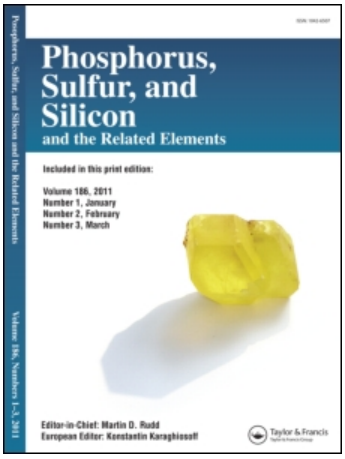

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PHOSPHORUS-NITROGEN COMPOUNDS. PART 63.[1] THE REACTION OF 6,6-BIS-t-BUTYLAMINO-2,2,4,4-TETRACHLOROCYCLOTRIPHOSPHAZATRIENE WITH DIFUNCTIONAL ALCOHOLS, AMINES, AND AMINOALCOHOLS. THE ^{31}P AND ^{1}H N.M.R. SPECTRA OF THE PRODUCTS

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PHOSPHORUS–NITROGEN COMPOUNDS. PART 63.[1] THE REACTIONS OF 6,6-BIS-t-BUTYLAMINO-2,2,4,4-TETRACHLOROCYCLOTRIPHOSPHAZATRIENE WITH DIFUNCTIONAL ALCOHOLS, AMINES, AND AMINOALCOHOLS. THE ^{31}P AND ^{1}H N.M.R. SPECTRA OF THE PRODUCTS†

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The reactions of geminal $N_3P_3(NHBu^t)_2Cl_4$ with difunctional alcohols, amines, and aminoalcohols were investigated and a series of spiro derivatives, $N_3P_3(NHBu^t)_2[X(CH_2)_nY]Cl_2$ (X = Y = O, NH: $n = 2, 3, 4$; X = O, Y = NH, $n = 2, 3, 4$; X = Y = NMe, $n = 2, 3$; X = NH, Y = NMe; $n = 2, 3$; X = O, Y = NMe, $n = 2$), $N_3P_3(NHBu^t)_2[O(CH_2)_nO]_2Cl_2$ ($n = 3, 4$) as well as a monodentate compound, $N_3P_3(NHBu^t)_2[O(CH_2)_3OH]Cl_3$, were isolated. The phosphorus-31 and proton n.m.r. spectra of these compounds are discussed. Degeneracies in the phosphorus-31 n.m.r. spectra could be reduced by the use of lanthanide shift reagents and by solvent effects.

INTRODUCTION

Four types of product are in principle possible from the reactions of cyclotriphosphazatrienes with difunctional reagents: (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) monodentate structures (only one end of the difunctional reagent is attached to the phosphazene ring).

Previous studies of the reactions of cyclotriphosphazatrienes with difunctional reagents show that the major products of these reactions are spirocyclic compounds.[2–20] Monodentate structural types[2,5,8,20] as well as bridged compounds[13,20] have also been observed. Ansa structures have proved more elusive. Only four authentic cases have so far been reported.[21–24] Recently the simplest type of ansa structure, $N_3P_3[O(CH_2)_3O]Cl_4$, has now also been obtained in trace amounts.[20]

The reactions of $N_3P_3Cl_6$ with 1,3-propane-diol suggested that ansa formation was more favourable when a pair of geminal chlorine atoms had been replaced by

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a spiro dioxy group.[20,22] The electron supply towards the remaining $\equiv PCl_2$ groups has thus been increased. An earlier study by us[19] has investigated whether the transition from $N_3P_3Cl_6$ to geminal $N_3P_3Ph_2Cl_4$ affected the potential product types (i)–(iv), since basicity studies indicate that a phenyl group increase the basicity by about the same amount as an alkoxy group.[19]

t-Butylamino groups would be expected to be rather more electron releasing than phenyl groups and we have therefore investigated the reactions of geminal $N_3P_3(NHBu^t)_2Cl_4$ (**1**) with difunctional reagents. Furthermore, basicity data of mono spiro products could be obtained, which allowed calculation of basicity substituent constants for spirocyclic groups which were required for structure-property relationships.[25] These could be compared with values obtained for analogous diphenyl compounds.[25] Earlier studies have shown that basicity constants were conformation dependent.[26,27] In particular recent work on the conformation of the most powerful electron releasing substituent $NPPh_3$ shows that the basicity substituent constant α_R ($R = NPPh_3$) can vary from 10.3[27] to 7.2.[28]

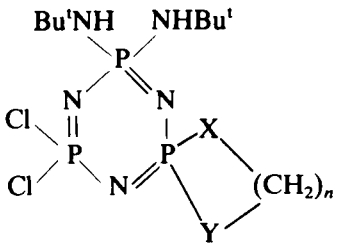
We have already reported the use of higher field strengths and the temperature dependence of ^{31}P n.m.r. spectra in the analysis of degenerate spectra of phenyl substituted cyclophosphazenes.[19,29] In contrast to the dramatic temperature effect observed in the ^{31}P n.m.r. spectra of e.g. $N_3P_3Ph_2[O(CH_2)_3O]Cl_2$, we found no noticeable change in the spectrum of the t-butylamino analogue $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ (**2**) with temperature. In the present study we have used lanthanide shift reagents and differential solvent shifts to remove degeneracies in spiro derivatives of geminal $N_3P_3(NHBu^t)_2Cl_4$ (**1**).

