REACTIONS OF CHLOROCYCLOPHOSPHAZENES WITH DIFUNCTIONAL REAGENTS

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Abstract- The reactions of chlorocyclophosphazenes with aliphatic and aromatic difunctional reagents are described. The reaction pathways involved, product preferences and stability of products are discussed. Structural data including ^{31}P nmr parameters and X ray crystallographic data are presented.

Contents:

1. Introduction

Chlorocyclophosphazenes, $N_3P_3Cl_6$ (1) and $N_4P_4Cl_8$ (2) are important inorganic heterocyclic compounds whose chemistry has received wide spread atten-

tion in recent years.[1-3] The P-Cl bond in these molecules can be substituted by a number of monofunctional nucleophilic reagents such as amines, alcohols and organometallic reagents.[3-6] The reactions tend to become complex from the fact that after the mono substitution several isomeric structures are possible. These are summarized in the Figures 1 and 2.

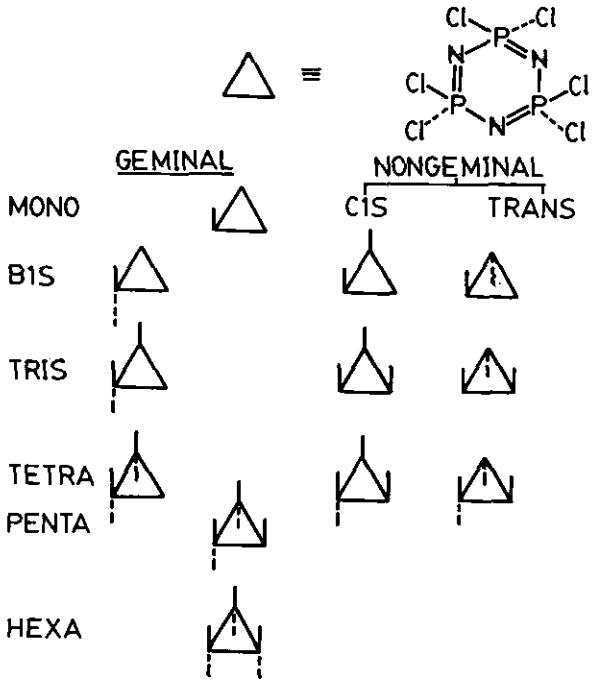


Figure 1. Geminal and nongeminal modes of replacement of chlorine atoms from $N_3P_3Cl_6$ (1). (The corners of the triangle represent phosphorus atoms; the full and broken lines denote the orientation of the substituents above and below the N_3P_3 ring plane, respectively; chlorine and ring nitrogen atoms are not shown.). From Ref. 3.

This aspect is now fairly well studied and the product distribution arising from a given nucleophile and the possible reaction mechanism responsible for the mode of substitution is now reasonably well understood.[3] Another important reason for the study of these heterocyclic compounds arises from

the fact that the six membered hexachlorocyclotriphosphazene can easily ring open to give rise to linear macromolecules(Scheme 1)[7]

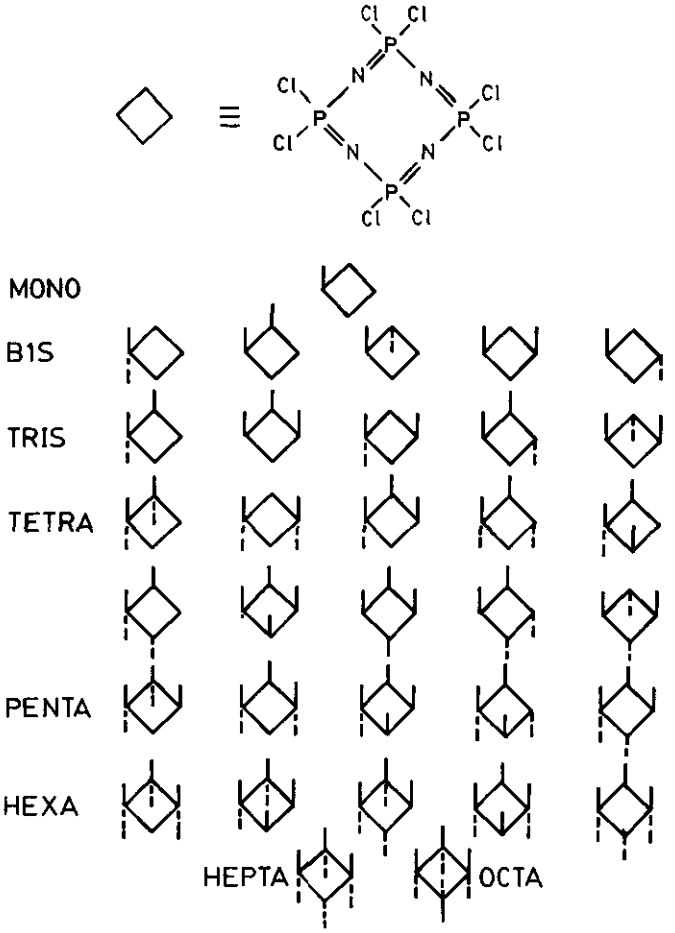
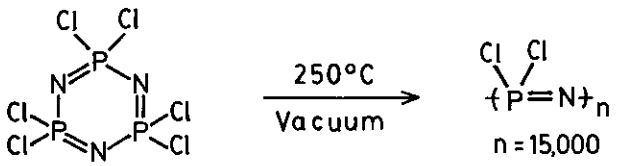


Figure 2. Possible substitution products from $N_4P_4Cl_8$ (2). (The corners of the square represent phosphorus atoms; the full and broken lines denote the orientation of substituents above and below the N_4P_4 ring plane, respectively; chlorine and ring nitrogen atoms are not shown.). From ref.3.

The P-Cl bonds are again extremely labile in the polymer, making this quite unstable hydrolytically. However, this feature can at once be turned into an advantage, because several nucleophiles can be substituted readily on



Scheme 1

the phosphorus greatly varying the polymer architechture and property.[8-12]

This review would focus on the reactions of the six membered and eight membered chlorocyclophosphazene ring compounds with difunctional nucleophilic reagents, such as diamines, diols, amino alchohols etc. Apart from the interest of this study from a view point of reactivity and structure, these reactions also throw light on the possibility of condensation polymers involving chlorocyclophosphazenes as one of the components of the polymer.

In contrast to the reactions of monofunctional nucleophilic reagents, the reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ with any difunctional reagent can lead to the formation of four types of products.[13-15](Figure 3)

(i) The spirocyclic product results from the substitution of both the chlorines on the same phosphorus atom by the difunctional reagent.

(ii) The ansa product is formed as a result of substitution of chlorines on different phosphorus atoms.

(iii) In the open chain compound only one end of the difunctional reagent reacts with the phosphazene; this kind of a behaviour can be expected when the reactivities of both the ends of the reagent are not the same ex as in the case of an amino alcohol such as $H_2N(CH_2)_3OH$.

(iv) The bridging compound which is the model compound for a condensation polymer results from two or more different molecules being bridged by the difunctional reagent.

The following account tries to summarize some of the reaction pathways followed and the structural parameters obtained for several products from a

variety of reactions that have been studied in the recent years.

