865
ATOM H03	1.22089	.92490	1.00492	.17805
ATOM H161	.43225	.47146	.78029	.09122
ATOM H162	.34142	.49181	.70625	.06709
ATOM H163	.50219	.51093	.66781	.11050
ATOM H171	.18739	.71394	.81876	.10787
ATOM H172	.15141	.62023	.78909	.14072
ATOM H173	.23160	.61246	.87679	.15875
ATOM H181	.41794	.68709	.60102	.23680
ATOM H182	.28095	.68192	.63040	.09603
ATOM H183	.30590	.77917	.65945	.13447
ATOM H191	.86918	.67811	.86496	.15310
ATOM H192	.84712	.71239	.95956	.10672
ATOM H193	.78668	.61611	.95609	.15017
ATOM H201	.56190	.63065	1.04024	.18812
ATOM H202	.61007	.71313	1.07791	.11165
ATOM H203	.46809	.73456	1.03891	.24304
ATOM H211	.55538	.89771	.92906	.21478
ATOM H212	.68253	.88068	.97269	.08300
ATOM H213	.70923	.88934	.85830	.11546
ATOM H221	1.16193	.30206	.80065	.08361
ATOM H222	1.05656	.21632	.85201	.10649
ATOM H223	1.11024	.24047	.72954	.09581
ATOM H231	.80309	.42206	.91482	.09470
ATOM H232	.88553	.31654	.95107	.07622
ATOM H233	.95708	.42996	.91450	.11354
ATOM H241	.85658	.26809	.71326	.12239
ATOM H242	.81535	.23689	.82568	.10055
ATOM H243	.72971	.34956	.78777	.09063
ATOM H251	.48428	1.08080	.83382	.09194
ATOM H252	.35656	1.13898	.78853	.08917
ATOM H253	.39241	1.00806	.80286	.09294
ATOM H261	.40805	1.02719	.61866	.08777
ATOM H262	.36224	1.14789	.61311	.13174
ATOM H263	.51273	1.10350	.53493	.09458
ATOM H271	.63594	1.22691	.59271	.10734
ATOM H272	.48199	1.26082	.66256	.08621
ATOM H273	.60727	1.21870	.71372	.08162
ATOM H411	1.13761	.98914	.57469	.11316
ATOM H412	1.07272	1.07318	.61756	.12593
ATOM H413	1.10993	.96919	.68786	.18747
ATOM H111	1.29427	.45862	.46570	.13826
ATOM H112	1.27441	.57843	.43462	.13681
ATOM H113	1.33731	.52300	.50895	.16267