RESULTS AND DISCUSSION

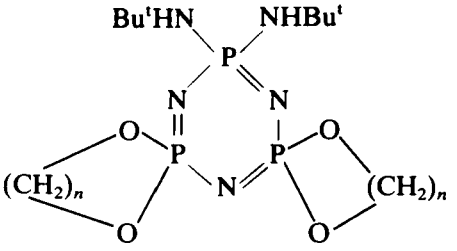
Alkylamino groups have larger basicity substituent constants (α_R) than aryl groups, e.g. $NHBu^t = 6.2$, $Ph = 4.2$. This greater electron supply at the demand of the proton is also reflected in the reactivity of the $\equiv PCl_2$ group of $N_3P_3(NHBu^t)_2Cl_4$ (**1**) towards nucleophilic attack. The initial reaction is undoubtedly $S_N2(P)$. All reactions of compound (**1**) with a given reagent were significantly slower than with its diphenyl analogue, $N_3P_3Ph_2Cl_4$.[19] For both series the amines reacted considerably more readily than the alcohols. This reduced reactivity permitted in the present study the relatively easy isolation of a monodentate intermediate $N_3P_3(NHBu^t)_2[O(CH_2)_3OH]Cl_3$ (**3**), whose intramolecular conversion to the spiro compound $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ (**2**) at room temperature could be readily followed by ^{31}P n.m.r. spectroscopy.

It has been shown earlier,[30] that it is more difficult to prepare specific substitution stages of chlorine atoms by alkoxy groups than by amino groups. Thus in the present study dispiro compounds (**4**) and (**16**) based on 1,3-propane-diol and 1,4-butane-diol were isolated along with their mono spiro analogues (**2**) and (**15**) under stoichiometric conditions aimed to prepare the latter. Dispiro derivatives with the amine reagents under similar conditions were not observed. The following compounds (**2–18**) were prepared.

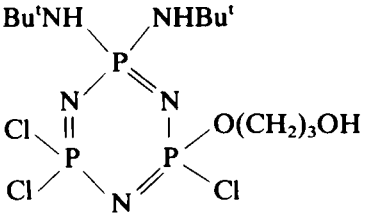
^{31}P n.m.r. spectra were obtained for a series of mono spiro derivatives (**2**, **5–15**,



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



(4) $n = 3$
(16) $n = 4$



(3)

17, 18) of $N_3P_3(NHBu^t)_2Cl_4$ (1). The system is similar to that of the monospiro derivatives of geminal $N_3P_3Ph_2Cl_4$ reported previously by us,[19] inasmuch as all three nuclei differ. Thus, in principle, we may obtain AMX, ABX, ABC type spectra. However, in the case of the $N_3P_3(NHBu^t)_2[X(CH_2)_nY]Cl_2$ compounds the coupling $J(PCl_2–P(NHBu^t)_2/[\nu PCl_2–\nu P(NHBu^t)_2]$ tended to be small as a result of a large shift difference, $[\nu PCl_2–\nu P(NHBu^t)_2]$, in contrast to the much smaller shift difference, $(\nu PCl_2–\nu Ph_2)$, observed in the $N_3P_3Ph_2[X(CH_2)_nY]Cl_2$ series.

In addition, the ^{31}P n.m.r. spectra of the dispiro compounds $N_3P_3(NHBu^t)_2[O(CH_2)_nO]_2$ (where $n = 3, 4$) (4), (16) were obtained and give rise to A_2B type spectra.

In the reaction of geminal $N_3P_3(NHBu^t)_2Cl_4$ (6) with propane-1,3-diol a compound was obtained with a formula $N_3P_3(NHBu^t)_2[O(CH)_3O]Cl_2$. Initial n.m.r. investigations suggested, erroneously, a rearranged[31,32] ansa structure[8].

X-ray crystallography[8] and a detailed investigation of the n.m.r. data show conclusively that the non-rearranged spiro structure (2) is, however, the correct assignment. The misleading A_2B appearance of the $^{31}P\{^1H\}$ n.m.r. spectrum and the triplet structures in the ^{13}C n.m.r. spectrum result from the very close chemical shifts of the $\equiv P(NHBu^t)_2$ and the $\equiv P$spiro group $[\nu P(NHBu^t)_2–\nu P\text{spiro}]$ (0.2 p.p.m.) compared with the coupling constant $J[P\text{spiro-}P(NHBu^t)_2]$ (65.4 Hz) such that second order effects are very strong. Closer inspection of the spectrum at 162.0 MHz reveals peaks of low intensity in the high field part of the spectrum. It was possible to assign these to the weak outer transitions of the ab

subspectra. A full analysis of the spectrum could be carried out and the n.m.r. parameters extracted. The spectrum was simulated and a very satisfactory agreement between line positions of the simulated and experimental spectrum was found as shown in Figure 1.

The X part of the spectrum does not collapse when a $^{31}P-H$ n.m.r. spectrum of $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ (**2**) is run and hence could be readily assigned to the $\equiv PCl_2$ group.

The X-ray crystal structure of $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ (**2**) showed interesting features in its hydrogen bonding.[8] Both of the N*H* protons donate a hydrogen bond to the same ring nitrogen atom [*para* to the $\equiv P(NHBu^t)_2$ group] in another molecule resulting in an infinite chain containing six-membered hydrogen bonded rings. The pattern of hydrogen bonding is consistent with a fairly broad band at 3340 cm^{-1} in the NH stretching region of the spectrum.