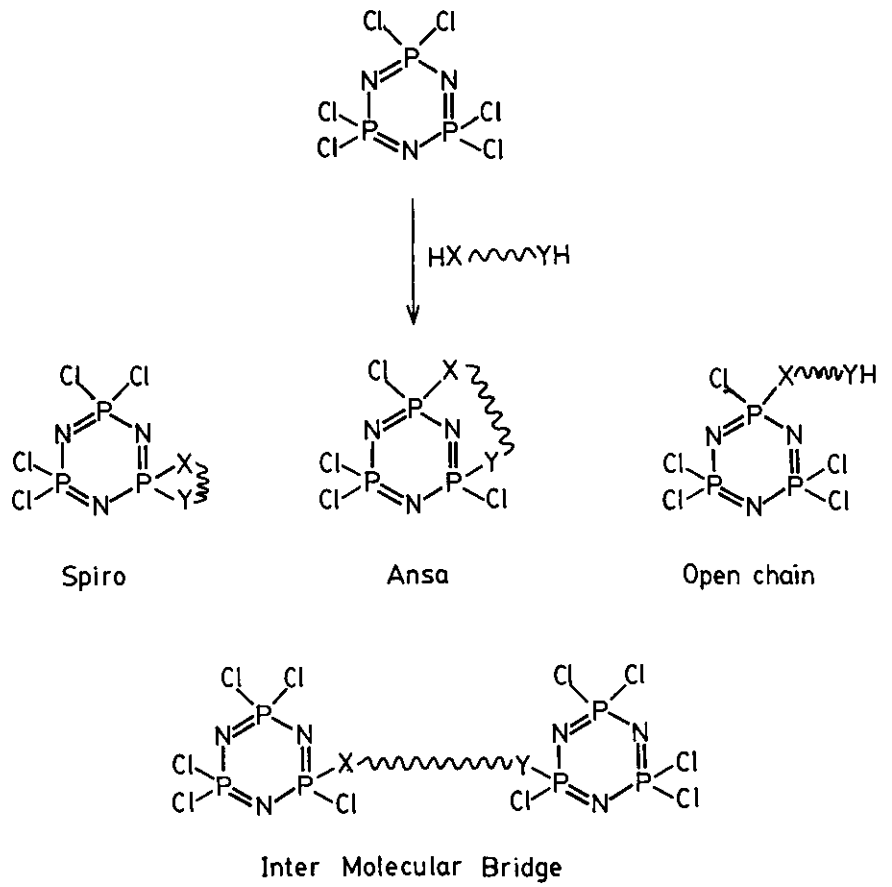


Figure 3

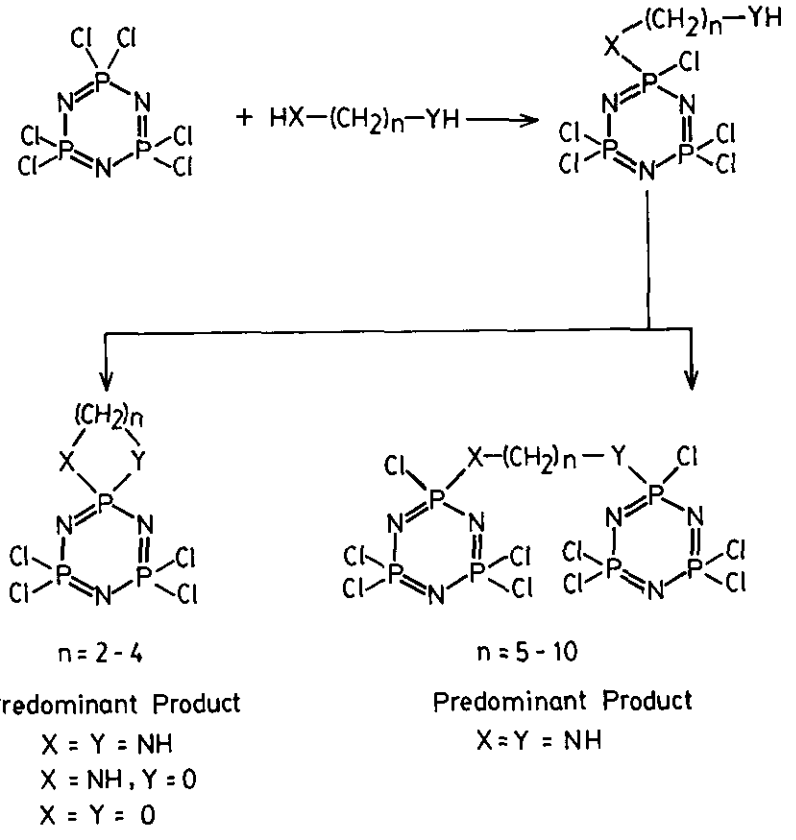
2.0 Reactions of chlorocyclophosphazenes with aliphatic difunctional reagents

2.1 Trimeric System

The reactions of hexachlorocyclotriphosphazene $N_3P_3Cl_6$[13-17] and its derivatives 2,2-diphenyl-4,4,6,6-tetrachlorocyclotriphosphazene $N_3P_3Cl_4Ph_2$[18](3) and 2,2-bis-(t-butylamino-4,4,6,6-tetrachlorocyclotriphosphazene $N_3P_3Cl_4(NHC_4H_9^t)_2$[19](4) with several aliphatic difunctional reagents have now been well studied. In general the reactions of 3 and 4 proceed

much slower than 1, but the product distribution is nearly the same. The results are summarized in Table 1.

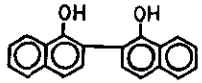
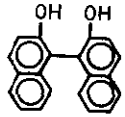
As has been seen there are four possible reaction pathways that a difunctional reagent can choose in its reactions with chlorocyclophosphazenes. From the results of Table 1 it can easily be seen that by far the majority of the products isolated belong to the type of 'spirocyclic' structures where the difunctional reagent is attached tothe same phosphorus atom. In a number of instances the spirocyclic product is obtained exclusively. It has been rationalized that the spirocyclic pathway is preferred for reagents that lead upto 5, 6, or 7 membered rings, because of the ease of ring closure in preference to inter molecular bridging: Scheme 2 summarizes this result.



Scheme 2

Table 1. Products from the reactions of $N_3P_3Cl_6$(1) and difunctional reagents[a)]

Difunctional reagent	Mono Spiro	Di Spiro	Tri Spiro	Ansa	Open Chain	Bridging	Reference
$H_2NCH_2CH_2NH_2$	+[b)]	-	-	-	-	-	16, 17
$H_2NCH_2CH(CH_3)NH_2$	+	-	-	-	-	-	15
$HN(CH_3)CH_2CH_2NH(CH_3)$	+	+	+	-	-	-	28, 29
$H_2N(CH_2)_3NH_2$	+	+	+	-	-	-	13,14,51
$NH(CH_3)(CH_2)_3NH(CH_3)$	+	-	-	-	-	-	52
$H_2N(CH_2)_4NH_2$	+	(+)	-	-	-	(+)	13, 51, 53, 54
$H_2N(CH_2)_5NH_2$	(+)	-	-	-	-	+	21, 51
$H_2N(CH_2)_nNH_2$ n = 6-10	-	-	-	-	-	+	21
$H_2N(CH_2)_2OH$	+	(+)[c)]	-	-	-	-	16, 17
$NH(CH_3)(CH_2)_2OH$	+	+[c)]	+[c)]	-	-	-	13, 14
$H_2N(CH_2)_3OH$[d)]	+	+[c)]	-	-	-	-	49
$NH_2\text{-}(CH_2)_2$>O, $NH_2\text{-}(CH_2)_2$	+e)	-	-	+	-	-	21
$NH_2(CH_2)_3\text{-}O\text{-}(CH_2)_2$, $H_2N\text{-}(CH_2)_3$	+e)	-	-	+	-	-	24
$HOCH_2\text{-}CH_2\text{-}OH$	+	+	+	-	-	-	20
$HOCH_2\text{-}CH_2\text{-}CH_2\text{-}OH$	+	+[f)]	+	(+)	(+)	(+)	20
$HOCH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$	+	+	+	-	(+)	(+)	20

catechol	+	+	+	-	-	-	33
1,2-diaminobenzene	+	-	+	-	-	-	2, 33
2,3-dihydroxynaphthalene	-	-	+	-	-	-	33
toluene-3-4-dithiol	-	-	+	-	-	-	33
2,2'-dihydroxybiphenyl	-	-	+	-	-	-	33
	+	-	-	-	-	-	50
	+	+	-	-	-	-	50

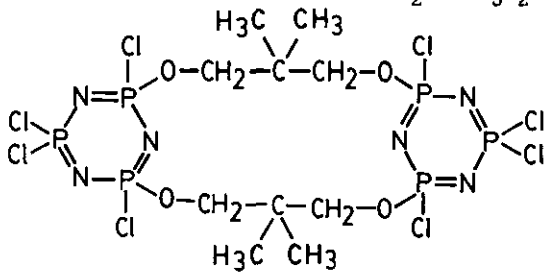
a) + : excellent yields; (+) : Moderate yields - traces. b) Further stages of substitution afforded only resinous material (see Text). c) Cis and trans isomers possible and isolated. d) 1-amino propanol reacts with $N_3P_3Cl_5CH_3$ to first give an open chain compound $N_3P_3Cl_4(CH_3)[NH(CH_2)_3OH]$; this product is cyclized by use of a base to the ansa product $N_3P_3Cl_3(CH_3)[NH(CH_2)_3O]$.[22] e) The spiro and ansa products are formed exclusively under different reaction conditions. f) Spiro ansa product was also isolated in a small yield.[20] g) The gem disubstituted phosphazenes $N_3P_3Cl_4Ph_2$[18] and $N_3P_3Cl_4(NHC_4H_9{}^t)_2$[19] react with several aliphatic difunctional reagents listed to give mono spiro products. Besides an ansa product is formed $N_3P_3Cl_2Ph_2[O(CH_2)_3O]$ and an open chain $N_3P_3Cl_3(NHC_4H_9{}^t)_2[O(CH_2)_3OH]$. h) $N_4P_4Cl_8$[32] gives the following spiro cyclic products $N_4P_4(N(CH_3)_2)_6[N(CH_3)CH_2CH_2O]$, $N_4P_4(OCH_3)_6[O(CH_2)_3O]$, $N_4P_4Cl_6(HN(CH_2)_3NH]$, $N_4P_4Cl_6[O(CH_2)_nO]$, $N_4P_4Cl_4[O(CH_2)_nO]_2$ dispiro[2,2,4,4 and 2,2,6,6], $N_4P_4Cl_2[O(CH_2)_nO]_3$ trispiro, n = 3,4 and $N_4P_4[O(CH_2)_nO]_4$.