Compound 2.48

	x	y	z	U(eq)
P(2A)	1750(2)	6686(1)	6857(2)	50(1)
P(4A)	336(2)	6287(1)	4998(2)	56(1)
P(2B)	5751(2)	10243(1)	9260(2)	53(1)
P(4B)	5572(2)	10658(1)	7414(2)	56(1)
O(1A)	2844(5)	7184(3)	6621(4)	48(2)
O(2A)	903(5)	6536(3)	4086(4)	59(2)
O(1B)	4702(5)	10728(3)	9564(4)	46(2)
O(2B)	4443(6)	11255(3)	6934(4)	58(2)
N(1A)	484(6)	6987(4)	5834(6)	51(2)
N(3A)	1619(6)	5978(4)	6027(6)	51(2)
N(1B)	6368(7)	10889(4)	8712(5)	50(2)
N(3B)	4938(7)	10020(4)	7970(5)	49(2)
C(1)	4496(7)	6653(4)	6205(6)	40(2)
C(2)	4073(7)	6917(4)	6959(6)	39(2)
C(3)	4780(8)	6950(5)	8046(6)	47(2)
C(4)	5970(8)	6694(5)	8407(6)	52(2)
C(5)	6503(7)	6399(5)	7712(7)	49(2)
C(6)	7726(9)	6104(6)	8086(9)	70(3)
C(7)	8239(10)	5826(6)	7395(11)	84(4)
C(8)	7537(10)	5828(6)	6314(9)	71(3)
C(9)	6342(9)	6086(5)	5912(8)	58(3)
C(10)	5785(7)	6377(5)	6592(6)	41(2)
C(11)	2857(8)	7197(5)	4485(6)	44(2)
C(12)	1581(9)	7147(5)	4036(7)	53(2)
C(13)	850(10)	7696(6)	3371(8)	66(3)
C(14)	1387(10)	8279(6)	3191(7)	68(3)
C(15)	2703(10)	8381(5)	3652(7)	57(3)
C(16)	3303(13)	8991(6)	3492(9)	77(3)
C(17)	4564(14)	9084(6)	3956(10)	80(4)
C(18)	5312(11)	8549(6)	4623(9)	77(3)
C(19)	4728(10)	7950(6)	4763(8)	63(3)
C(20)	3442(9)	7841(5)	4325(6)	46(2)
C(21)	3668(8)	6581(5)	5044(6)	48(2)
C(22)	-306(9)	7617(6)	5788(9)	65(3)
C(23)	468(10)	8286(5)	5821(9)	81(4)
C(24)	-1454(9)	7576(6)	4777(9)	90(4)
C(25)	-710(11)	7610(7)	6753(10)	98(4)
C(26)	1886(9)	5213(5)	6326(8)	53(2)
C(27)	3149(9)	5179(6)	7223(8)	73(3)
C(28)	1958(11)	4839(6)	5375(9)	83(3)
C(29)	883(11)	4913(6)	6683(11)	102(5)
C(1B)	2545(8)	10448(5)	8719(6)	43(2)
C(2B)	3639(8)	10369(5)	9567(6)	42(2)
C(3B)	3733(9)	9927(5)	10419(7)	56(3)
C(4B)	2747(9)	9536(6)	10422(8)	66(3)
C(5B)	1584(10)	9570(6)	9544(8)	58(3)
C(6B)	568(10)	9138(7)	9520(9)	79(4)
C(7B)	-547(12)	9151(7)	8669(10)	90(4)
C(8B)	-702(10)	9625(7)	7830(9)	84(4)
C(9B)	287(8)	10052(6)	7853(8)	68(3)
C(10B)	1448(8)	10046(5)	8692(7)	49(2)
C(11B)	3107(8)	11610(5)	7929(6)	47(2)
C(12B)	4021(8)	11753(5)	7505(7)	51(2)
C(13B)	4524(10)	12437(6)	7551(8)	64(3)
C(14B)	4150(11)	12969(6)	8039(9)	78(3)
C(15B)	3273(10)	12865(6)	8517(7)	61(3)
C(16B)	2870(12)	13419(6)	9021(9)	76(3)
C(17B)	1947(12)	13302(7)	9404(9)	81(3)
C(18B)	1393(10)	12639(7)	9357(8)	72(3)
C(19B)	1780(9)	12087(6)	8888(7)	60(3)
C(20B)	2703(8)	12169(5)	8456(7)	48(2)
C(21B)	2441(8)	10910(5)	7752(7)	48(2)
C(22B)	7476(9)	11141(6)	9228(7)	63(3)
C(23B)	8581(10)	10895(7)	9940(10)	97(4)
C(24B)	7848(10)	11685(7)	8372(8)	95(4)
C(25B)	7128(11)	11899(7)	9897(9)	99(4)
C(26B)	4609(9)	9282(5)	7507(8)	59(3)
C(27B)	5777(9)	8895(6)	7521(9)	81(3)
C(28B)	3994(10)	8893(6)	8198(9)	77(3)
C(29B)	3674(10)	9359(6)	6980(8)	81(3)

Compound 2.59

	x	y	z	U(eq)
P(1)	1820(1)	7204(1)	1167(1)	43(1)
P(2)	2583(1)	8614(1)	2101(1)	53(1)
O(1)	3017(1)	8293(2)	2716(1)	78(1)
N(1)	1741(1)	5353(2)	1232(1)	49(1)
N(2)	2765(1)	7722(2)	1562(1)	51(1)
N(3)	1713(1)	7966(2)	1804(1)	56(1)
C(1)	1380(1)	4349(2)	734(1)	45(1)
C(2)	674(1)	3595(3)	778(1)	65(1)
C(3)	303(2)	2543(3)	260(2)	89(1)
C(4)	854(2)	1362(3)	183(1)	77(1)
C(5)	1557(2)	2108(3)	137(1)	75(1)
C(6)	1923(1)	3149(3)	657(1)	70(1)
C(7)	3400(1)	7935(3)	1325(1)	54(1)
C(8)	3454(2)	6491(4)	983(2)	90(1)
C(9)	4142(2)	8084(5)	1844(2)	87(1)
C(10)	3277(2)	9335(5)	941(2)	104(1)
C(8A)	3088(15)	7803(30)	634(7)	77(7)
C(9A)	3958(16)	6755(28)	1593(12)	98(10)
C(10A)	3728(17)	9606(21)	1450(13)	92(9)
C(11)	1016(1)	8273(3)	1951(1)	54(1)
C(12)	1262(4)	8448(9)	2643(2)	56(1)
C(13)	689(4)	9754(8)	1677(3)	64(2)
C(14)	475(3)	6921(8)	1777(4)	60(2)
C(12A)	990(6)	9796(12)	2208(6)	70(3)
C(13A)	289(5)	8196(14)	1345(4)	58(2)
C(14A)	962(7)	6953(12)	2325(6)	69(3)
C(12B)	1188(13)	7805(27)	2576(7)	69(7)
C(13B)	346(11)	7392(22)	1537(9)	62(6)
C(14B)	861(12)	10021(15)	1890(10)	53(5)
C(12C)	667(12)	6666(15)	2033(10)	52(5)
C(13C)	1224(12)	9063(23)	2546(7)	65(7)
C(14C)	442(11)	9176(24)	1477(8)	69(6)