By contrast geminal $N_3P_3(NHBu^t)_2Cl_4$ whose structure was studied crystallographically by Sowerby and co-workers[33] forms discrete dimers, in which only one group of each monomer is involved in hydrogen bonding to the ring nitrogen atom [*ortho* to the $\equiv P(NHBu^t)_2$ group] of the other resulting in an eight-membered hydrogen bonded ring.

$N_3P_3(NHBu^t)_2[HN(CH_2)_2NMe]Cl_2$ (**12**) gives rise to a deceptively simple AX_2 type spectrum using $CDCl_3$ as solvent, even at higher fields (162.0 MHz). The compound has a spiro structure and the degeneracy of the ^{31}P n.m.r. spectrum

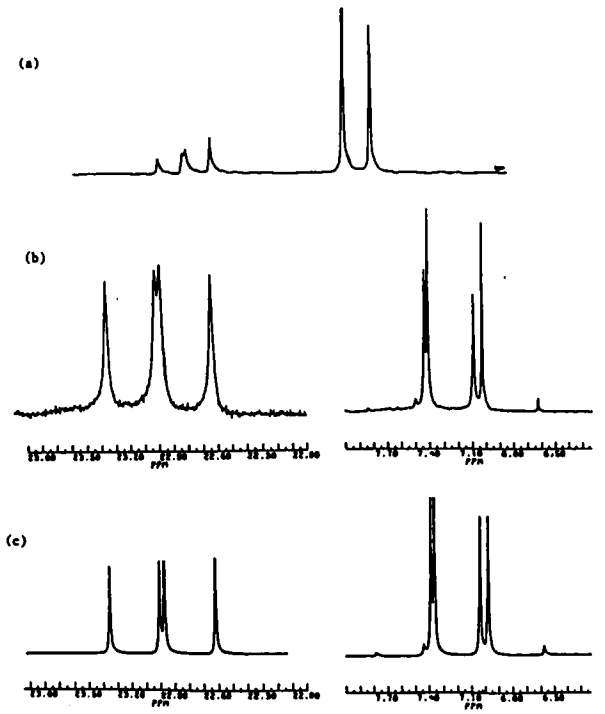


FIGURE 1 The $^{31}P\{^1H\}$ n.m.r. spectra of $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ (**2**) (room temperature) (*a*) 24.15 MHz ($CDCl_3$, (*b*) 162.0 MHz $CDCl_3$ (*c*) simulation of spectrum at 162.0 MHz.

arises from the accidental isochrony of the $\equiv P$spiro and $\equiv PCl_2$ nuclei. Second order coupling effects are observed in both the ^{13}C and ^{1}H n.m.r. spectra of the spiro ring, but not in those of the $NHBu^t$ groups, since the coupling $J[P(NHBu^t)_2\text{-}PCl_2]/vP(NHBu^t)_2\text{-}vPCl_2$ is small.

In a previous study,[19] we demonstrated the use of variable temperature ^{31}P n.m.r. spectrometry to remove degeneracies in the $^{31}P\{^1H\}$ n.m.r. spectra of a number of derivatives of geminal $N_3P_3Ph_2Cl_4$. Varying the temperature did not, however, alter the AB_2 appearance of the $^{31}P\{^1H\}$ spectrum of $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ (**2**) at 24.15 MHz.

Lanthanide shift reagents[34,35] and solvent effects[34–36] have been found valuable in the interpretation of degenerate spectra and these techniques have been applied to the analysis of the $^{31}P\{^1H\}$ n.m.r. spectra of $N_3P_3(NHBu^t)_2[O(CH_2)_3]Cl_2$ (**2**) [accidental isochrony of the $\equiv P(NHBu^t)_2$ and $\equiv P$spiro nuclei] and $N_3P_3(NHBu^t)_2[NH(CH_2)_2NMe]Cl_2$ (**12**) (accidental isochrony of the $\equiv PCl_2$ and $\equiv P$spiro nuclei) in the study presented here.

LANTHANIDE SHIFT REAGENTS

Figure (2) shows the pronounced effects that are observable in the appearance of the $^{31}P\{^1H\}$ n.m.r. spectrum of $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ (**2**) at 24.15 MHz

