Phosphorus–Nitrogen Compounds. Part 55.[1] The Reactions of 2,2,4,4-Tetrachloro-6,6-diphenylcyclotriphosphazatriene with Aliphatic Difunctional Alcohols, Amines, and Aminoalcohols. Proton and Phosphorus-31 Nuclear Magnetic Resonance Spectroscopic Studies of the Products

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The reactions of geminal $N_3P_3Ph_2Cl_4$ with aliphatic difunctional alcohols, amines, and aminoalcohols have been investigated. A series of monospiro derivatives, $N_3P_3Ph_2[X(CH_2)_nY]Cl_2$ [X = Y = O or NH, n = 2—4; X = O, Y = NH, n = 2—4; X = Y = NMe, n = 2 or 3; X = NH, Y = NMe, n = 2 or 3; X = O, Y = NMe, n = 2] were obtained and the ^{31}P and ^1H n.m.r. spectra investigated. The field and temperature dependences of the ^{31}P n.m.r. spectra were used in the study of degenerate spectra. Non-equivalence of methylene protons in the spiro rings is observed in the ^1H n.m.r. spectra of these compounds.

The reactions of difunctional reagents with phosphazenes give rise in principal to four types of structures: (*i*) spiro (both functional groups of the reagent attached to the same phosphorus atom), (*ii*) ansa (the two functional groups attached to different atoms in the same molecule), (*iii*) bridging (each functional group is attached to different phosphazene rings), and (*iv*) dangling structures (only one end of the difunctional reagent is attached to the phosphazene ring). These have been summarised elsewhere.[2]

From the reaction of $N_3P_3Cl_6$ with propane-1,3-diol two isomeric $N_3P_3[O(CH_2)_3O]_2Cl_2$ derivatives were obtained. The n.m.r. spectra suggested and the crystal structures proved them to be the first example of dispiro/spiro–ansa isomerism in phosphazene chemistry.[3] The formation of the spiro–ansa compound is likely to proceed *via* the monospiro compound, $N_3P_3[O(CH_2)_3O]Cl_4$, which is by far the major product, although recently the ansa isomer has been isolated in trace amounts.[4]

The present study was undertaken with two aims in mind. (*a*) The reactions of $N_3P_3Cl_6$ with propane-1,3-diol suggested that ansa formation was more favourable when a pair of geminal chlorine atoms had been replaced by a spiro dioxy group (see above). The electron supply towards the remaining $\equiv PCl_2$ groups has then been increased. As in basicity studies phenyl groups increase the basicity by about the same amount as alkoxy groups, geminal $N_3P_3Ph_2Cl_4$ (**1**) seemed a good choice (particularly as it is readily available by a Friedel–Crafts reaction[5]) to see how the transition from $N_3P_3Cl_6$ to geminal $N_3P_3Ph_2Cl_4$ (**1**) affected the potential product types (*i*)—(*iv*). (*b*) Basicity measurements on the monospiro products allow calculation of basicity substituent constants which were required for structure–property relationships.[6] Spiro substituents are more conformationally constrained than acyclic substituents and earlier studies had shown that basicity constants were conformation dependent.[7]

Here, ^{31}P n.m.r. spectroscopic data are presented and we show how the use of higher field strengths and variable-temperature ^{31}P n.m.r. spectroscopy can be used in the elucidation of degenerate spectra. The dispiro compound $N_3P_3[O(CH_2)_3O]_2Cl_2$ has given rise to a highly complex ^1H n.m.r. spectrum as a result of the non-equivalence of the methylene protons.[8] For this reason we have also investigated the proton n.m.r. spectra of monospiro derivatives, $N_3P_3Ph_2[X(CH_2)_nY]Cl_2$, to observe whether similar complexities exist.

Results and Discussion

In the reactions of chlorocyclotriphosphazatrienes with α,ω derivatives of ethane and propane (and to a lesser extent of butane) spiro products predominate.[2] The scarcity of ansa structures and the increasing incursion of bridging derivatives of butane[4,9,10] and higher homologues can be rationalised as follows: generally, reactions leading to five- and six-membered rings confer stability on their products. Larger rings form progressively with lesser ease. Hence bridging derivatives compete successfully with spiro compounds. This occurs for butane derivatives, and for higher difunctional amines only bridging compounds have been reported.[4,9,10] The only ansa structures of this family so far reported are those based on propane reagents.[3,4,11] These form eight-membered rings and are highly strained.[6,12] Ethane reagents would give rise to seven-membered rings, but the strain would be greatly increased. With butane derivatives such strain would be absent, but the ring would be now nine-membered.

The reactions of diols and aminoalcohols with geminal $N_3P_3Ph_2Cl_4$ are very much slower than corresponding reactions with diamines. Reactions were found to proceed far more efficiently in the presence of pyridine as a tertiary base than when triethylamine is used, although the basicity of triethylamine is greater. The greater effectiveness of pyridine compared to triethylamine in facilitating chlorine replacement is presumably related to steric demands. The compounds isolated are shown below.

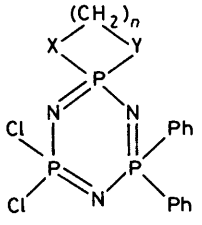
Their ^{31}P n.m.r. spectra were obtained and provide examples where all three nuclei differ. These may be considered as AMX (first order), ABX, or ABC spin systems depending on the extent of phosphorus–phosphorus coupling $J(PP)/\nu_0\delta$. A number of different cases arise and are discussed below. The ^{31}P n.m.r. data are presented in Table 1. The spectra were run both proton coupled and decoupled and this greatly simplified assignment of lines in the ^{31}P-$\{^1H\}$ n.m.r. spectra since the signals from $\equiv PCl_2$ remain unsplit in both cases, whereas those of the $\equiv PPh_2$ and ≡P(spiro) group collapse in the ^{31}P–H spectra.