Nearly all the products formed are spirocyclic when the chain length in the difunctional reagent $HX\text{-}(CH_2)_n\text{-}YH$ does not exceed n = 4. This would of course lead to a maximum spirocyclic ring size of seven. In reactions with aliphatic diols $HO\text{-}(CH_2)_n\text{-}OH$ n = 2-4, Shaw and coworkers have noticed formation of ansa, open chain and bridging products along with spirocyclic, but the former three are found only in trace amounts.[20]

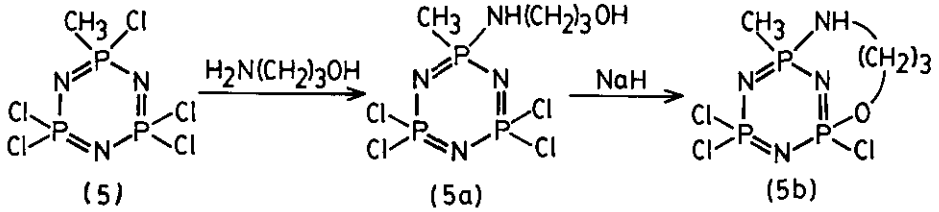
Only when the chain length exceeds n = 5 in the aliphatic diamines $NH_2(CH_2)_nNH_2$ does a reversal of product distribution take place, now the major product formed being of the bridging type.[21]

Surprisingly, there does not seem to be any competing crosslinking reactions that would lead to cyclomatrix polymers. Also, there has been no evidence for formation of any intermolecular condensation polymers. Details on these reactions are scanty and further work is required to clearly delineate the reaction conditions necessary to generate a true condensation polymer involving the cyclophosphazene ring system.

Shaw and coworkers have reported formation of interesting bridging derivatives from the reaction of (1) with $HO\text{-}CH_2\text{-}C(CH_3)_2\text{-}CH_2\text{-}OH$:[2]

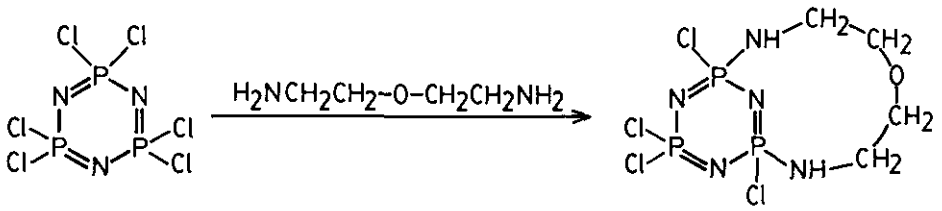


Ansa products have remained rare. The first 'ansa' compound was prepared by an indirect route:[22]



(5) (5a) (5b)

The amino propanol reacts with 5 at the $\delta P(CH_3)(Cl)$ centre affording the open chain derivative (5a), which subsequently is cyclized by the use of a strong base affording the 'ansa' product. More recently Labarre and coworkers have succeeded in the synthesis of 'ansa' products directly from $N_3P_3Cl_6$ (1) by the reaction with oxygen bridged diamines:[21,23-26]



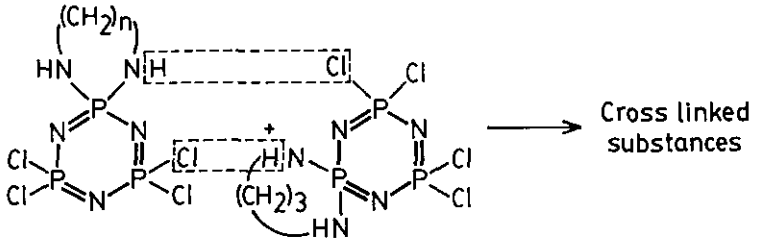
Shaw and coworkers reported the formation of an interesting compound from the reaction of $N_3P_3Cl_6$ and 1,3-propanediol that contains both a spirocyclic ring and an ansa arch, $N_3P_3Cl_2[O(CH_2)_3O]_2$.[27] (Vide infra).

2.2 Stability of spirocyclic products

While spirocyclic pathway has been shown to be the dominant pathway, the stability of the products obtained seems to be governed by two factors:[14]

(i) presence of reactive NH and chlorine substituents in the product.
(ii) ring size of the spirocyclic ring.

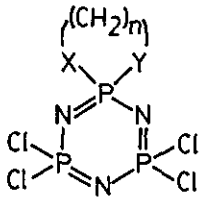
Thus a spirocyclic compound that still possesses reactive units in the form of residual NH protons and chlorines can undergo intermolecular cross-linking reactions affording resinous substances:



The tendency to crosslink is most predominant when n = 2. This can be inhibited by replacement of chlorines by nonreactive groups such as $N(CH_3)_2$ or OCH_3.[14-17]

The extent of spirocyclic substitution by the difunctional group on cyclophosphazenes is also governed by the above "destructive" side reaction. Thus, with ethylenediamine (which would leave residual NHs) only monospiro product[17] has been isolated; with N,N-dimethylethylenediamine,[28-29] N-methylethanolamine,[13-14] and ethyleneglycol[20] where such effects are absent, all the three stages of spirocyclic substitution have been realized.

The size of the spirocyclic ring also contributes significantly to the stability of the product(s). It is shown that a product with a five membered spirocyclic ring is much less stable compared to the one possessing a six membered spirocyclic ring:[2,14]



$n = 2 \ll 3 \backsimeq 4$

This phenomenon is similar to what has been observed by Westheimer and coworkers in the hydrolysis studies of cyclic phosphates containing five and six membered rings.[30] It has been shown by Westheimer that the five membered ring systems undergo rapid hydrolysis and this rate is approximately 10^6 times as fast as what is observed for the six membered ring systems. Westheimer attributed the fast rate to a relief of ring strain experienced by the five membered ring systems. Although such detailed studies are absent in the cyclophosphazene derivatives, it is reasonable to expect similar effects to operate in these systems also, accounting for the observed phenomenon.

2.3 Tetrameric Systems

The tetramer $N_4P_4Cl_8$(2) is considerably more reactive than the trimer $N_3P_3Cl_6$(1) towards nucleophilic reagents. This feature is manifested in the reactions with difunctional reagents also. Thus, reactions with

ethylenediamine and ethyleneglycol resulted in only hydrolysed derivatives. Attempts to stabilise products by derivatisation also lead to hydrolysis products.[31]

$$N_4P_4Cl_8 \xrightarrow{\quad} [N_4P_4Cl_6HN(CH_2)_2NH] \xrightarrow{HN(CH_3)_2}$$

$N_4P_4[N(CH_3)_2]_6[HN(CH_2)_2NH]$ Expected

$N_4P_4[N(CH_3)_2]_7OH$ Isolated

However, reactions with N-methylethanolamine, 1,3-propanediol and 1,3-diaminopropane afforded monospiro products. More recently an investigation of the reactions of $N_4P_4Cl_8$ with 1,3-propanediol and 1,4-butanediol revealed that monospiro, dispiro, trispiro and tetraspiro products are formed, showing once again the preponderance of the spirocyclic pathway in these systems also.[32]

3.0 Aromatic difunctional reagents

Allcock and coworkers have found that $N_3P_3Cl_6$ reacts readily with several aromatic difunctional reagents affording readily trispiro derivatives.[33] Attempts at restricting the substitution to monospiro and dispiro have only recently been successful.[2]

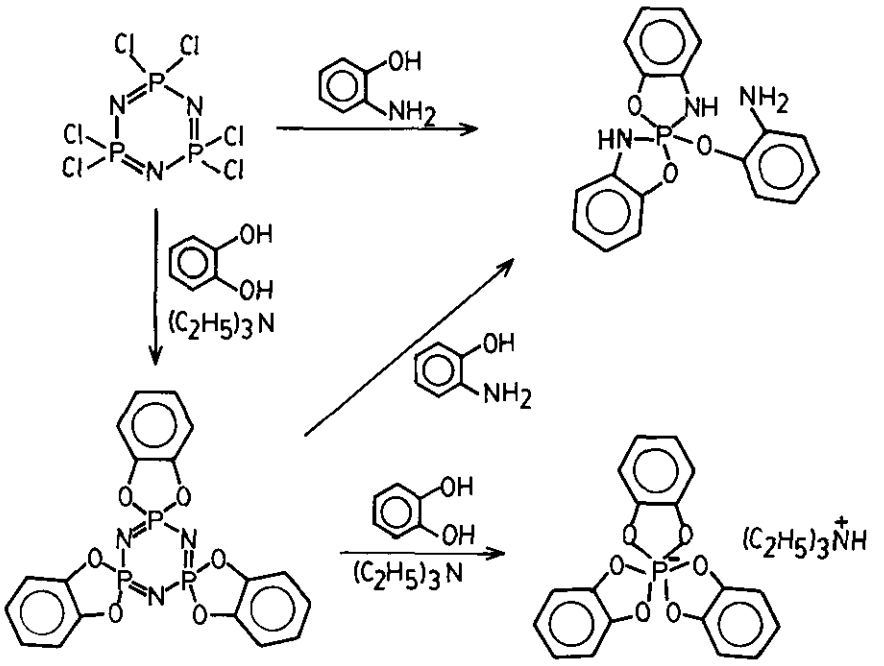
An interesting feature of the reaction of $N_3P_3Cl_6$ with aromatic difunctionals is the ease of decomposition of the products to cyclic phosphoranes[34] (Scheme 3).