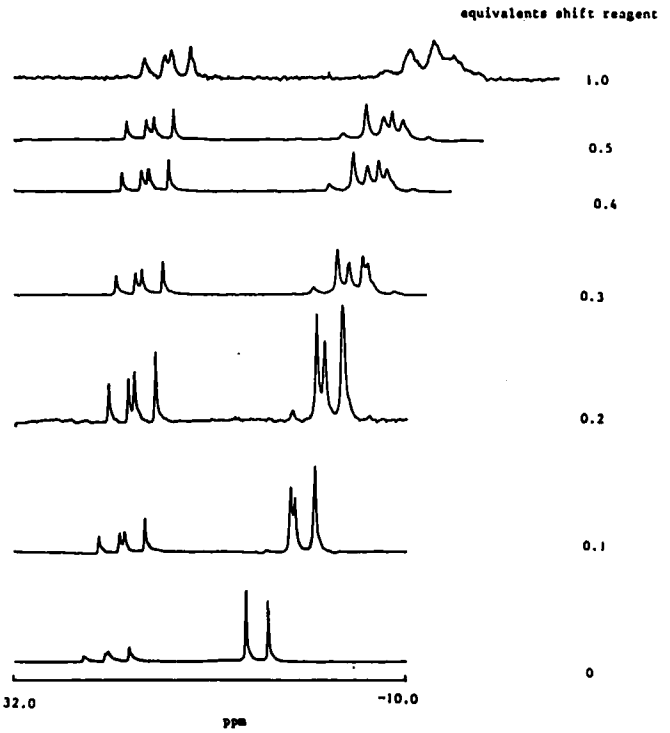


FIGURE 2 The $^{13}P\{^1H\}$ n.m.r. spectrum of $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ (**2**) in $CDCl_3$ (room temperature) at 24.15 MHz showing effect of the addition of lanthanide shift reagent, $Pr(fod)_3$.

with increasing concentration of $Pr(fod)_3$ [tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-1-3,5-octanedionato)-praseodymium]. The spectrum shows an increasing complexity as the difference in chemical shift between the $\equiv P$spiro group and the $\equiv P(NHBu^t)_2$ group increases. A number of additional transitions become apparent and the spectrum can be identified as being of the ABX type.

A general shift to lower frequencies of all signals is observable. The differential shift is markedly smaller for the X part of the spectrum [associated with the $\equiv PCl_2$ group] than for the AB part of the spectrum [associated with the $\equiv P(NHBu^t)_2$ and $\equiv$Pspiro groups]. Addition of 0.5 equivalent of shift reagent causes an upfield movement of the $\equiv PCl_2$, $\equiv$Pspiro, and $\equiv P(NHBu^t)_2$ signals of approximately 4, 12, and 15 p.p.m., respectively.

Unfortunately addition of shift reagent results in paramagnetic broadening of the peaks in the spectra, particularly in the case of the $\equiv P$spiro and $\equiv P(NHBu^t)_2$ nuclei and is quite severe with one equivalent of reagent resulting in the coalescence of a number of signals. This differential shift can be rationalised, by assuming that co-ordination of the shift reagent is likely to occur preferentially to the most basic nitrogen atom of the phosphazene ring, i.e. the nitrogen atom bridging the $\equiv P(NHBu^t)_2$ and $\equiv P$spiro moieties.

$Pr(fod)_3$ was also used to show the presence of three phosphorus environments in $N_3P_3(NHBu^t)_2[HN(CH_2)_2NMe]Cl_2$ (**12**). The resonances due to all three phosphorus environments are clearly separated after the addition of only 0.3 equivalents of $Pr(fod)_3$ as a result of the increased chemical shift difference between the $\equiv P$spiro and the $\equiv PCl_2$ nuclei. As in the case of $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ (**2**), much larger upfield movements are observed for the $\equiv$Pspiro and $\equiv P(NHBu^t)_2$ than for the $\equiv PCl_2$ nuclei. addition of 0.3 equivalents of $Pr(fod)_3$ to compound (**12**) results in upfield movements of the $\equiv PCl_2$, $\equiv$Pspiro and $\equiv P(NHBu^t)_2$ groups of approximately 4, 11, and 7 p.p.m., respectively. Paramagnetic broadening is observed for all lines, but is particularly severe for the $\equiv$Pspiro group and is least for the $\equiv PCl_2$ groups. (Figure 3) [cf. compound (**2**), Figure 2].

Solvent effects

Changing the solvent from $CDCl_3$ to benzene has a dramatic effect on the appearance of the $^{31}P\{^1H\}$ n.m.r. spectrum of $N_3P_3(NHBu^t)_2[HN(CH_2)_2NMe]Cl_2$ (**12**), (Figure 3). The accidental equivalence of the chemical shift of the $\equiv PCl_2$ and $\equiv$Pspiro groups could be removed by changing the solvent from $CDCl_3$ to benzene (Figure 3). As a result, extraction of n.m.r. parameters was possible in the latter. [νPspiro$-\nu PCl_2 = 1.2$ p.p.m., using benzene as solvent].

The ^{31}P n.m.r. data of mono spiro derivatives (**2**, **5**–**15**, **17**, **18**) of geminal $N_3P_3(NHBu^t)_2Cl_4$ (**1**) are given in Table I.

The ^{31}P n.m.r. spectra of $N_3P_3(NHBu^t)_2[O(CH_2)_3NH]Cl_2$ (**5**) and $N_3P_3(NHBu^t)_2[HN(CH_2)_3NH]Cl_2$ (**6**) could be treated as ABX type systems at 24.15 MHz. The chemical shift difference νPspiro$-\nu P(NHBu^t)_2$ was sufficiently large in comparison to the coupling constant $J[P$spiro-$P(NHBu^t)_2]$ for a clear analysis of spectra to be possible.