The spectra of $N_3P_3Ph_2[X(CH_2)_3Y]Cl_2$ [X = Y = O or NH; X = O, Y = NH; X = NH, Y = NMe (**2**)—(**5**)] are of the ABX type. The AB part of the spectra arises from the $\equiv PPh_2$ and $\equiv PCl_2$ groups as a result of the small chemical shift difference between them. The ^{31}P-$\{^1H\}$ n.m.r. spectra of these compounds at 24.15 MHz give rise to poorly resolved spectra in which the inner transitions of the ab subspectra coalesce and the outer transitions are weak. Extraction of parameters is as a

Table 1. Phosphorus-31 n.m.r. data of monospiro derivatives of *gem*-$N_3P_3Ph_2Cl_4$ [a]

	δ/p.p.m.			δ(PPh$_2$) − δ(PCl$_2$)/	J/Hz		
	P(spiro)	PPh$_2$	PCl$_2$	p.p.m.	P(spiro)–PCl$_2$	P(spiro)–PPh$_2$	PCl$_2$–PPh$_2$
$N_3P_3Ph_2Cl_4$ [b]		20.6	18.1	2.5			12.7
$N_3P_3Ph_4Cl_2$ [b]		18.1	15.8	2.3			9.2
$N_3P_3Ph_6$ [b]		14.7					
(2) $N_3P_3Ph_2[O(CH_2)_3O]Cl_2$ [c]	5.4	22.1	21.9	0.2	45.1	34.0	16.8
(3) $N_3P_3Ph_2[O(CH_2)_3NH]Cl_2$ [c]	10.0	21.1	20.6	0.5	33.0	28.0	18.4
(4) $N_3P_3Ph_2[HN(CH_2)_3NH]Cl_2$ [c]	10.9	20.0	20.4	−0.4	22.0	19.4	23.0
(5) $N_3P_3Ph_2[HN(CH_2)_3NMe]Cl_2$ [c]	15.0	20.2	20.7	−0.5	17.2	20.1	19.5
(6) $N_3P_3Ph_2[MeN(CH_2)_3NMe]Cl_2$ [c]	19.4	20.1	21.7	−1.6	6.5	24.1	21.5
(7) $N_3P_3Ph_2[O(CH_2)_2O]Cl_2$ [c]	26.7	23.1	25.2	−2.1	50.3	29.0	20.1
(8) $N_3P_3Ph_2[O(CH_2)_2NH]Cl_2$ [b]	26.4	20.8	23.7	−2.9	39.3	21.2	20.8
(9) $N_3P_3Ph_2[HN(CH_2)_2NH]Cl_2$ [d]	25.4	20.3	22.8	−2.5	30.1	18.4	22.6
(10) $N_3P_3Ph_2[HN(CH_2)_2NMe]Cl_2$ [d]	24.0	20.6	23.3	−2.7	27.6	18.4	23.8
(11) $N_3P_3Ph_2[MeN(CH_2)_2NMe]Cl_2$ [d]	22.9	20.8	24.0	−3.2	25.2	18.3	23.7
(12) $N_3P_3Ph_2[O(CH_2)_2NMe]Cl_2$ [d]	25.2	22.1	24.4	−2.3	35.7	22.5	22.3
(13) $N_3P_3Ph_2[O(CH_2)_4O]Cl_2$ [c]	12.5	22.0	23.6	−1.6	53.9	31.4	17.9
(14) $N_3P_3Ph_2[O(CH_2)_4NH]Cl_2$ [c]	16.9	20.7	22.9	−2.2	44.2	23.2	19.1
(15) $N_3P_3Ph_2[HN(CH_2)_4NH]Cl_2$ [c]	14.5	18.7	21.4	−2.7	32.0	19.9	20.8

[a] In $CDCl_3$ solution; external reference 85% H_3PO_4. [b] Spectra obtained at 24.15 MHz. [c] Spectra obtained at 162.0 MHz. [d] Spectra obtained at 80.95 MHz.



		n
(2)	X = Y = O	3
(3)	X = O, Y = NH	3
(4)	X = Y = NH	3
(5)	X = NH, Y = NMe	3
(6)	X = Y = NMe	3
(7)	X = Y = O	2
(8)	X = O, Y = NH	2
(9)	X = Y = NH	2
(10)	X = NH, Y = NMe	2
(11)	X = Y = NMe	2
(12)	X = O, Y = NMe	2
(13)	X = Y = O	4
(14)	X = O, Y = NH	4
(15)	X = Y = NH	4

consequence difficult and in some cases spectra may be misleading in the assignment of structure. The second-order effects and degeneracy could be reduced in two ways in these compounds: (*a*) increase of field strength and (*b*) lowering of temperature.

(*i*) At higher field strengths, 80.95 and 162.0 MHz, the frequency spread is increased and hence spectra are better resolved and second-order perturbations of the AB parts of the spectra are reduced. Figure 1(*a*) and (*b*) show the spectrum of $N_3P_3Ph_2[HN(CH_2)_3NH]Cl_2$ (**4**) at low (24.15 MHz) and high field (162.0 MHz) respectively, both at room temperature.