Compound 2.61

	x	y	z	U(eq)
Se(1)	3321(1)	1300(1)	1821(1)	53(1)
Se(2)	264(1)	232(1)	2586(1)	54(1)
P(1)	3138(1)	155(1)	2343(1)	34(1)
P(2)	1585(1)	-369(1)	2750(1)	33(1)
O(1)	1439(2)	-1265(2)	3100(2)	37(1)
O(2)	4131(2)	-306(2)	2407(3)	38(1)
N(1)	2631(3)	33(3)	3293(3)	32(1)
N(2)	2186(3)	-399(3)	1853(3)	36(1)
C(1)	1985(4)	-1706(3)	3846(3)	30(1)
C(2)	1502(4)	-1958(3)	4562(3)	36(1)
C(3)	2109(4)	-2286(3)	5319(4)	40(1)
C(4)	3101(4)	-2398(3)	5363(4)	40(1)
C(5)	3512(4)	-2219(3)	4591(3)	36(1)
C(6)	2954(4)	-1895(3)	3810(3)	33(1)
C(7)	3325(3)	-1888(3)	2894(3)	32(1)
C(8)	4389(4)	-1712(3)	2896(3)	32(1)
C(9)	5045(4)	-2363(3)	3068(4)	41(1)
C(10)	6021(4)	-2270(4)	3019(4)	44(1)
C(11)	6343(4)	-1525(4)	2773(4)	43(1)
C(12)	5735(4)	-856(3)	2555(3)	33(1)
C(13)	4749(3)	-982(3)	2644(3)	30(1)
C(14)	387(4)	-1908(4)	4563(4)	41(1)
C(15)	104(5)	-1055(5)	4832(6)	76(2)
C(16)	-203(4)	-2110(5)	3606(5)	66(2)
C(17)	76(5)	-2531(6)	5221(6)	85(3)
C(18)	3713(5)	-2750(4)	6206(4)	57(2)
C(19)	6716(5)	-2980(4)	3192(6)	74(2)
C(20)	6124(4)	-65(3)	2193(4)	40(1)
C(21)	5606(5)	74(4)	1201(4)	53(2)
C(22)	5997(4)	657(4)	2786(4)	53(2)
C(23)	7222(4)	-146(4)	2143(5)	60(2)
C(24)	2849(4)	508(3)	4184(4)	42(1)
C(25)	2378(5)	63(4)	4900(4)	56(2)
C(26)	2429(6)	1377(4)	4069(5)	65(2)
C(27)	3934(5)	544(6)	4446(5)	73(2)
C(28)	1870(4)	-616(4)	855(4)	50(2)
C(29)	1154(5)	-1304(5)	821(4)	68(2)
C(30)	1395(6)	113(5)	328(5)	81(3)
C(31)	2779(5)	-877(6)	488(4)	73(2)