Downfield movements of the chemical shift of the $\equiv$Pspiro group are observed

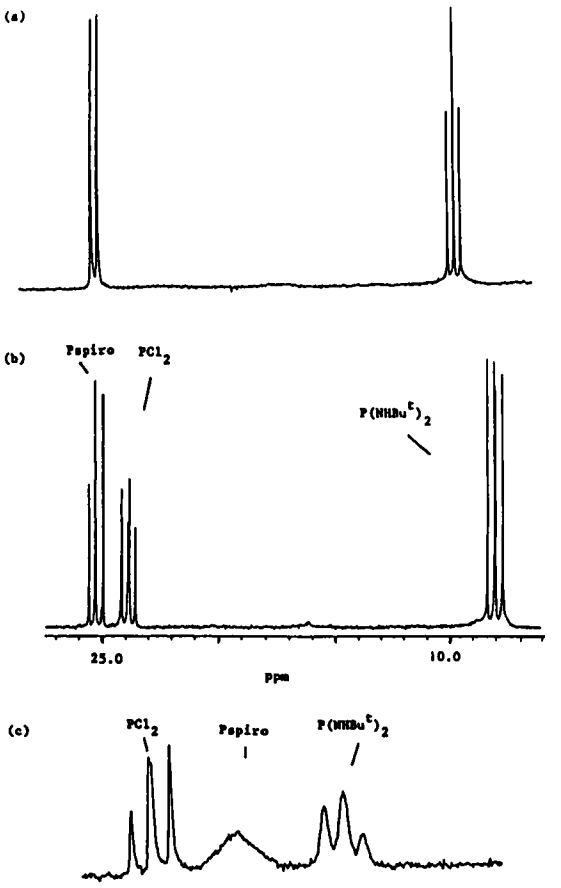


FIGURE 3 $^{31}P\{^1H\}$ n.m.r. spectra of $N_3P_3(NHBu^t)_2[HN(CH_2)_2NMe]Cl_2$ (**12**) room temperature, (*a*) 162.0 MHz ($CDCl_3$), (*b*) 162.0 MHz (benzene), (*c*) 24.15 MHz $CDCl_3$ 0.3 equivalents of $Pr(fod)_3$.

on methylation of the nitrogen atoms of the spiro rings in the six-membered ring series, whilst changes in chemical shift of the $\equiv PCl_2$ and $\equiv P(NHBu^t)_2$ are very small by comparison. In the spectrum of $N_3P_3(NHBu^t)_2[HN(CH_2)_3NMe]Cl_2$ (**7**) the resonances of the three groups are well separated at 24.15 MHz, although second order perturbation of the intensity of lines may be observed.

The $^{31}P\{^1H\}$ n.m.r. spectrum of $N_3P_3(NHBu^t)_2[MeN(CH_2)NMe]Cl_2$ (**8**) gives rise to an ABX type spectrum, where the AB part of the spectrum arises from the interaction of the $\equiv PCl_2$ and $\equiv$Pspiro groups (Figure 4).

The mono five-membered spiro ring derivatives of geminal $N_3P_3(NHBu^t)_2Cl_4$ (**1**) give rise to ABX type spectra, where the AB part of the spectra arises from the interaction of the $\equiv$Pspiro and the $\equiv PCl_2$ groups, e.g. in compound (**10**) (Figure 4). In the case of $N_3P_3(NHBu^t)_2[HN(CH_2)_2NMe]Cl_2$ (**12**) the spectrum has a deceptively simple AX_2 appearance when $CDCl_3$ is used as a solvent (Figure 3).

The mono seven-membered spiro derivatives give rise to systems in which the resonances due to the $\equiv P(NHBu^t)_2$, $\equiv PCl_2$ and $\equiv$Pspiro groups are well

TABLE I

^{31}P n.m.r. data of spiro derivatives of geminal $N_3P_3(NHBu^t)_2Cl_4$[a]

Compound	δPspiro p.p.m.	δPR_2[f] p.p.m.	δPCl_2 p.p.m.	J(*P*spiro-PCl_2) Hz	J(*P*spiro-PR_2)[f] Hz	J(PCl_2-PR_2)[f] Hz
$N_3P_3Cl_6$[c]			19.9			
$N_3P_3(NHBu^t)_2Cl_4$[c] (**1**)		1.0	18.0			44.0
$N_3P_3(NHBu^t)_4Cl_2$[c]		3.9	19.7			52.7
$N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$[c] (**2**)	7.1	7.3	23.0	67.1	65.4	51.2
$N_3P_3(NHBu^t)_2[O(CH_2)_3NH]Cl_2$[c] (**5**)	9.3	6.8	21.4	55.1	54.0	46.9
$N_3P_3(NHBu^t)_2[HN(CH_2)_3NH]Cl_2$[d] (**6**)	10.7	5.4	21.3	46.6	40.7	47.4
$N_3P_3(NHBu^t)_2[HN(CH_2)_3NMe]Cl_2$[c] (**7**)	14.7	6.3	21.9	38.5	43.4	47.5
$N_3P_3(NHBu^t)_2[MeN(CH_2)_3NMe]Cl_2$[c] (**8**)	18.4	6.4	22.4	31.7	43.9	50.2
$N_3P_3(NHBu^t)_2[O(CH_2)_2O]Cl_2$[c] (**9**)	26.8	7.0	24.5	72.6	56.3	57.3
$N_3P_3(NHBu^t)_2[O(CH_2)_2NH]Cl_2$[c] (**10**)	27.0	6.4	23.7	54.3	50.6	59.8
$N_3P_3(NHBu^t)_2[HN(CH_2)_2NH]Cl_2$[c] (**11**)	25.3	5.9	23.1	49.5	42.6	56.9
$N_3P_3(NHBu^t)_2[HN(CH_2)_2NMe]Cl_2$[b,e] (**12**)	25.3[b]	8.1[b]	24.1[b]	44.5[b]	47.4[b]	56.8[b]
$N_3P_3(NHBu^t)_2[MeN(CH_2)_2NMe]Cl_2$[d] (**13**)	22.9	7.4	24.4	45.9	40.5	57.8
$N_3P_3(NHBu^t)_2[O(CH_2)_2NMe]Cl_2$[d] (**14**)	25.0	7.2	24.3	50.2	49.5	60.4
$N_3P_3(NHBu^t)_2[O(CH_2)_4O]Cl_2$[c] (**15**)	13.0	5.9	23.5	76.6	64.1	48.8
$N_3P_3(NHBu^t)[O(CH_2)_4NH]Cl_2$[c] (**17**)	16.9	5.7	22.6	65.3	51.1	49.1
$N_3P_3(NHBu^t)_2[HN(CH_2)_4NH]Cl_2$[e] (**18**)	15.5	6.0	23.2	51.8	45.5	51.2
$N_3P_3(NHBu^t)_2[O(CH_2)_3O]_2$[d] (**4**)	12.3	13.2			63.2	
$N_3P_3(NHBu^t)_2[O(CH_2)_4O]_2$[c] (**16**)	19.4	10.8			65.9	