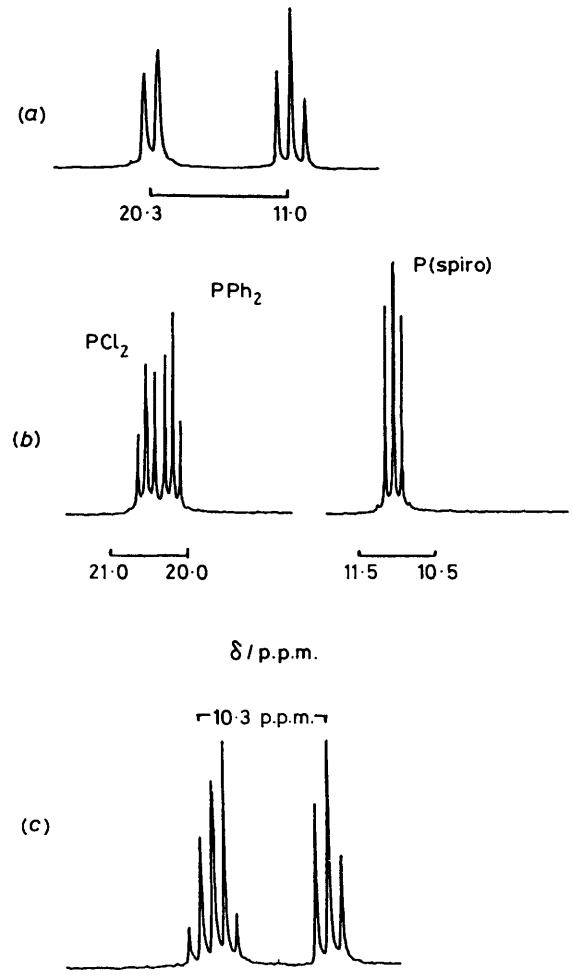


Figure 1. $^{31}P-\{^1H\}$ N.m.r. spectra of $N_3P_3Ph_2[HN(CH_2)_3NH]Cl_2$ (**4**) in $CDCl_3$: (*a*) at 24.15 (room temperature), (*b*) at 162.0 (room temperature), and (*c*) 24.15 MHz (−50 °C)

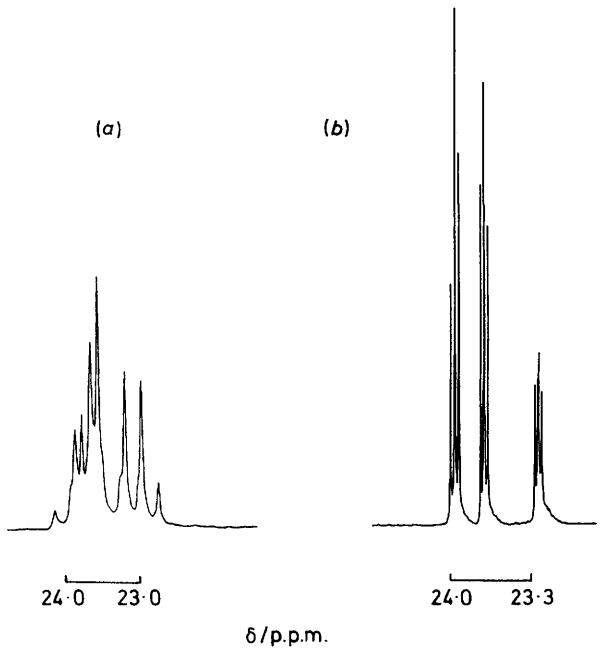


Figure 2. $^{31}P-\{^1H\}$ N.m.r. spectrum of $N_3P_3Ph_2[MeN(CH_2)_2NMe]Cl_2$ (**11**) in $CDCl_3$ (room temperature) at (*a*) 24.15 and (*b*) 162.0 MHz

(*ii*) Lowering the temperature at 24.15 MHz to −50 °C results in a dramatic change in the $^{31}P-\{^1H\}$ n.m.r. spectra of these compounds, with a number of previously overlapping transitions resolved and a decrease in second-order perturbation. This allows the spectra to become more amenable to interpretation. These changes result from an increase in the chemical shift difference [$\nu(PPh_2) - \nu(PCl_2)$] with decrease of temperature. Figure 1(*c*) illustrates this temperature effect for $N_3P_3Ph_2[HN(CH_2)_3NH]Cl_2$, (**4**), which has a deceptively simple A_2X appearance at room temperature.

The compound $N_3P_3Ph_2[MeN(CH_2)_3NMe]Cl_2$, (**6**), gives rise to a poorly resolved ABC type spectrum at 24.15 MHz, caused by the anomalously high chemical shift of the ≡P[$MeN(CH_2)_3NMe$] group (19.4 p.p.m.) compared with that of the analogous non-methylated six-membered ring compound, $N_3P_3Ph_2[HN(CH_2)_3NH]Cl_2$ (**4**), where the chemical shift of the ≡P[$HN(CH_2)_3NH$] group is only 10.9 p.p.m. Eleven out of 12 lines anticipated for an AMX/ABX type spectrum were observed, when the spectrum was run at 162.0 MHz.

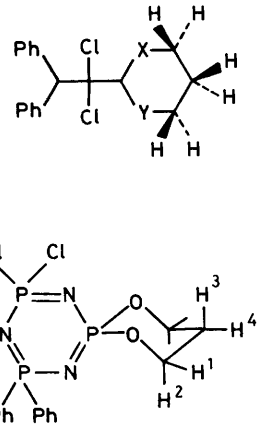
A large downfield movement (14—21 p.p.m.) of the ≡P(spiro) group is observed on passing from six-membered [except for compound (**6**), see above] to the five-membered spiro ring series. The result is that the resonances of all three phosphorus nuclei occur in the same region of the spectrum and at lower field strengths (24.15 MHz) strong second-order effects are observable in the five-membered ring series giving in general ABC-type spectra. At higher field strengths (80.95 and 162.0 MHz) second-order effects are considerably reduced, particularly in the case of $N_3P_3Ph_2[X(CH_2)_2Y]Cl_2$ [X = Y = O or NH; X = O, Y = NH; X = O, Y = NMe, (**7**)—(**9**) and (**12**)], where the resonances of all three nuclei are distinctly separated. The effect of field strength on the appearance of the spectrum is illustrated for $N_3P_3Ph_2[MeN(CH_2)_2NMe]Cl_2$ (**11**) in Figure 2.