The mechanisms of these reactions have now been established.[35] An important point to note is that this decomposition pathway occurs only for spirocyclic rings that are five membered, underlying the greater stability of the higher membered ring systems.

An additional feature of interest of the triscatecholate derivative $N_3P_3(O_2C_6H_4)_3$ is its ability to form inclusion clathrates with several

solvents.[36] This feature has been taken advantage of cleverly by entrapping acrylate monomers in the channels of this molecule and polymerising it in a stereoregular fashion.[37]

In view of the greater reactivity of the tetrameric ring system, all reactions with aromatic difunctionals such as catechol lead only to the formation of cyclic phosphoranes.



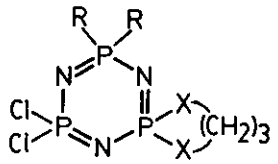
Scheme 3

4.0 Structural Studies

4.1 Nmr

Phosphorus nmr is an extremely useful technique for deriving structural information. Most monospiro products of the trimeric system give well resolved AB_2 or AX_2 type of spectra. In some instances ex. $N_3P_3Cl_4HN(CH_2)_2NH$ and $N_3P_3Cl_4[HN(CH_2)O]$ a single line is observed in ^{31}P.[17]

However, this accidental isochrony can be removed by recording the spectra at higher field strength. A similar feature is present for some of the spirocyclic products obtained from $N_3P_3Cl_4Ph_2$ or $N_3P_3Cl_4(NHC_4H_9^t)_2$:[18-19]



R = Ph or $NHC_4H_9^t$
X = NH or O

As can be seen from the structure, there are three different types of phosphorus nuclei and one should expect an ABX, AMX or ABC type of a spin system depending on the extent of closeness of chemical shifts and the resulting second order effects. However as can be seen in Figure 4,

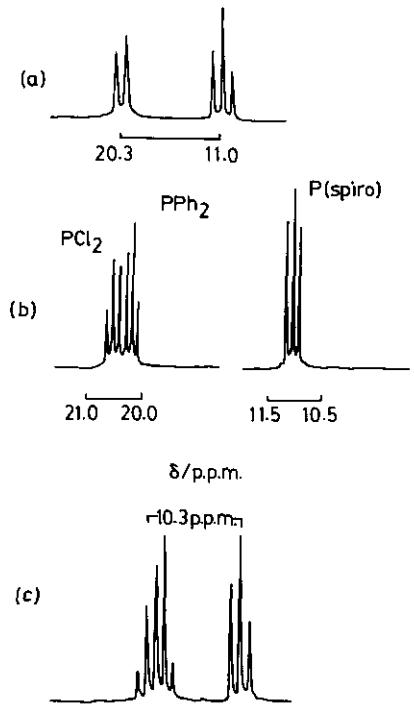


Figure 4. $^{31}P-[^1H]$Nmr spectra of $N_3P_3Ph_2[HN(CH_2)_3NH]Cl_2$(49) in $CDCl_3$: (a) at 24.15 (room temperature). (b) at 162.0 (room temperature), and (c) 24.15 MHz (-50°C). From ref. 18

the spectrum at room temperature shows an AX_2 patttern. This could be misleading and lead to wrong structural conclusions. A careful variation of temperature, solvent and field strength removes the isochrony of chemical shifts and the expected spin pattern is realized.

Another feature of the chemical shifts (Table 2) is the δP(spiro) for a five membered spirocyclic ring system is considerably more deshielded than a phosphorus bearing a six membered ring.[14,38] The trend is reversed albeit to a small extent with seven membered rings, the latter almost resembling the acyclic systems. Theoretical calculations have shown that a phosphorus atom in a five membered ring system has a greater positive charge than that in an acyclic or a six membered analogue.[39] Since the five membered ring is subject to steric strain (vide infra) there is a decrease of π-electron release to the phosphorus atoms from exocyclic substituents. Interestingly a similar variation is also observed for 2-oxo-2-thiooxo-2-R-1,3-2-dithiaphospha ring systems[40] and the cyclic phosphates, 2-oxo-2-phenoxy-1-3-2-dioxophospha compounds.[41]

Unless the difunctional reagent is an asymmetrical one it is difficult from ^{31}P data alone to distinguish between the various structural forms. Thus consider the following examples:

$[N_3P_3Cl_4HN(CH_2)_3NH]$ (Case 1) and $N_3P_3Cl_4[N(CH_3)CH_2CH_2O]$ (Case 2)

The former has a symmetrical difunctional group and the latter an asymmetric.

In Case 2 we have a clear distinction possible between the two structures based on ^{31}P alone. Thus structure C has two types of phosphorus nuclei and would be expected to show an AB_2 or AX_2 spectrum where as structure D would show 3 types of phosphorus environments in the form of a three spin system. This distinction is difficult in Case 1 where both structures would exhibit a two spin pattern. In most instances this difficulty can be over come by derivatising the chloroprecursor with groups such as -F, $-NCH_3$ or $-OCH_3$.

Table 2. Phosphorus - 31 nmr data[a)]

Compound	Structure[b)]	δPCl_2(A)	δP Spiro(B)	δPR_2(C)	J(P-N-P)	J(Other)	Ref.
1	2	3	4	5	6	7	8
$N_3P_3Cl_4[HNCH_2CH_2NH]$ (6)	Spiro (5)	23.5[d)]	22.9[d)]	-	47.1	-	17, 20
$N_3P_3F_4[HNCH_2CH_2NH]$ (6a)	Spiro (5)	-	30.06	10.18	c)	-	49
$N_3P_3(N(CH_3)_2)_4[HNCH_2CH_2NH]$(6b)	Spiro(5)	-	35.5	26.7	40.0	-	17
$N_3P_3Cl_4[HNCH_2CH(CH_3)NH]$ (7)	Spiro (5)	22.5	21.3	-	46.0	-	15
$N_3P_3Cl_4[CH_3NCH_2CH_2NCH_3]$ (8)	Spiro (5)	23.8	20.4	-	41.8	-	29, 49
$N_3P_3Cl_2[CH_3NCH_2CH_2NCH_3]_2$ (9)	Dispiro(5)	29.1	24.9	-	54.3	-	29
$N_3P_3[CH_3NCH_2CH_2NCH_3]_3$ (10)	Trispiro(5)	-	29.40	-	-	-	29
$N_3P_3Cl_4[HN(CH_2)_3NH]$ (11)	Spiro (6)	21.5	7.50	-	45.5	-	13, 14
$N_3P_3F_4[HN(CH_2)_3NH]$ (11a)	Spiro (6)	-	16.34	10.57	95.0	-	49
$N_3P_3Cl_2[HN(CH_2)_3NH]_2$ (12)	Dispiro (6)	23.10	12.30	-	43.7	-	49
$N_3P_3F_2[HN(CH_2)_3NH]_2$ (12a)	Dispiro (6)	-	17.08	10.12	74.0	-	49
$N_3P_3Cl_4[HN(CH_2)_4NH]$ (13)	Spiro (7)	20.82	13.07	-	46.0	-	13, 14
$N_3P_3Cl_4[HN(CH_2)_2O]$ (14)	Spiro (5)	24.90[d)]	24.30	-	53.9	-	16,17,20
$N_3P_3(N(CH_3)_2)_4[HN(CH_2)_2O]$(14a)	Spiro (5)	-	36.5	27.3	46.0	-	17
$N_3P_3Cl_2[HNCH_2CH_2O]_2$ (15)	Dispiro (5)	29.0	29.0	-	-	-	17
$N_3P_3Cl_4[HN(CH_2)_3O]$ (16)	Spiro (6)	22.40	7.20	-	53.9	-	49
$N_3P_3F_4[HN(CH_2)_3O]$ (16a)	Spiro (6)	-	15.06	10.20	c)	-	49

1	2	3	4	5	6	7	8
$N_3P_3Cl_2[HN(CH_2)_3O]_2$ (17)	Dispiro(6)[e]	12.74	23.83	-	50.5	-	49
		12.48	23.67	-	53.8	-	
$N_3P_3F_2[HN(CH_2)_3O]_2$ (17a)	Dispiro(6)[e]	-	17.66	10.11	84.0	-	49
			17.66	9.16	84.0		
$N_3P_3Cl_4(CH_3)[HN(CH_2)_3OH]$(18)	Open-chain	19.8	-	25.0[f]	-	19.5(A-C)	22
$N_3P_3Cl_3(CH_3)[HN(CH_2)_3O]$ (19)	Ansa	24.5	-	31.2[g]	-	48.8	22
				29.3	-	9.8	
						4.0	
$N_3P_3Cl_4[CH_3NCH_2CH_2O]$ (20)	Spiro (5)	25.1	22.40	-	53.9	-	14
$N_3P_3F_4[CH_3NCH_2CH_2O]$ (20a)	Spiro (5)	-	30.56	13.95	c)	-	49
$N_3P_3(N(CH_3)_2)_4[CH_3NCH_2CH_2O]$(20b)	Spiro (5)	-	32.5	28.3	46.0	-	10, 14
$N_3P_3(OCH_3)_4[CH_3NCH_2CH_2O]$(20c)	Spiro (5)	-	33.7	21.9	67.5	-	10, 14
$N_3P_3Cl_2[CH_3NCH_2CH_2O]_2$ (21)	Dispiro[h](5)	30.7	28.5	-	62.90	-	14
$N_3P_3(N(CH_3)_2)_2[CH_3NCH_2CH_2O]_2$(21a)	Dispiro[h](5)	-	33.40	29.7	52.50	-	14
$N_3P_3F_2[CH_3NCH_2CH_2O]_2$ (21b)	Dispiro[h](5)	-	31.62	14.42	98.0	-	14, 49
$N_3P_3[CH_3NCH_2CH_2O]_3$ (22)	Trispiro(5)	-	33.6 (1)[h]	-	-	-	
			25.4 (2)[h]	-	-	-	14
$N_3P_3Cl_4(20202)$[1] (23)	Ansa	21.36	-	21.82[m]	-	48.5	26
$N_3P_3Cl_4(30203)$[1] (24)	Ansa	21.33	-	21.79[m]	-	47.5	26
$N_3P_3Cl_4(30403)$[1] (25)	Ansa	21.28	-	21.76[m]	-	47.5	26
$N_3P_3Cl_4(3020203)$[1] (26)	Ansa	21.0	-	21.60[m]	-	44.0	24