[a] $CDCl_3$ solution (unless otherwise indicated); [b] Data obtained using benzene as solvent; [c] Spectra obtained at 24.15 MHz; [d] Spectra obtained at 80.95 Mhz; [e] Spectra obtained at 162.0 Mhz; [f] R = $NHBu^t$.

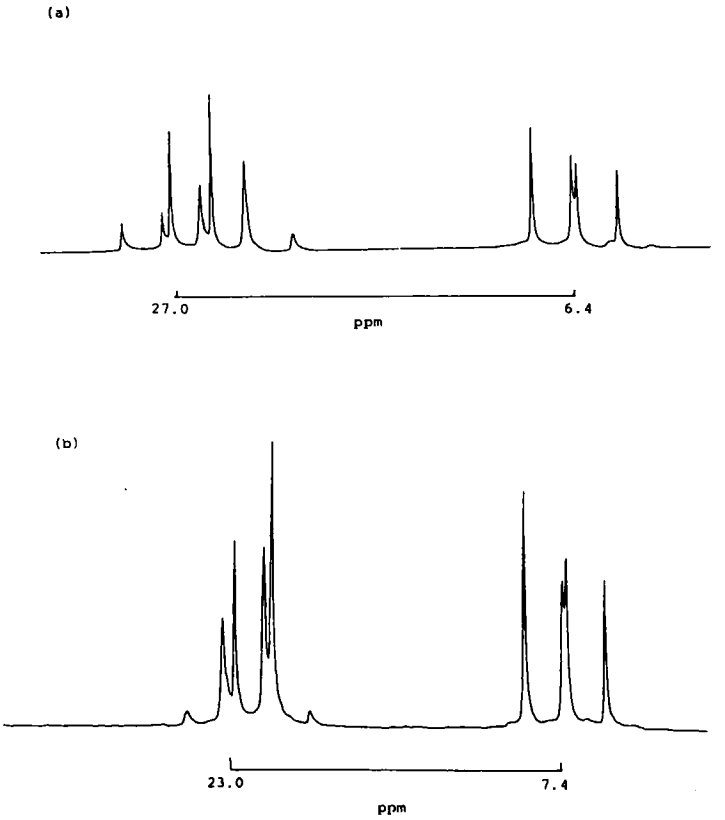


FIGURE 4 The $^{31}P\{^{1}H\}$ n.m.r. spectra measured at 24.15 MHz (in $CDCl_3$ at room temperature) (*a*) $N_3P_3(NHBu^t)_2[O(CH_2)_2NH]Cl_2$ (**10**), (*b*) $N_3P_3(NHBu^t)_2[MeN(CH_2)_3NMe]Cl_2$ (**8**).

separated, even at low field. A downfield movement of the chemical shift of the ≡Pspiro group is observed, when a further two chlorine atoms of the mono spiro compound $N_3P_3[X(CH_2)_nY]Cl_4$ are replaced geminally by either a second spiro group, two t-butylamino or phenyl groups. The resultant chemical shift of the ≡Pspiro group is very similar in both, diphenyl and bis t-butylamino derivatives, although the electron releasing capacities of the t-butylamino group are somewhat larger than those of the phenyl group. If, however, we turn to the bis-spiro derivatives, e.g. $N_3P_3[O(CH_2)_nO]_2Cl_2$, which have the same degree of substitution of chlorine as the mono spiro derivatives of geminal $N_3P_3Ph_2Cl_4$ and geminal $N_3P_3(NHBu^t)_2Cl_4$, larger downfield chemical shifts of the ≡Pspiro group are observed. This is best illustrated for the alkane dioxy derivatives, where the most complete set of ^{31}P n.m.r. data is available (Table II).