A smaller downfield movement (4—7 p.p.m.) of the chemical shift of the ≡P(spiro) group is observed on passing from the six- to the seven-membered spiro ring than is observed on passing from the six- to the five-membered ring series. In the seven-membered ring series the ≡P(spiro) group is relatively well separated from the resonances of the $\equiv PPh_2$ and the $\equiv PCl_2$ groups. Furthermore, the chemical shift difference [$\nu(PPh_2) - \nu(PCl_2)$] is noticeably larger in the seven- than in the six-membered spiro derivatives and hence fewer degeneracies are observed in their spectra. The spectra are unambiguous, even at lower field (24.15 MHz), whilst at 162.0 MHz the $^{31}P-\{^1H\}$ n.m.r. spectra could be treated as first-order ones.

The effect of OPO bond angles in PO_2N_2 tetrahedra (which themselves are dependent on spiro ring size) on chemical shift has been investigated in a series of alkoxy derivatives of cyclophosphazenes.[13] It was shown that relatively small changes in bond angles resulted in large changes of chemical shift.

Inspection of Table 1 reveals a number of interesting trends. If we consider the chemical shift of the ≡P(spiro) nucleus in $N_3P_3Ph_2[X(CH_2)_nY]Cl_2$, we note the following. (*i*) For the six- and seven-membered ring series (n = 3 or 4) the big changes (≈4.5 p.p.m.) occur from X = Y = O to X = O, Y = NH, with only a smaller change on replacement of the second oxygen atom by an NH group. (*ii*) Further large changes in shift (4.2 p.p.m.) occur for six-membered spiro rings on methylation of nitrogen atoms. (*iii*) The total chemical shift range for effects (*i*) and (*ii*) for the six-membered ring series (n = 3) is 14 p.p.m., whilst for the five-membered analogues (n = 2) it is only 3.8 p.p.m. and this is in the *opposite sense* to that for n = 3. (*iv*) Whilst methylation in the six-membered series (NH ⟶ NMe) is accompanied by ≈4.2 p.p.m. *deshielding* per NMe group, in the five-membered series a *shielding* of ≈1.2 p.p.m. per NMe group is noted. With the structural data available we suggest that the latter effect may well be connected with the increased electron supply on replacing NH by NMe, whilst in the six-membered ring series[14,15] changes in the stereochemistry around the nitrogen atoms and concomitant P–N bond length increases are the paramount factors. It is interesting to observe differences in the relative shift of the $\equiv PPh_2$ and $\equiv PCl_2$ groups for different spiro rings (Table 1).

For the monospiro derivatives of the type $N_3P_3Ph_2[X(CH_2)_nY]Cl_2$ additional information can be obtained from their ^1H n.m.r. spectra (Table 2) compared with those of the monospiro derivatives of the type $N_3P_3[X(CH_2)_nY]Cl_4$, since in the former case differing chemical environments are provided for the methylene protons of the $XCH_2(YCH_2)$ and CCH_2 groups. This is illustrated below for $N_3P_3Ph_2[X(CH_2)_3Y]Cl_2$.



In both cases, at room temperature, rapid interconversion of the two chair forms occurs. Hence differences between these two, as well as possible axial–equatorial environments, become equivalent, through fast exchange and only differences due to asymmetric substitution of the N_3P_3 ring are observable.

Table 2. Proton n.m.r. data[a] of monospiro derivatives of geminal $N_3P_3Ph_2Cl_4$

Compound	δ/p.p.m. OCH_2	NCH_2	CCH_2	NCH_3	NH	^3J/Hz $POCH_2$	$PNCH_2$	$PNCH_3$
$N_3P_3Ph_2[O(CH_2)_3O]Cl_2$[b]	4.36		1.76			12.9		
	4.54		2.22					
$N_3P_3Ph_2[O(CH_2)_3NH]Cl_2$	4.4*	3.2*	1.69		2.5	*	*	
			2.01					
$N_3P_3Ph_2[HN(CH_2)_3NH]Cl_2$		3.16	1.68		2.5		15.0	
		3.25	1.82					
$N_3P_3Ph_2[HN(CH_2)_3NMe]Cl_2$		3.0*	1.7*	2.35			*	*
			2.2*					
$N_3P_3Ph_2[MeN(CH_2)_3NMe]Cl_2$		3.1*	1.72	2.35	2.5		*	14.0
			1.92					
$N_3P_3Ph_2[O(CH_2)_2O]Cl_2$	4.45					11.5		
$N_3P_3Ph_2[O(CH_2)_2NH]Cl_2$	4.4*	3.5*			2.6	*	*	
$N_3P_3Ph_2[HN(CH_2)_2NH]Cl_2$		3.37			2.5		9.2	
$N_3P_3Ph_2[HN(CH_2)_2NMe]Cl_2$		3.2*		2.40	2.5		*	14.2
		3.4*						
$N_3P_3Ph_2[MeN(CH_2)_2NMe]Cl_2$		3.2*		2.44			*	14.2
$N_3P_3Ph_2[O(CH_2)_2NMe]Cl_2$	4.2*	3.2*		2.45		*	*	14.0
$N_3P_3Ph_2[O(CH_2)_4O]Cl_2$[b]	4.19		2.93			*		
	4.21							
$N_3P_3Ph_2[O(CH_2)_4NH]Cl_2$	4.2*	3.1*		1.7	2.9	*	*	
				1.9				
$N_3P_3Ph_2[HN(CH_2)_4NH]Cl_2$[c]		3.14	1.57		2.9		12.5	
		3.16						

An asterisk indicates a complex overlap of lines.

[a] At 199.5 MHz except where indicated. [b] At 250.48 MHz. [c] At 400.0 MHz.