1	2	3	4	5	6	7	8
$N_3P_3Cl_4(20202)$[1] (27)	Spiro (8)	21.83	10.98	-	45.0	-	26
$N_3P_3Cl_4(30203)$[1] (28)	Spiro (13)	21.72	9.39	-	43.9	-	26
$N_3P_3Cl_4(30403)$[1] (28)	Spiro (15)	21.71	9.38	-	43.9	-	26
$N_3P_3Cl_4(3020203)$[1] (29)	Spiro (16)	21.14	9.51	-	41.2	-	24
$N_3P_3Cl_4(202)$[1] (30)	Ansa	28.96	-	22.5	-	58.1	21
$N_3P_3Cl_4[OCH_2CH_2O]$ (31)	Spiro (5)	26.5	24.5	-	68.0	-	20
$N_3P_3Cl_2[OCH_2CH_2O]_2$ (32)	Dispiro (5)	31.3	30.95	-	76.8	-	20
$N_3P_3[OCH_2CH_2O]_3$ (33)	Trispiro(5)	-	37.40	-	-	-	20
$N_3P_3Cl_4[O(CH_2)_3O]$ (34)	Spiro (5)	24.1	3.4	-	69.2	-	20
$N_3P_3Cl_4[O(CH_2)_3O]$ (35)	Ansa	29.5	-	30.05[i]	-	-	20
$[N_3P_3Cl_5]_2[O(CH_2)_3O]$ (36)	bridging	23.4	-	16.0[i]	63.0	-	20
$N_3P_3Cl_5[O(CH_2)_3OH]$ (37)	open chain	23.5	-	16.1[i]	61.7	-	20
$N_3P_3F_4[O(CH_2)_3O]$ (34a)	Spiro (6)	-	15.16	8.9	c)	-	20
$N_3P_3Cl_2[O(CH_2)_3O]_2$ (38)	Dispiro (6)	26.5	9.1	-	70.8	-	20
$N_3P_3Cl_2[O(CH_2)_3O]_2$ (39)	Spiro(6)Ansa	-	10.1	31.2[i]	-	73.0(B-C)	20
$N_3P_3[OCH_2CH_2CH_2O]_3$ (40)	Trispiro (6)	-	14.1	-	-	-	20
$N_3P_3Cl_4[O(CH_2)_4O]$ (41)	Spiro (7)	24.1	10.3	-	70.5	-	20
$N_3P_3Cl_5[O(CH_2)_4OH]$ (42)	open chain	23.5	-	15.9[i]	62.1	-	20
$[N_3P_3Cl_5]_2[O(CH_2)_4O]$ (43)	Bridging	23.5	-	15.9[i]	61.9	-	20
$N_3P_3Cl_2[O(CH_2)_4O]_2$ (44)	Dispiro (7)	27.8	16.0	-	76.9	-	20
$N_3P_3[O(CH_2)_4O]_3$ (45)	Trispiro(7)	-	21.7	-	-	-	20

1	2	3	4	5	6	7	8
$N_3P_3Cl_2Ph_2[HNCH_2CH_2NH]$ (46)	Spiro (5)	22.8	25.4	20.3	30.1	18.4(B-C) 22.6(A-C)	18
$N_3P_3Cl_2Ph_2[HN(CH_2)_2NCH_3]$(47)	Spiro (5)	23.3	24.0	20.6	27.6	18.4 23.8	18
$N_3P_3Cl_2Ph_2[CH_3N(CH_2)_2NCH_3]$(48)	Spiro (5)	24.0	22.9	20.8	25.2	18.3 23.7	18
$N_3P_3Cl_2Ph_2[HN(CH_2)_3NH]$ (49)	Spiro (6)	20.4	10.9	20.0	22.0	19.4 23.0	18
$N_3P_3Cl_2Ph_2[CH_3N(CH_2)_3NH]$(50)	Spiro (6)	20.7	15.0	20.2	17.2	20.1 19.5	18
$N_3P_3Cl_2Ph_2[CH_3N(CH_2)_3NCH_3]$(51)	Spiro (6)	21.7	19.4	20.1	6.5	24.1 21.5	19
$N_3P_3Cl_2Ph_2[NH(CH_2)_4NH]$ (52)	Spiro (7)	21.4	14.5	18.7	32.0	19.9 20.8	18
$N_3P_3Cl_2Ph_2[OCH_2CH_2NH]$ (53)	Spiro (5)	23.7	26.4	20.8	39.3	21.2 20.8	18
$N_3P_3Cl_2Ph_2[OCH_2CH_2NCH_3]$ (54)	Spiro (5)	24.4	25.2	22.1	35.7	22.5 22.3	18
$N_3P_3Cl_2Ph_2[O(CH_2)_3NH]$ (55)	Spiro (6)	20.6	10.0	21.1	33.0	28.0 18.4	18
$N_3P_3Cl_2Ph_2[O(CH_2)_4NH]$ (56)	Spiro (7)	22.9	16.9	20.7	44.2	23.2 19.1	18

1	2	3	4	5	6	7	8
$N_3P_3Cl_2Ph_2[O(CH_2)_2O]$ (57)	Spiro (5)	25.2	26.7	23.1	50.3	29.0 20.1	18
$N_3P_3Cl_2Ph_2[O(CH_2)_3O]$ (58)	Spiro (6)	21.9	5.4	22.1	45.1	34.0 16.8	18
$N_3P_3Cl_2Ph_2[O(CH_2)_4O]$ (59)	Spiro (7)	23.6	12.5	22.0	53.9	31.4 17.9	18
$N_3P_3Cl_2R_2^J[HN(CH_2)_2NH]$ (60)	Spiro (5)	23.1	25.3	5.9	49.5	42.6 56.9	19
$N_3P_3Cl_2R_2[HN(CH_2)_2NCH_3]$ (61)	Spiro (5)	24.1	25.3	8.1	44.5	47.4 56.8	19
$N_3P_3Cl_2R_2[CH_3N(CH_2)_2NCH_3]$(62)	Spiro (5)	24.4	22.9	7.4	45.9	40.5 57.8	19
$N_3P_3Cl_2R_2[HN(CH_2)_3NH]$ (63)	Spiro (6)	21.3	10.7	5.4	46.6	40.7 47.4	19
$N_3P_3Cl_2R_2[HN(CH_2)_3NCH_3]$(64)	Spiro (6)	21.9	14.7	6.3	38.5	43.4 47.5	19
$N_3P_3Cl_2R_2[CH_3N(CH_2)_3NCH_3]$(65)	Spiro (6)	22.4	18.4	6.4	31.7	43.9 50.2	19
$N_3P_3Cl_2R_2[HN(CH_2)_4NH]$ (66)	Spiro (7)	23.2	15.5	6.0	51.8	45.5 51.2	19
$N_3P_3Cl_2R_2[HN(CH_2)_2O]$ (67)	Spiro (5)	23.7	27.0	6.4	54.3	50.6 59.8	19