The effect of the replacement of two chlorine atoms of geminal $N_3P_3(NHBu^t)_2Cl_4$ by a spiro group on the chemical shift of the $\equiv P(NHBu^t)_2$ group and the $\equiv PCl_2$ group may be noted. An increase in chemical shift of the $\equiv P(NHBu^t)_2$ group is observed in passing from the gem $N_3P_3(NHBu^t)_2Cl_4$ compound to the mono spiro derivatives $N_3P_3(NHBu^t)_2[X(CH_2)_nY]Cl_2$. These shifts do not appear to depend greatly on the size of the spiro ring and would

TABLE II

Phosphorus-31 n.m.r. data of alkanedioxy spiro ring derivatives of chlorocyclotriphosphazatrienes at room temperature

	δPspiro p.p.m.	δPR_2[a] p.p.m.	δPCl_2 p.p.m.
$N_3P_3[O(CH_2)_3O]Cl_4$[b]	4.7		25.6
$N_3P_3[O(CH_2)_3O]_2Cl_2$[b]	9.1		26.5
$N_3P_3[O(CH_2)_3O]_3$[b]	14.1		
$N_3P_3Ph_2[O(CH_2)_3O]Cl_2$	5.4	22.1	21.9
$N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$	7.1	7.3	23.0
$N_3P_3(NHBu^t)_2[O(CH_2)_3O]_2$	12.3	13.2	
$N_3P_3[O(CH_2)_2O]Cl_4$[b]	23.8		25.5
$N_3P_3[O(CH_2)_2O]_2Cl_2$[b]	30.95		31.3
$N_3P_3[O(CH_2)_2O]_3$[b]	37.3		
$N_3P_3Ph_2[O(CH_2)_2O]Cl_2$	26.7	23.1	25.2
$N_3P_3(NHBu^t)_2[O(CH_2)_2O]Cl_2$	26.3	7.0	24.5
$N_3P_3[O(CH_2)_4O]Cl_4$[b]	11.7		25.6
$N_3P_3[O(CH_2)_4O]_2Cl_2$[b]	16.0		27.8
$N_3P_3[O(CH_2)_4O]_3$[b]	21.7		
$N_3P_3Ph_2[O(CH_2)_4O]Cl_2$	12.5	22.0	23.6
$N_3P_3(NHBu^t)_2[O(CH_2)_4O]Cl_2$	13.0	5.9	23.4
$N_3P_3(NHBu^t)_2[O(CH_2)_4O]_2$	19.4	10.8	

[a] R = Ph, $NHBu^t$. [b] Reference 20.

imply that the extent of deshielding of the $\equiv P(NHBu^t)_2$ group is not greatly affected by the electron releasing capacity of the ≡Pspiro group. For example, the chemical shift of the ≡Pspiro group of $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ (**2**) is 7.1 p.p.m. in contrast to that of $N_3P_3(NHBu^t)_2[O(CH_2)_2O]Cl_2$ (**9**) at 26.3 p.p.m., whilst the chemical shifts of the $\equiv P(NHBu^t)_2$ group in these two compounds are almost identical.

A number of empirical observations can be made for $^2J(PP)$ values in spiro derivatives of geminal $N_3P_3(NHBu^t)_2Cl_4$. It has been suggested that these values in cyclotriphosphazatrienes depend on the electronegativities of the substituents involved.[37] However, errors in certain compounds were attributed to the non-additivity of substituent constants.[38]

(i) Comparison of $^2J(PP)$ of the dioxy, primary diamino and primary aminoalkoxy derivatives suggests a decrease in $J(P\text{spiro-}PCl_2)$ and $J[P\text{spiro-}P(NHBu^t)_2]$ for a given spiro ring in the order.

$$N_3P_3(NHBu^t)_2[O(CH_2)_nO]Cl_2 > N_3P_3(NHBu^t)_2[O(CH_2)_nNH]Cl_2 > N_3P_3(NHBu^t)_2[HN(CH_2)_nNH]Cl_2,$$

where $n = 2, 3, 4$. Considerably smaller variations are observed in $^2J[PCl_2\text{-}P(NHBu^t)_2]$.

(ii) The greatest variation on N-methylation on the coupling constants in the six-membered diamino series is observed for $J(P\text{spiro-}PCl_2)$. The secondary amino spiro derivative $N_3P_3(NHBu^t)_2[MeN(CH_2)_3NMe]Cl_2$, (**8**), has a $J(P\text{spiro-}PCl_2)$ value of 31.7 Hz compared to 46.6 Hz for the primary amino spiro derivative $N_3P_3(NHBu^t)_2[HN(CH_2)_3NH]Cl_2$ (**6**). We have recently related a decrease in $^3J(PNCC)$ values on passing from $N_3P_3[NH(CH_2)_3NH]Cl_4$ to $N_3P_3[NMe(CH_2)_3NMe]Cl_4$ to an increase in pyramidality of the substituent

nitrogen atom and its P–N bond length in the latter.[39] It is likely that the above variation in $^2J(PP)$ can be attributed to the same structural effects. Considerably smaller variations of $J(P\text{spiro-}PCl_2)$ are observed in the corresponding five-membered ring series.

(iii) Comparison of phosphorus-phosphorus spin-spin coupling constants of mono spiro derivatives of geminal $N_3P_3(NHBu^t)_2Cl_4$ and geminal $N_3P_3Ph_2Cl_4$ show that in the latter case significantly lower coupling constants are observed[19] (although similar trends within each series may be noted).