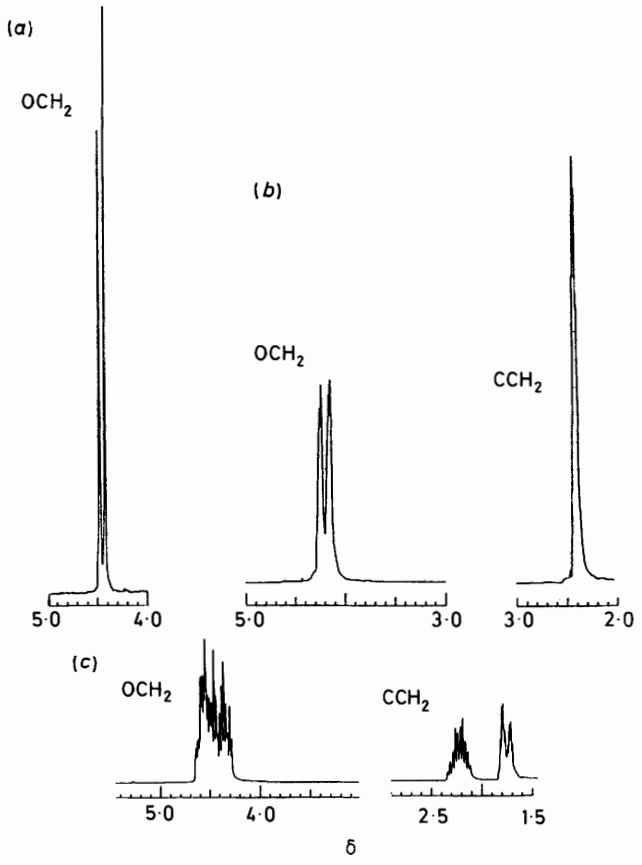


Figure 3. Proton n.m.r. spectra of alkanedioxy derivatives of *gem*-$N_3P_3Ph_2Cl_4$ (room temperature) in $CDCl_3$ at 199.50 MHz of (*a*) $N_3P_3Ph_2[O(CH_2)_2O]Cl_2$ (**7**), (*b*) $N_3P_3Ph_2[O(CH_2)_4O]Cl_2$ (**13**), and (*c*) $N_3P_3Ph_2[O(CH_2)_3O]Cl_2$ (**2**)

The ^1H n.m.r. spectra of some monospiro dioxy derivatives of geminal $N_3P_3Ph_2Cl_4$ are given in Figure 3. The six-membered monospiro derivatives of geminal $N_3P_3Ph_2Cl_4$ have highly complex ^1H n.m.r. spectra. The XCH_2, YCH_2, and CCH_2 protons gives rise to AB quartets depending on whether a proton 'observes' preferentially the $\equiv PPh_2$ or the $\equiv PCl_2$ group. In addition, further coupling with the adjacent protons and phosphorus is possible. This is illustrated for $N_3P_3Ph_2[O(CH_2)_3O]Cl_2$ (**2**) in Figure 3(*c*).

Homonuclear decoupling of the $X(Y)CH_2$ protons of the symmetric six-membered spiro derivatives of $N_3P_3Ph_2[X(CH_2)_3Y]Cl_2$, where X = Y = O, NH, or NMe, results in simplification of the CCH_2C signals to a quartet structure. Simplification of the XCH_2 resonances was also observed on decoupling of the CCH_2C protons, although coupling of the XCH_2 protons with phosphorus is evident. For $N_3P_3Ph_2[O(CH_2)_3O]Cl_2$ (**2**) it was not possible to irradiate the resonances due to the two CCH_2 protons simultaneously, as a result of the relatively large shift difference between them.

The ^1H-$\{^{31}P\}$ n.m.r. spectrum of $N_3P_3Ph_2[O(CH_2)_3O]Cl_2$ (**2**) was recorded and with the aid of further selective proton-decoupling experiments a simulation of the ^1H-$\{^{31}P\}$ spectrum of the CCH_2C protons was possible as shown in Figure 4. Details are given in Table 3 and compared with the coupling constants of related phosphorinanes.[16] The protons are labelled H^1 to H^4 according to the decrease in their chemical shift values. H^1 and H^2 correspond to the OCH_2 protons and H^3 and H^4 to the CCH_2C protons, respectively.

The coupling constants between protons of the spiro ring of $N_3P_3Ph_2[O(CH_2)_3O]Cl_2$ (**2**) are of the same sign and similar magnitude to those of 2-fluoro- and 2-chloro-1,3,2-dioxaphosphorinanes.[16] This would suggest that the spiro ring takes up similar conformations, in compound (**2**) and in the above phosphorinanes. (Values obtained by Hacklin *et al.*[16] for 2-chloro-1,3,2-dioxaphosphorinane are given in parentheses.) The methylene protons (particularly the CCH_2C protons) give

rise to a distinctly asymmetric multiplet structure, which arises from the different values of the coupling constants of the CCH_2 protons with the neighbouring OCH_2 protons.

Comparison of the ^1H chemical shift data of $N_3P_3Ph_2[O(CH_2)_3O]Cl_2$ (**2**) with those of $N_3P_3[O(CH_2)_3O]Cl_4$[4,8] suggests that H^1 of the OCH_2 group and H^3 of the CCH_2 group preferentially 'observe' the $\equiv PCl_2$ group whilst H^2 and H^4 preferentially 'observe' the $\equiv PPh_2$ group. A considerably smaller chemical shift difference ($\nu_A - \nu_B$) is observed between the OCH_2 protons (0.18 p.p.m.) than between the two CCH_2C protons (0.44 p.p.m.).

The compound $N_3P_3Ph_2[O(CH_2)_2O]Cl_2$ (**7**) gives rise to a doublet structure [Figure 3(*a*)] due to splitting of a single resonance by phosphorus indicating that the two environments of the OCH_2 protons are not resolved at this field strength in contrast to that of the six-membered ring analogue $N_3P_3Ph_2[O(CH_2)_3O]Cl_2$ (**2**). (An indication of non-equivalence is just observable at 400.00 MHz.)