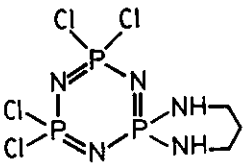
1	2	3	4	5	6	7	8
$N_3P_3Cl_2R_2[O(CH_2)_2NCH_3]$ (68)	Spiro (5)	24.3	25.0	7.2	50.2	49.5	19
						60.4	
$N_3P_3Cl_2R_2[O(CH_2)_3NH]$ (70)	Spiro (6)	21.4	9.3	6.8	55.1	54.0	19
						46.9	
$N_3P_3Cl_2R_2[O(CH_2)_4NH]$ (71)	Spiro (7)	22.6	16.9	5.7	65.3	51.1	19
						49.1	
$N_3P_3Cl_2R_2[O(CH_2)_2O]$ (72)	Spiro (5)	24.5	26.8	7.0	72.6	56.3	19
						57.3	
$N_3P_3Cl_2R_2[O(CH_2)_3O]$ (73)	Spiro (6)	23.0	7.1	7.3	67.1	65.4	19
						51.2	
$N_3P_3R_2[O(CH_2)_3O]_2$ (74)	Dispiro (6)	-	12.3	13.2	-	63.2	19
$N_3P_3Cl_2R_2[O(CH_2)_4O]$ (75)	Spiro (7)	23.5	13.0	5.9	76.6	64.1	19
						48.8	
$N_3P_3R_2[O(CH_2)_4O]_2$ (76)	Dispiro (7)	-	19.4	10.8	-	65.9	19
$N_3P_3Cl_4O_2(C_{20}H_{12})$ (77)	Spiro (7)	23.48	14.98	-	70.96	-	50
$N_3P_3Cl_2(O_2C_{20}H_{12})_2$ (78)	Dispiro (7)	28.56	20.26	-	57.30	-	50
$N_3P_3Cl_4[O_2C_{20}H_{12}]$ (79)	Spiro (7)	24.29	13.61	-	70.96	-	50
$N_3P_3[O_2C_6H_4]_3$ (80)	Trispiro(5)	-	11.80[n]	-	-	-	33
$N_3P_3Cl_4[(NH)_2C_6H_4]$ (81)	Spiro (5)	-	20.0[n]	-	-	-	33
$N_3P_3[(NH)_2C_6H_4]_3$ (82)	Trispiro(5)	-	23.0[n]	-	-	-	33
$N_4P_4[N(CH_3)_2]_6[NH(CH_2)_3NH]$(83)	Spiro (6)	-	1.6	8.9(2)[k]	42.2	-	31
				7.2(1)	36.8		

1	2	3	4	5	6	7	8
$N_4P_4Cl_6[CH_3NCH_2CH_2NCH_3]$ (84)	Spiro (5)	-8.3 -6.2	6.1	-	42.1 27.1	-	31
$N_4P_4Cl_6[O(CH_2)_3O]$ (85)	Spiro(6)	-5.5(1)[k] -4.3(2)	-10.5	-	59.0	29.9	32
$N_4P_4Cl_6[O(CH_2)_4O]$ (86)	Spiro (7)	-5.7(1)[k] -4.1(2)	-2.05	-	62.5	29.3	32
$N_4P_4Cl_4[O(CH_2)_3O]_2$ (87)	Dispiro(6) [2,2,6,6]	-2.3	-9.6	-	57.9	36.5	32
$N_4P_4Cl_4[O(CH_2)_3O]_2$ (88)	Dispiro(6) [2,2,4,4]	-4.7	-6.6	-	58.2	82.9	32
$N_4P_4Cl_4[O(CH_2)_4O]_2$ (89)	Dispiro(7) [2,2,6,6]	-1.0	-1.0	-	-	-	32
$N_4P_4Cl_4[O(CH_2)_4O]_2$ (90)	Dispiro(7) [2,2,4,4]	-2.6	1.4	-	60.7	89.2	32
$N_4P_4Cl_2[O(CH_2)_3O]_3$ (91)	Trispiro(6)	-2.6	-2.1(1)[k] -5.7(2)	-	53.7	79.4	32
$N_4P_4Cl_2[O(CH_2)_4O]_3$ (92)	Trispiro(7)	-0.2	5.5(1)[k] 2.2(2)	-	54.2 -	86.1 39.9	32
$N_4P_4[O(CH_2)_4O]_4$ (93)	Tetraspiro(7)	-	7.1	-	-	-	32

a) : The chemical shift values are reported with respect to ext. H_3PO_4 as 0.0 ppm. Upfield shifts are negative relative to downfield shifts. The chemical shifts are in ppm and the J values in Hz. b) : The number in parenthesis represents the size of spirocyclic ring c) : Not determined d) At low field only a single line is observed at 23.3 ppm for compound (6) 22.0 ppm for compound (14). e) : The values are for the two geometrical isomers possible, cis and trans. f) : $\delta P(CH_3)(NH(CH_2)_3OH)$. g) $\delta P(CH_3)(NHR)$: 31.2; $\delta P(Cl)(O)$ 29.3; h) : The cis isomer i) : $\delta P(O)Cl$ j) : R = $NHC_4H_9{}^t$ k) : Numbers in parentheses represents the relative number of nuclei. l) : 202 = $[NH(CH_2)_2O(CH_2)_2NH]$; 20202 = $[NH(CH_2)_2O\text{-}(CH_2)_2\text{-}O\text{-}(CH_2)_2NH]$ etc. m) : $\delta P(NHR)(Cl)$ n) : Chemical shifts with respect to triethylphosphite as 0.0 ppm.

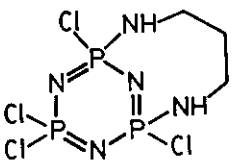
Thus a derivative would show two fluorine environments, two $-NCH_3$ and two $-OCH_3$ signals respectively for the ansa and only one for the spiro in Case 1 example.

Case 1



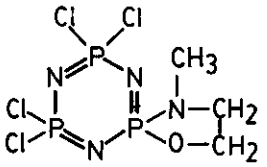
Spiro (A)

or

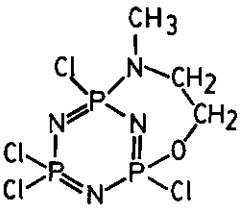


Ansa (B)

Case 2



C



D

Alternatively by observing second order effects in the ^1H nmr it is possible to derive additional structural information. Thus in the ^1H nmr of the spiro $N_3P_3Cl_4[HN(CH_2)_2NH]$ the N-CH_2 signals appear as a doublet due to coupling with phosphorus. However, because of the closeness of chemical shifts of δP(spiro) and δPCl_2 a second order effect manifests in the ^1H nmr in the form a broad hump between the doublets. This feature is called "virtual coupling".[16,42-44] Upon derivatisation with $HN(CH_3)_2$ the resultant compound $N_3P_3[N(CH_3)_2]_4[HNCH_2CH_2NH]$ shows only one type of NCH_3 signals in ^1H nmr, confirming its spiro structure and therefore of its chloroprecursor. Additionally the N-CH_3 signals now show virtual coupling [because of the equivalence of chemical shifts of $\delta P(NCH_3)$] and the N-CH_2 signals are free of the second order effects (Figure 5). Thus, second order effects in ^1H nmr can be used effectively as supporting evidence for structure determination.

It is also known that if one measures ^3J(P-H) in geminal compounds and non-

geminal compounds in cyclophosphazenes the coupling constant of the geminal derivative is always lower by 4-5 Hz. [3]

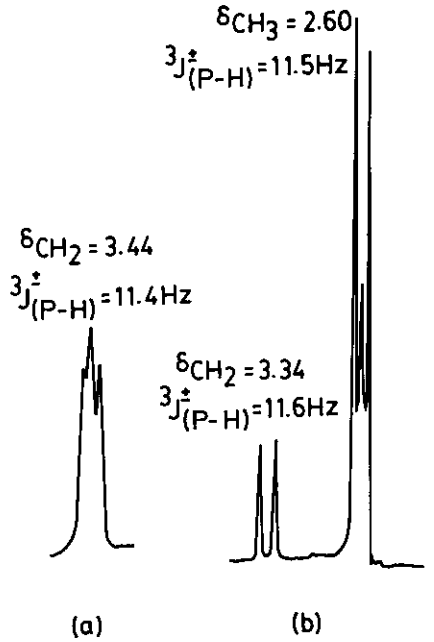
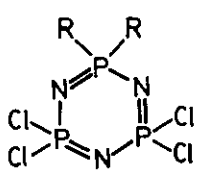
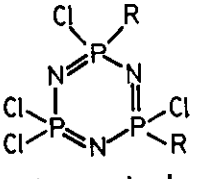
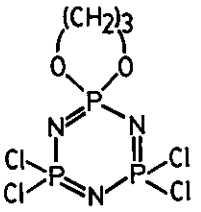


Figure 5. ^{1}H nmr spectra (100 MHz, $CDCl_3$) of (a) $N_3P_3Cl_4(NHCH_2CH_2NH)$ (6) and b) $N_3P_3(NCH_3)_4(NHCH_2CH_2NH)$ (6b)(NH regions not shown). From ref. 16







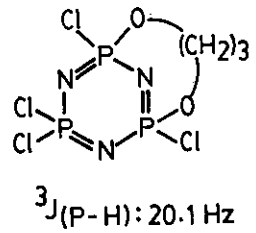
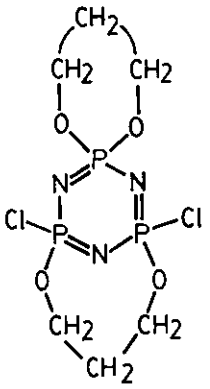


Figure 6

In examples where both products have been isolated from the same reagent this expectation is realized [20] (Figure 6).