Compound 3.27.H_2O

	x	y	z	U(eq)
Cl(1)	3751.2(3)	9660.5(6)	4902.7(4)	69.2(2)
O(4)	5022(1)	9033(3)	4110(1)	105(1)
P(1)	3631.2(2)	6162.0(6)	2897.2(3)	51.4(2)
O(1)	3421(1)	4820(2)	2594(1)	83(1)
O(2)	4066(1)	6953(1)	2381(1)	51(1)
O(3)	3047(1)	7130(2)	3008(1)	69(1)
N(1)	3652(1)	4219(2)	4511(1)	54(1)
N(2)	3519(1)	6480(2)	4845(1)	60(1)
C(1)	4116(1)	6105(2)	3797(1)	44(1)
C(2)	4804(1)	5501(3)	3775(1)	58(1)
C(3)	4862(1)	4017(3)	3524(1)	72(1)
C(4)	4576(1)	2954(3)	4011(1)	73(1)
C(5)	3853(1)	3107(2)	4018(1)	64(1)
C(6)	3311(2)	3740(3)	5138(2)	81(1)
C(7)	3271(2)	4775(3)	5703(2)	58(1)
C(7A)	2929(3)	4756(4)	5453(5)	69(2)
C(8)	3141(2)	6161(3)	5460(2)	78(1)
C(9)	3745(1)	5550(2)	4406(1)	45(1)
C(10)	4113(1)	8463(2)	2397(1)	52(1)
C(11)	3451(1)	9142(2)	2349(1)	51(1)
C(12)	3099(1)	8635(3)	2997(1)	67(1)
C(13)	3556(2)	10707(3)	2420(2)	99(1)
C(14)	3053(1)	8820(3)	1619(1)	59(1)

Compound 3.34

Atom	x	y	z	Ueq)
P	4919(1)	9083(1)	2717(2)	58(1)
O(3)	5000	10000	3364(8)	59(2)
O(4)	4670(4)	9045(4)	1235(6)	81(2)
O(2)	5796(3)	8695(3)	3041(6)	57(1)
O(1)	4277(3)	8645(3)	3739(6)	58(1)
C(1)	3977(4)	8894(4)	5088(8)	51(2)
C(2)	3127(5)	9051(5)	5237(9)	56(2)
C(3)	2882(5)	9319(6)	6587(10)	72(2)
C(4)	3409(5)	9383(6)	7746(9)	69(2)
C(5)	4233(5)	9198(4)	7533(9)	59(2)
C(6)	4532(5)	8968(4)	6217(8)	53(2)
C(7)	3067(7)	9674(9)	9178(11)	107(4)
C(8)	2484(5)	8969(5)	4000(9)	67(2)
C(9)	1610(6)	9010(9)	4558(13)	112(4)
C(10)	2571(7)	8128(7)	3226(16)	119(4)
C(11)	2627(6)	9703(7)	3003(11)	87(3)
C(12)	5489(4)	8842(4)	6031(8)	52(2)
C(13)	5742(4)	8016(5)	5341(8)	55(2)
C(14)	5938(4)	7963(4)	3888(8)	54(2)
C(15)	6273(4)	7254(5)	3259(8)	57(2)
C(16)	6368(5)	6578(5)	4171(9)	62(2)
C(17)	6138(5)	6592(5)	5584(10)	64(2)
C(18)	5835(5)	7308(4)	6152(9)	56(2)
C(19)	6283(7)	5823(5)	6521(14)	97(3)
C(20)	6549(5)	7206(5)	1684(10)	70(2)
C(21)	5780(7)	7233(7)	700(12)	99(4)
C(22)	7155(7)	7904(7)	1379(14)	101(3)
C(23)	7011(7)	6386(6)	1558(12)	96(3)