The ^1H n.m.r. spectra of the seven-membered spiro derivatives $N_3P_3Ph_2[X(CH_2)_4Y]Cl_2$, where X = Y = O or NH, show considerably less fine structure than those of the six-membered ring analogues. Figure 3(*b*) illustrates this for $N_3P_3Ph_2[O(CH_2)_4O]Cl_2$ (**13**). The ^1H-$\{^{31}P\}$ n.m.r. spectrum of (**13**) shows that the OCH_2 methylene protons form part of an ABXX′ system (Figure 5). Extraction of n.m.r. parameters is

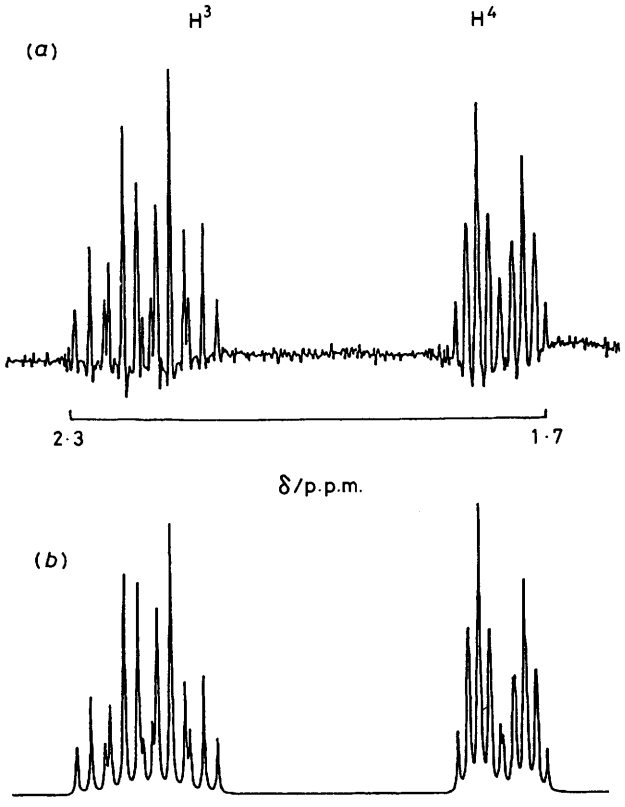


Figure 4. ^1H-$\{^{31}P\}$ N.m.r. spectrum at 250.48 MHz (room temperature) of $N_3P_3Ph_2[O(CH_2)_3O]Cl_2$ (**2**) showing the CCH_2C region: (*a*) observed; (*b*) simulated

Table 3. Proton n.m.r. parameters[a] of $N_3P_3Ph_2[O(CH_2)_3O]Cl_2$ (**2**) and a comparison with coupling constants of the related 2-chloro-1,3,2-dioxaphosphorinane

$\delta(H^1)$ 4.54	$\delta(H^1)-\delta(H^2)$ 0.18
$\delta(H^2)$ 4.36	
$\delta(H^3)$ 2.20	$\delta(H^3)-\delta(H^4)$ 0.44
$\delta(H^4)$ 1.76	
$J(H^1\text{–}H^2)$ −11.46 (−11.1)[b]	$J(H^2\text{–}H^3)$ 4.37 (4.6)
$J(H^1\text{–}H^3)$ 10.48 (13.0)	$J(H^3\text{–}H^4)$ −14.58 (−14.5)
$J(H^1\text{–}H^4)$ 3.07 (2.5)	$J(H^2\text{–}H^4)$ 0.0 (0.0)

[a] *J* In Hz. [b] Values in parentheses refer to 2-chloro-1,3,2-dioxaphosphorinane.[16]

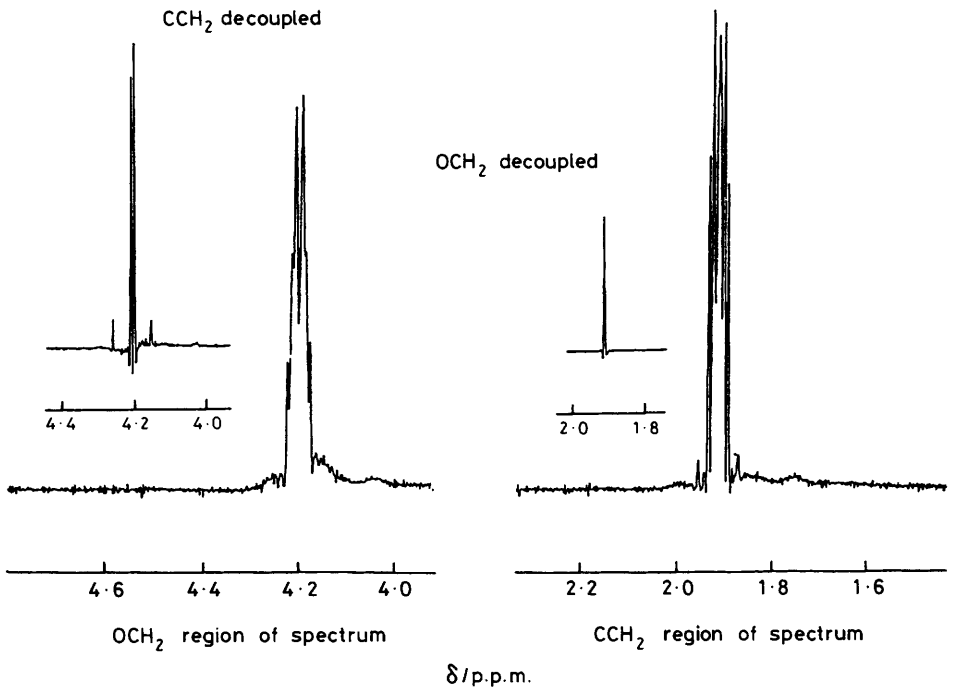


Figure 5. ^1H-$\{^{31}P\}$ N.m.r. spectrum of $N_3P_3Ph_2[O(CH_2)_4O]Cl_2$ (**13**) in $CDCl_3$ (room temperature) at 250.48 MHz