Similarly the unique 'spiro-ansa' derivative shows both types of coupling constants:[20]

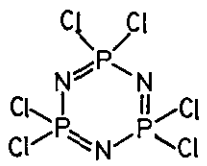


$^{3}J_{(P-H)}$ (Spiro ring) 12.8 Hz
$^{3}J_{(P-H)}$ (Ansa ring) 20.0 Hz

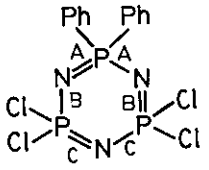
4.2 X ray

The X ray structural details of several spirocyclic, ansa and bridging compounds are summarised in Table 3. From the studies of Mani, Ahmed and Wagner it is well known that substitution of chlorines on phosphorus by other susbstituents causes significant changes in bond lengths:[45-46]

The observed differences are readily accountable by the theories of bonding existing in cyclophosphazenes.[3]



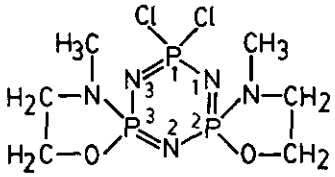
All bond lengths
equal = 1.581 A



Bond lengths not equal
A > B < C

Similar bond length differences exist for a number of mono and dispiro cyclophosphazenes. Thus for example in the dispiro compound

$N_3P_3Cl_2[N(CH_3)CH_2CH_2O]_2$[14] the P(1)-N(1) and P(1)-N(3) distances are relatively short (mean 1.565 A) compared to the other ring distances (mean 1.602 A).



The general trends of bondlength - bond angle relationships observed in other cyclophosphazenes seem to be holding true for spiro cyclophosphazenes: thus a decrease in the ring P-N bond length (effected by an increase of *electronegativity of* the substituent) is accompanied by a decrease in the angle subtended by the exocyclic substituents at the phosphorus, an increase in the ring NPN angle and a decrease in ring PNP angle. The planar character of the cyclotriphosphazene ring seems to remain unaffected largely in many of the spirocyclic compounds. Puckering of the spirocyclic ring is observed in most instances and generally the two rings are perpendicular to each other, although there is a great variation in the extent of dihedral angles from compound to compound.

In contrast to spiro compounds, ansa compounds are found with significant ring puckering. This is undoubtedly the influence of the ansa arch which connects two phosphorus atoms of the same molecule.[23,47] Attempts have been made to correlate the observed structural features with nmr parameters. Thus Shaw and coworkers have measured the ^3J(P-O-C-C) in a *series of compounds* and related it to the dihedral angle/or exocyclic nitrogen atom planarity:[3]

	Dihedral Angle	^3J P-O-C-C
$N_3P_3[O(CH_2)_4O]\ Cl_4$ (41)	90°	0.0
$N_3P_3[O(CH_2)_3O]\ Cl_4$ (34)	53°	7.3 Hz
$N_3P_3[NH(CH_2)_3NH]\ Cl_4$ (11)	62°	6.6 Hz
$N_3P_3[N(CH_3)(CH_2)_3N(CH_3)]Cl_4$ (11a)	49°	2.6 Hz

Table 3. X ray Structural Parameters

(a) Spirocyclic Phosphazenes

(i) Monospiro

Compound	Phosphazene ring Conformation	Conformation of spirocyclic group	Average ring P-N bond length	Average endocyclic bond angles (O)			Dihedral angle between ring NPN and exocyclic X-P̂-Y	Ref.
				P-N̂-P	N-P̂-N	X-P̂-Y		
1	2	3	4	5	6	7	8	9
$N_3P_3[N(CH_3)_2]_4[HN(CH_2)_2NH]$(6b)	Non-linear	Envelope	1.594	123.6	115.8	95.5	101.3	55
$N_3P_3Cl_4[HN(CH_2)_2O]$(14)	Planar	Nonplanar	1.593	124.6	112.9			
			1.554	118.3	118.8	95.6	a)	56
			1.585					
$N_3P_3Cl_4[N(CH_3)(CH_2)_2O]$ (20)	Planar	Planar	1.568	124.3	113.3			
			1.556	119.3	119.3	95.7	a)	56
			1.568					
$N_3P_3Cl_4[O(CH_2)_2O]$ (31)	Planar	Twist boat	1.581	122.9	115.5			
			1.561	119.6	119.1	98.3	92.0	56
			1.571					
$N_3P_3Cl_4[HN(CH_2)_3NH]$ (11)	Planar	Nonplanar	1.609	125.1	111.5			
		(Twist boat)	1.553	118.8	119.9	101.1	99.0	56, 57
			1.579					

1	2	3	4	5	6	7	8	9
$N_3P_3Cl_4[N(CH_3)(CH_2)_3N(CH_3)]$	Planar	Nonplanar	1.619	123.9	111.3			
		(Chair)	1.553	117.9	120.5	103.8	a)	56
			1.584					
$N_3P_3Cl_4[NH(CH_2)_3O](16)$	Planar	Nonplanar	1.594	124.3	113.2			
		Distorted	1.557	118.4	119.6	102.2	a)	56
		chair	1.585					
$N_3P_3Cl_4[O(CH_2)_3O]$ (35)	Planar	Nonplanar	1.582	122.4	116.6			
		chair	1.561	120.4	119.2	105.4	90	38, 56
			1.571					
$N_3P_3Cl_4[HN(CH_2)_4NH]$ (13)	Nonplanar	Nonplanar	1.60	125.3	113.5			
			1.59	118.5	118.0	105.2	99.2	51
			1.57					
$N_3P_3Cl_4[O(CH_2)_4O]$ (41)	Planar	Nonplanar	1.592	122.3	116.1			
			1.561	120.1	119.3	106.1	98.0	38
			1.575					
(ii) Dispiro								
$N_3P_3Cl_2[N(CH_3)(CH_2)_2O]_2(21)$	Planar	Planar	1.565	127.0	114.4	95.7	89.9	14,56
			1.602	120.7	121.5	96.2	89.1	
			1.579					

1	2	3	4	5	6	7	8	9
$N_3P_3Cl_2[O(CH_2)_2O]_2$ (32)	a)	a)	1.563 1.587 1.572	121.7 124.7	119.6 116.1 (spiro)	97.8	a)	56
(iii) Trispiro								
$N_3P_3[HN(CH_2)_3NH]_3$	Planar	Nonplanar	1.598	122.4	114.9	102.2	a)	51
$N_3P_3[O_2(C_6H_4)]_3$	Planar	Planar	1.576	122.0	119.0	97.0	107.0	59
$N_3P_3[O_2(C_6H_4)_2]_3$	Distorted	b)	1.572	121.0	118.4	102.7	105.6	60
(iv) Bridging								
$[N_3P_3Cl_5]_2[HN(CH_2)_4NH]$	Planar	-	1.599 1.547 1.574	121.6 121.0	117.2 119.3	107.6	-	51
(v) Ansa								
$N_3P_3Cl_3CH_3[HN(CH_2)_3O]$	Nonplanar	-	1.622 1.577 1.599	122.0 117.0	112.0 119.1	104.6[c] 103.0[d]	-	51
$N_3P_3Cl_4[HN(CH_2)_2O(CH_2)_2NH]$	Nonplanar[e]	-	1.579 1.602	119.3 116.0	121.5 124.3	100.1	-	23

a): not mentioned in the original reference. b) : Two of the $O_2(C_6H_4)_2$ groups are twisted in a 'propeller' fashion at 43° in one direction while the third is twisted at 52° in the opposite direction. c) : $H_3C\text{-}\hat{P}\text{-}N$. d) : $Cl\text{-}\hat{P}\text{-}O$. e) : Only one ring nitrogen atom out of plane by 0.22 A.

As the dihedral angle becomes 90° according to Karplus relationship the coupling constant becomes a minimum. But in the last two examples the variation in coupling constant cannot be explained by dihedral angle variations alone. Shaw[3] suggests that the reasons of variation are due to the (non) planarity of exocyclic nitrogen atoms. Thus compound (11) has a pyramidal nitrogen (sum of angles around nitrogen = 351.1°) and shows a lower coupling constant while compound (11a) has a planar nitrogen (360°) and a larger coupling constant. There have also been attempts to correlate the observed ^{31}P chemical shift values with changes in exocyclic bond angles.[14,38,48] However, more examples and more detailed studies are required for a thorough understanding of the correlation of observed nmr parameters with that of the solid-state structures.

5.0 Summary

The reactions of $N_3P_3Cl_6$(1) and its derivatives, $N_3P_3Cl_4Ph_2$(3) and $N_3P_3Cl_4(NHC_4H_9{}^t)_2$(4) with several difunctional reagents proceed predominantly via the spirocyclic pathway. Bridging compounds result when the chain length in the reagent $H_2N\text{-}(CH_2)_n\text{-}NH_2$ is $n > 4$. Ansa products, although isolated, remain rare. The tetrameric system has not been studied to the same extent as the trimeric one owing to the instability of the products as well as the inherent complexity. However, available data suggests here also the preponderance of spirocyclic products.

Multinuclear nmr has proved to be a versatile and powerful technique for the elucidation of the structures of the products. However, care must be taken to analyze dubious second order effects as well as isochronous chemical shifts. Further attempts are required for a proper and a fuller understanding of the correlation between X ray and nmr data.

Future directions in this field would include development of suitable precursor cyclophosphazene derivatives that can be used for condensation polymerizations, use of macrocyclic spiro and ansa rings as novel ligating systems, and study of the effect of the spirocyclic ring on further

substitutions of the P-Cl bond by other nucleophiles.