Compound 3.**36**.1.5H_2O

	x	y	z	U(eq)
P(1)	5904(1)	3233(2)	818(2)	51(1)
O(1)	6313(2)	3333(4)	1162(5)	50(2)
O(3)	5867(2)	3386(4)	-446(6)	63(2)
O(2)	5825(2)	2373(3)	1063(5)	53(2)
O(4)	5703(2)	3630(4)	1706(6)	63(2)
N(1)	5734(3)	3451(6)	-4586(9)	74(3)
N(2)	5732(2)	3795(5)	-2648(8)	69(3)
C(18)	5534(3)	4105(8)	-4969(12)	86(4)
C(19)	5350(4)	4418(8)	-3980(13)	112(5)
C(20)	5559(3)	4480(6)	-2872(11)	79(4)
C(21)	5808(3)	3314(7)	-3489(9)	69(4)
C(22)	5974(4)	2602(7)	-3142(10)	84(4)
C(23)	6334(4)	2586(9)	-3494(12)	100(5)
C(24)	6392(4)	2319(9)	-4751(12)	103(5)
C(25)	6221(4)	2847(11)	-5654(13)	114(7)
C(26)	5845(4)	2909(9)	-5549(11)	93(5)
O(5)	5000	4092(7)	2500	109(4)
C(1)	6588(2)	3243(5)	380(9)	44(2)
C(2)	6760(3)	3842(5)	-69(9)	48(3)
C(3)	7020(3)	3675(5)	-885(9)	56(3)
C(4)	7124(3)	2985(5)	-1210(9)	51(2)
C(5)	6953(3)	2413(6)	-700(9)	54(3)
C(6)	6687(2)	2531(5)	114(9)	49(2)
C(7)	6512(3)	1889(5)	702(9)	48(2)
C(8)	6207(2)	1576(5)	38(8)	43(2)
C(9)	6257(3)	1029(5)	-789(8)	52(2)
C(10)	5985(3)	723(5)	-1408(9)	52(3)
C(11)	5652(3)	982(5)	-1156(9)	57(3)
C(12)	5584(2)	1528(5)	-347(8)	47(2)
C(13)	5867(2)	1835(5)	205(9)	49(2)
C(14)	6686(3)	4618(6)	295(9)	57(3)
C(15)	7415(3)	2871(7)	-2112(11)	71(4)
C(16)	6040(3)	108(7)	-2269(11)	77(4)
C(17)	5209(3)	1754(6)	-125(10)	60(3)
C(14A)	6669(4)	4698(9)	1626(13)	108(5)
C(14B)	6955(3)	5160(7)	-137(12)	90(4)
C(14C)	6336(3)	4892(8)	-198(12)	99(4)
C(17A)	4956(4)	1214(9)	-621(14)	121(5)
C(17B)	5130(5)	2450(9)	-722(14)	122(6)
C(15A)	7759(5)	2941(10)	-1486(16)	139(6)
C(16A)	5800(5)	175(12)	-3352(18)	154(8)
C(17C)	5121(5)	1847(10)	1174(15)	132(6)
C(15B)	7410(5)	3385(11)	-3139(18)	146(8)
C(15C)	7390(5)	2152(11)	-2817(18)	152(8)
C(16B)	5966(7)	-614(14)	-1740(2)	195(10)
C(16C)	6380(6)	161(13)	-2900(2)	197(10)
O(6)	2767(9)	330(2)	-110(3)	405(16)

Compound 3.46

	x	y	z	U_{eq}
Sb	0.3167 (1)	0.4322 (1)	0.6419 (1)	0.043 (1)
P	−0.0563 (1)	0.7097 (1)	0.7213 (1)	0.031 (1)
Cl(1)	0.5719 (1)	0.2780 (2)	0.5488 (1)	0.072 (1)
Cl(2)	0.2299 (1)	0.2454 (1)	0.6895 (1)	0.059 (1)
Cl(3)	0.3982 (2)	0.3664 (2)	0.8180 (2)	0.083 (1)
Cl(4)	0.0011 (2)	0.7939 (1)	0.5488 (1)	0.055 (1)
O	0.0706 (3)	0.5612 (3)	0.7493 (2)	0.042 (1)
N(1)	−0.0852 (4)	0.8345 (3)	0.7853 (3)	0.033 (1)
C(1)	−0.1322 (5)	0.7976 (5)	0.9151 (3)	0.044 (1)
C(2)	−0.2438 (6)	0.9377 (6)	0.9580 (4)	0.059 (1)
C(3)	−0.1804 (7)	1.0544 (6)	0.9148 (5)	0.067 (2)
C(4)	−0.1425 (7)	1.0907 (5)	0.7836 (5)	0.064 (1)
C(5)	−0.0326 (5)	0.9555 (5)	0.7316 (4)	0.045 (1)
C(6)	0.0023 (7)	0.7056 (6)	0.9782 (4)	0.071 (2)
C(7)	0.1342 (6)	0.9072 (7)	0.7375 (6)	0.078 (2)
N(2)	−0.2147 (3)	0.6938 (3)	0.7438 (3)	0.031 (1)
C(8)	−0.3621 (4)	0.8288 (4)	0.7351 (4)	0.037 (1)
C(9)	−0.4870 (5)	0.7994 (6)	0.8344 (4)	0.054 (1)
C(10)	−0.4963 (6)	0.6587 (6)	0.8378 (5)	0.064 (1)
C(11)	−0.3425 (6)	0.5275 (6)	0.8520 (4)	0.058 (1)
C(12)	−0.2127 (5)	0.5475 (4)	0.7545 (4)	0.039 (1)
C(13)	−0.4082 (6)	0.8833 (5)	0.6174 (4)	0.053 (1)
C(14)	−0.2145 (6)	0.5253 (5)	0.6398 (5)	0.060 (1)