Table 4. Experimental details of the reactions of geminal $N_3P_3Ph_2Cl_4$ with difunctional reagents using dichloromethane as solvent

gem $N_3P_3Ph_2Cl_4$		Difunctional	Amount		Tertiary	Amount		Solvent used for column		Yield	M.p. (°C) of		
g	mmol	reagent	g	mmol	base	g	mmol	chromatography	Product	(%)	product	M^+	M
1.50	3.48	$HO(CH_2)_3OH$	0.265	3.48	Pyridine	0.550	6.96	CH_2Cl_2	(**2**)	65	168—169	433	433
1.50	3.48	$HO(CH_2)_3NH_2$	0.261	3.48	Pyridine	0.550	6.96	CH_2Cl_2–OEt_2 (8:1)	(**3**)	32	158—160	432	432
1.00	2.32	$H_2N(CH_2)_3NH_2$	0.172	2.32	NEt_3	0.470	4.64	CH_2Cl_2–OEt_2 (3:1)	(**4**)	60	153	431	431
1.50	3.48	$H_2N(CH_2)_3NMeH$	0.306	3.48	NEt_3	0.704	6.96	CH_2Cl_2–OEt_2 (4:1)	(**5**)	45	109	445	445
1.50	3.48	$HMeN(CH_2)_3NMeH$	0.355	3.48	NEt_3	0.704	6.96	CH_2Cl_2–OEt_2 (15:1)	(**6**)	35	136	459	459
1.50	3.48	$HO(CH_2)_2OH$	0.216	3.48	Pyridine	0.550	6.96	CH_2Cl_2	(**7**)	53	174—175	419	419
1.50	3.48	$HO(CH_2)_2NH_2$	0.212	3.48	Pyridine	0.550	6.96	CH_2Cl_2–OEt_2 (6:1)	(**8**)	45	155—156 (154*)	418	418
1.50	3.48	$H_2N(CH_2)_2NH_2$	0.209	3.48	NEt_3	0.704	6.96	CH_2Cl_2–OEt_2 (1:1)	(**9**)	55	143 (145*)	417	417
1.50	3.48	$H_2N(CH_2)_2NMeH$	0.258	3.48	NEt_3	0.704	6.96	CH_2Cl_2–OEt_2 (4:1)	(**10**)	52	139	431	431
1.50	3.48	$HMeN(CH_2)_2NMeH$	0.306	3.48	NEt_3	0.704	6.96	CH_2Cl_2–OEt_2 (6:1)	(**11**)	45	91	445	445
1.50	3.48	$HO(CH_2)_2NMeH$	0.261	3.48	Pyridine	0.550	6.96	CH_2Cl_2–OEt_2 (20:1)	(**12**)	30	99—100	430	430
1.50	3.48	$HO(CH_2)_4OH$	0.313	3.48	Pyridine	0.550	6.96	CH_2Cl_2	(**13**)	40	194—195	447	447
1.00	2.32	$HO(CH_2)_4NH_2$	0.206	2.32	Pyridine	0.367	4.64	CH_2Cl_2–OEt_2 (1:1)	(**14**)	33	174	446	446
1.50	3.48	$H_2N(CH_2)_4NH_2$	0.306	3.48	NEt_3	0.704	6.96	CH_2Cl_2–OEt_2 (9:1)	(**15**)	45	148—150	445	445

* From ref. 17.

Table 5. Analytical data (%)* for derivatives of geminal $N_3P_3Ph_2Cl_4$

Compound	C	H	N
(**2**) $N_3P_3Ph_2[O(CH_2)_3O]Cl_2$	41.7 (41.5)	3.8 (3.7)	9.6 (9.7)
(**3**) $N_3P_3Ph_2[O(CH_2)_3NH]Cl_2$	41.2 (41.6)	4.0 (4.0)	12.5 (12.9)
(**4**) $N_3P_3Ph_2[HN(CH_2)_3NH]Cl_2$	41.5 (41.7)	4.1 (4.2)	16.2 (16.2)
(**5**) $N_3P_3Ph_2[HN(CH_2)_3NMe]Cl_2$	42.9 (43.1)	4.3 (4.5)	15.8 (15.7)
(**6**) $N_3P_3Ph_2[MeN(CH_2)_3NMe]Cl_2$	44.6 (44.4)	4.8 (4.8)	15.2 (15.2)
(**7**) $N_3P_3Ph_2[O(CH_2)_2O]Cl_2$	39.6 (40.0)	3.5 (3.4)	10.3 (10.0)
(**10**) $N_3P_3Ph_2[HN(CH_2)_2NMe]Cl_2$	41.8 (41.7)	4.3 (4.2)	16.2 (16.2)
(**11**) $N_3P_3Ph_2[MeN(CH_2)_2NMe]Cl_2$	42.8 (43.1)	4.6 (4.5)	15.5 (15.7)
(**12**) $N_3P_3Ph_2[O(CH_2)_2NMe]Cl_2$	41.3 (41.6)	4.0 (4.0)	13.1 (12.9)
(**13**) $N_3P_3Ph_2[O(CH_2)_4O]Cl_2$	42.8 (43.0)	4.2 (4.1)	9.4 (9.4)
(**14**) $N_3P_3Ph_2[O(CH_2)_4NH]Cl_2$	42.8 (43.0)	4.5 (4.3)	12.4 (12.5)
(**15**) $N_3P_3Ph_2[HN(CH_2)_4NH]Cl_2$	43.3 (43.1)	4.7 (4.5)	15.5 (15.7)

* Calculated values are given in parentheses.

difficult because of the coalescence of large numbers of lines. The spectrum of this compound was run with further selective decoupling. Decoupling of the OCH_2 protons resulted in a singlet in the CCH_2 region of the spectrum, whilst decoupling of the CCH_2 protons resulted in an AB quartet structure in the OCH_2 region of the spectrum due to a small chemical non-equivalence of these nuclei.