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REFERENCES

1. R. A. Shaw, Phosphorus and Sulfur, 1986, 28, 99.
2. R. A. Shaw, Phosphorus, Sulfur and Silicon, 1989, 45, 103.
3. S. S. Krishnamurthy, A. C. Sau, and M. Woods, Adv. Inorg. Chem. Rad. Chem., 1978, 21, 41.
4. H. R. Allcock, P. R. Suszko, L. J. Wagner, R. R. Whittle, and B. Boso, J. Am. Chem. Soc., 1984, 106, 4966; M. R. Welker, I. Manners, M. Pervez, and H. R. Allcock, J. Chem. Soc., Chem. Comm., 1989, 871.
5. H. R. Allcock, D. J. Brennen, B. S. Dunn, and M. Parvez, Inorg. Chem., 1988, 27, 3226; H. R. Allcock, I. Manners, M. N. Maug, and M. Parvez, Inorg. Chem., 1990, 29, 522.
6. H. R. Allcock, G. H. Riding, and R. R. Whittle, J. Am. Chem. Soc., 1984, 106, 5561.
7. S. Ganapathiappan, K. S. Dhathathreyyan and S. S. Krishnamurthy, Macromolecules, 1987, 20, 1501 and references there in; H. R. Allcock, "Encyclopedia of Polymer Science and Engineering", 1988, 13, 31 and references cited there in.
8. H. R. Allcock, D. J. Brennan, and B. S. Dunn, Macromolecules , 1989, 22, 1534.
9. H. R. Allcock, Chem. Eng. News., 1985, 63, 22.
10. H. R. Allcock, W. C. Hymer, and P. E. Austin, Macromolecules , 1983, 16, 1401.
11. H. R. Allcock and S. Kwon, Macromolecules , 1986, 19, 1502.
12. H. R. Allcock, M. N. Maug, G. S. McDonnell, and M. Parvez, Macromolecules , 1987, 20, 2060; H. R. Allcock and W. D. Coggio,

Macromolecules , 1990, 23, 1626.

13. V. Chandrasekhar, S. S. Krishnamurthy, A. R. Vasudeva Murthy, R. A. Shaw, and M. Woods, Inorg. Nucl. Chem. Letts., 1981, 17, 181.
14. V. Chandrasekhar, S. S. Krishnamurthy, H. Manohar, A. R. Vasudeva Murthy, R. A. Shaw, and M. Woods, J. Chem. Soc., Dalton Trans., 1984, 621.
15. V. Chandrasekhar and N. S. Reddy, Heterocycles , 1989, 28, 611.
16. S. S. Krishnamurthy, K. Ramachandran, A. R. Vasudeva Murthy, R. A. Shaw, and M. Woods, Inorg. Nucl. Chem. Letts., 1977, 13, 407.
17. S. S. Krishnamurthy, K. Ramachandran, A. R. Vasudeva Murthy, R. A. Shaw, and M. Woods, J. Chem. Soc., Dalton Trans., 1980, 840.
18. W. F. Deutsch and R. A. Shaw, J. Chem. Soc., Dalton Trans., 1988, 1757.
19. W. F. Deutsch and R. A. Shaw, Phosphorus, Sulfur and Silicon., 1990, 47, 119.
20. A. H. Alkubaisi, H. G. Parkes, and R. A. Shaw, Heterocycles , 1989, 28, 347.
21. P. Castera, J. P. Faucher, J. F. Labarre, and B. Perly, J. Mol. Struct., 1987, 160, 365; P. Castera, J. P. Faucher, G. Guerch, R. Lahana, A. Mahmoun, F. Sournies, and J. F. Labarre, Inorg. Chim. Acta., 1985, 108, 29.
22. P. J. Harris and K. B. Williams, Inorg. Chem., 1984, 23, 1496.
23. R. Enjalbert, J. Galy, P. Castera, and J. F. Labarre, Acta cryst., 1988, C44, 1813.
24. F. Sournies, A. E. Bakili, J. F. Labarre, and B. Perly, J. Mol. Struct. 1989, 196, 201.
25. R. Enjalbert, J. Galy, A. E. Bakili, P. Castera, J. P. Faucher, F. Sournies, and J. F. Labarre, J. Mol. Struct., 1989, 195, 207.
26. A. E. Bakili, P. Castera, J. P. Faucher, F. Sournies, and J. F. Labarre J. Mol. Struct., 1989,195, 21.
27. S. R. Contractor, M. B. Hursthouse, H. G. Parkes, L. S. Shaw, R. A. Shaw, and H. Yilmaz, J. Chem. Soc., Chem. Commun., 1984, 675.

28. T. Chivers and R. Hedgeland, Can. J. Chem., 1972, 50, 1017.

29. B. D. Ruiter, G. Kuipers, J. H. Bijlaart, and J. C. Van de Grampel, Z. Naturforsch., 1982, 37b, 1425.

30. F. H. Westheimer, Acc. Chem. Res., 1968, 1, 70.

31. V. Chandrasekhar, S. Karthikeyan, S. S. Krishnamurthy, and M. Woods, Ind. J. Chem., 1985, 24A, 379.

32. A. H. Alkubaisi and R. A. Shaw, Phosphorus, Sulfur and Silicon , 1989, 45, 7.

33. H. R. Allcock and R. L. Kugel, Inorg. Chem., 1966, 5, 1016.

34. H. R. Allcock and R. L. Kugel, J. Am. Chem. Soc., 1969, 91, 5452.

35. H. R. Allcock, R. L. Kugel, and G. Y. Moore, Inorg. Chem., 1975, 14, 2831.

36. H. R. Allcock and L. A. Siegel, J. Am. Chem. Soc., 1964, 86, 5140.

37. H. R. Allcock and M. L. Levin, Macromolecules , 1985, 18, 1324.

38. S. R. Contractor, M. B. Hursthouse, L. S. Shaw, R. A. Shaw, and H. Yilmaz, Acta Cryst., 1985, B41, 122.

39. R. L. Collin, J. Am. Chem. Soc., 1966, 88, 3281.

40. J. Martin and J. B. Robert, Org. Magn. Reson., 1981, 15, 87.

41. G. M. Blackburn, J. S. Cohen, and Lord Todd, Tetrahedron Lett., 1964, 2873.

42. E. G. Finer, J. Mol. Spectroscopy., 1967, 23, 104.

43. E. G. Finer, R. K. Harris, M. R. Band, R. Keat, and R. A. Shaw, J. Mol. Spectroscopy , 1970, 33, 72.

44. R. Keat, R. A. Shaw, and M. Woods, J. Chem. Soc., Dalton Trans., 1976, 1582.

45. N. V. Mani, F. R. Ahmed, and W. H. Barnes, Acta Cryst., 1965, 19, 693.

46. N. V. Mani, F. R. Ahmed, and W. H. Barnees, Acta Cryst., 1966, 21, 375.

47. F. Sournies, J. F. Labarre, P. J. Harris, and K. B. Williams, Inorg. Chim. Acta , 1984, 90, L61.

48. W. F. Deutsch, M. B. Hursthouse, Z. Kilic, H. G. Parkes, L. S. Shaw,

and R. A. Shaw, Phosphorus and Sulfur , 1987, 32, 81.

49. K. C. Kumaraswamy and S. S. Krishnamurthy, Ind. J. Chem., 1984, 23A, 717.

50. K. Brandt and Z. Jedlinski, J. Org. Chem., 1980, 45, 1672.

51. J. F. Labarre, Top. Curr. Chem., 1985, 129, 173.

52. W. F. Deutsch, M. B. Hursthouse, Z. Kilic, H. G. Parkers, L. S. Shaw, and R. A. Shaw, Phosphorus and Sulfur, 1987, 32, 81.

53. G. Guerch, J. F. Labarre, R. Lahana, R. Roques, and F. Sournies, J. Mol. Struct, 1983, 99, 275.

54. G. Guerch J. F. Labarre, R. Roques, and F. Sournies, J. Mol. Struct., 1982, 96, 113.

55. Y. Sudhakar Babu, H. Manohar, K. Ramachandran, and S. S. Krishnamurthy, Z. Naturforsch. Teil B ,1978, 33, 588.

56. A. H. Alkubaisi, H. A. Madfa, W. F. Deutsch, M. B. Hursthouse, H. G. Parkes, L. S. Shaw, and R. A. Shaw, Phosphorus and Sulfur , 1986, 28, 277.

57. G. Guerch, M. Greffenil, J. F. Labarre, R. Enjalbert, R. Lahana, and F. Sournies, J. Mol. Struct., 1982, 85, 237.

58. S. R. Contractor, M. B. Hursthouse, H. G. Parkes, L. S. Shaw, R. A. Shaw, and H. Yilmaj, J. Chem. Soc., Chem. Commun., 1984, 675.

59. L. A. Siegel and J. H. Van der Hande, J. Chem. Soc. A , 1967, 817.

60. H. R. Allcock, M. T. Stein, and J. A. Stanxo, J. Am. Chem. Soc., 1971, 93, 3173.

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