The spiro-N*H* resonance of $N_3P_3Ph_2[HN(CH_2)_2NH]Cl_2$ (**9**) has been previously noted[17] to appear as a well resolved doublet, in contrast to those of most primary aminocyclophosphazenes, which are generally observed as unresolved humps. More complex fine structure was observable for two seven-membered spiro derivatives, $N_3P_3Ph_2[NH(CH_2)_4NH]Cl_2$ (**15**) and $N_3P_3Ph_2[O(CH_2)_4NH]Cl_2$ (**14**).

For the symmetric spiro compounds, $N_3P_3Ph_2[X(CH_2)_nY]Cl_2$ (X = Y = O or NH) the non-equivalence of the XCH_2 protons is largest in the six-membered ring derivatives (**2**) and (**4**) and smallest in the five-membered analogues (**7**) and (**9**).

Experimental

Geminal $N_3P_3Ph_2Cl_4$ (**1**) was obtained by a modified Friedel–Crafts reaction.[5] Experimental details of the reactions of this compound with difunctional reagents are given in Table 4. $N_3P_3Ph_2[O(CH_2)_2NH]Cl_2$ (**8**) and $N_3P_3Ph_2[HN(CH_2)_2NH]Cl_2$ (**9**) were obtained previously.[17] For the purpose of the present study we re-isolated these compounds using column chromatography. Analytical data are presented in Table 5. Column chromatographic separations of phosphazene compounds were carried out using silica gel 60 (from E. Merck). Standard thin-layer chromatography (t.l.c.) techniques were used [plates precoated with silica gel $60F_{254}$ (from E. Merck)] to examine the reaction mixtures or fractions isolated by column chromatography. The plates were sprayed with ninhydrin reagent (0.5% solution in butan-1-ol) and heated at 110 °C for 5 min. Reactions were carried out typically in CH_2Cl_2 in the presence of a tertiary base such as pyridine or triethylamine. The reaction of geminal $N_3P_3Ph_2Cl_4$ with propane-1,3-diol is discussed in some detail, below, to exemplify our procedures.

The Reaction of 2,2,4,4-*Tetrachloro*-6,6-*diphenylcyclotriphosphazatriene, gem*-$N_3P_3Ph_2Cl_4$ (**1**) *with Propane*-1,3-*diol.*—Compound (**1**) (1.50 g, 3.50 mmol) was dissolved in dichloromethane (20 cm^3). To this solution were added propane-1,3-diol (0.226 g, 3.50 mmol) and pyridine (0.552 g, 6.99 mmol) dissolved in dichloromethane (5 cm^3). The reaction was initially slightly exothermic. It was judged to be complete 24 h after the start, since an examination of the reaction mixture by t.l.c. showed no change in intensity of the spots beyond this time. T.l.c. using CH_2Cl_2 as eluant revealed the formation of essentially a single major product (**2**). An intense spot was observed on the baseline of the t.l.c. plate due to a mixture of pyridine and pyridine hydrochloride, and possibly also due to small quantities of polymeric and hydrolysis products. Appreciable quantities of starting material, (**1**), were also observed. The pyridine hydrochloride was precipitated from the solution as long thin needle-like crystals. These were filtered off and the product (**2**) was isolated from the filtrate using column chromatography. The filtrate was applied to a column packed

with 80 g of silica gel using CH_2Cl_2 as eluant. The various fractions were examined by t.l.c. and those containing the same compound were combined and evaporated to dryness under reduced pressure. The product, $N_3P_3Ph_2[O(CH_2)_3O]Cl_2$ (**2**), was recrystallised from hexane–dichloromethane (1:1), m.p. 168—169 °C (0.95 g, 65%). The t.l.c. R_f value was 0.50 (using CH_2Cl_2 as eluant). The molecular ion (M^+) was observed at m/z 433. A peak at m/z 432 corresponding to the base peak may be assigned to $[M - H]^+$.

Chemicals and Instrumental Techniques.—Proton n.m.r. spectra were recorded using a JEOL JNM FX-200 (operating at 199.5 MHz), a Varian XL400 (at 400.00 MHz), and a Bruker WH 250 spectrometer (at 250.48 MHz). Samples were dissolved in $CDCl_3$ and placed in 5-mm n.m.r. tubes. Measurements were carried out using a $CDCl_3$ lock, $SiMe_4$ as internal reference, and sample concentrations of approximately 10 mg cm^{-3}. Phosphorus-31 n.m.r. spectra were recorded using a JEOL JNM FX-60 (operating at 24.15 MHz), a Varian XL-200 (at 80.98 MHz), and a Bruker WH 400 spectrometer (at 162.0 MHz), with 85% H_3PO_4 as an external reference

Runs at different temperatures were carried out by passing pre-cooled nitrogen gas over the sample. In the case of the Bruker WH 400 spectrometer, temperatures were measured using a thermocouple placed immediately below the sample, whilst with the JEOL JNM FX 60 instrument a thermometer was placed in the solution. Spectra were simulated using a JEOL program or the PANIC program from the Bruker software package.

Mass spectrometric data were obtained using a VG 7070H mass spectrometer (University College, London) or a VG ZAB IF spectrometer (School of Pharmacy). Melting points were obtained using a Mettler FP 82 hot-stage connected to a Mettler FP 800 central processor. Microanalyses were carried out by University College, London microanalytical service.

Reagent-grade solvents were used throughout. The basic starting material, $N_3P_3Cl_6$, was obtained from Shin Nisso Kako Co. Ltd. Other sources for chemicals were as follows: aluminium chloride, triethylamine, pyridine, ethane-1,2-diol, propane-1,3-diol, *N*-methylethanolamine (BDH Chem. Co. Ltd.); ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane (Aldrich Chem. Co. Ltd.); *N,N'*-dimethylethylenediamine, *N*-methylethylenediamine, *N*-methylpropane-1,3-diamine, ethanolamine, propanolamine, butanolamine (Fluka Ltd.); and *N,N'*-dimethylpropane-1,3-diamine (Lancaster Synthesis). Silica gel (grain size 0.043—0.063 mm) and silica gel 60_{254} t.l.c. plates were obtained from E. Merck.

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