The use of solvents to remove accidental degeneracy in the ^{31}P spectra of $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ (**2**) and $N_3P_3(NHBu^t)_2[HN(CH_2)_2NMe]Cl_2$ (**12**) has already been discussed. To investigate this phenomenon further we have included $N_3P_3(NHBu^t)_2[HN(CH_2)_4NH]Cl_2$ (**18**) and $N_3P_3(NHBu^t)_2[O(CH_2)_4O]Cl_2$ (**15**) in our investigations. Differential ^{31}P chemical shifts of spiro derivatives in $CDCl_3$ and deuteriobenzene are summarised in Table III.

In general, relatively large upfield movements of the ^{31}P shift of the $\equiv PCl_2$ group are observed in passing from $CDCl_3$ to the aromatic solvent benzene ($\Delta\delta \equiv PCl_2 = 1.2$ to 2.1 p.p.m.). Significantly smaller changes in ^{31}P shift are noted for the $\equiv$Pspiro group. Upfield movements are observed in passing from $CDCl_3$ to benzene for $N_3P_3(NHBu^t)_2[O(CH_2)_4O]Cl_2$ (**15**) and $N_3P_3(NHBu^t)_2[HN(CH_2)_4NH]Cl_2$ (**18**) ($\Delta\delta$Pspiro = 0.4 to 0.6 p.p.m.), whilst in the case of $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ (**2**) a small downfield shift can be seen ($\Delta\delta \equiv$Pspiro = −0.2 p.p.m.). Changes in the ^{31}P shift of the $\equiv P(NHBu^t)_2$ group using $CDCl_3$ and deuteriobenzene vary ($\Delta\delta = 0.2$ to 0.8 p.p.m.) in an upfield direction for the compounds given in Table III.

Extraction of chemical shift values in $CDCl_3$ of the $\equiv$Pspiro and $\equiv PCl_2$ groups is difficult in the case of $N_3P_3(NHBu^t)_2[HN(CH_2)_2NMe]Cl_2$ (**12**), because of the deceptively simple appearance of the spectrum in $CDCl_3$ and a full comparison of ^{31}P shift changes between $CDCl_3$ and C_6D_6 is as a result not possible. However, a downfield movement of the $\equiv P$spiro group (−0.4 p.p.m.) relative to an upfield movement of the $\equiv PCl_2$ (~1.0 p.p.m.) is observed on changing the solvent from $CDCl_3$ to deuteriobenzene. An upfield shift of 0.7 p.p.m. is observed for the $\equiv P(NHBu^t)_2$ group of $N_3P_3(NHBu^t)_2[HN(CH_2)_2NMe]Cl_2$ (**12**) for the same change in solvent systems.

An important contributory factor to the observed differential shifts is the solvent anisotropy of the benzene molecule. the benzene molecule will cause a shift of the resonances of the phosphorus nucleus through ring current effects

TABLE III

Differential phosphorus-31 chemical shifts of spiro derivative in $CDCl_3$ and C_6D_6

Compound		$\Delta\delta PCl_2$[a] p.p.m.	$\Delta\delta$Pspiro[a] p.p.m.	$\Delta\delta P(NHBu^t)_2$[a] p.p.m.
$N_3P_3(NHBu^t)_2[HN(CH_2)_4NH]Cl_2$	(**18**)	2.1	0.4	0.4
$N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$	(**12**)	1.2	−0.2	0.8
$N_3P_3(NHBu^t)_2[O(CH_2)_4O]Cl_2$	(**15**)	1.2	0.6	0.2
$N_3P_3(NHBu^t)_2[HN(CH_2)_2NMe]Cl_2$	(**12**)	~1	~−0.4	0.7

[a] $\Delta\delta PX_2 = \delta PX_2(CDCl_3) - \delta PX_2(C_6D_6)$[$X_2 = Cl_2$, spiro, $(NHBu^t)_2$].

causing shielding or deshielding. It appears that the magnitude of this effect is greater for the polar $\equiv PCl_2$ group than for the $\equiv$Pspiro or $\equiv P(NHBu^t)_2$ group, as indicated by the greater $\Delta\delta$ values of $\equiv PCl_2$.

The relative solvent shifts in ^{31}P n.m.r. spectroscopy on changing from $CDCl_3$ to deuteriobenzene resemble those observed in ^1H n.m.r. spectroscopy on aminocyclophosphazenes and mononuclear phosphorus compounds, where changes from CCl_4 to deuteriobenzene were studied.[40] In both groups of compounds increased substitution of electron withdrawing chlorine atoms by electron releasing dimethylamino groups decreased the solvent effect. In both cases the protons attached to the least electron rich phosphorus experienced the greatest shielding by the benzene solvent molecules. With the most highly aminolysed derivatives of cyclotriphosphazatrienes a small deshielding effect was observed. Extrapolation of this data would predict the greatest solvent effect for the $\equiv PCl_2$ group, which is what is observed.

It is likely that these aromatic shielding effects observed here are also related to the temperature dependence of the ^{31}P spectra observed for phenylated cyclotriphosphazatrienes,[19,29] as well as to the preferential formation of geminal $N_3P_3Cl_3(NR_2)_3$ derivatives in aromatic solvents.[41]

Much smaller shielding effects were observed for the $\equiv P(NHBu^t)_2$ group. The effects on the $\equiv$Pspiro group are also small, shielding and deshielding being observed for different compounds. There is an indication that these could be related to the size of the spiro ring.

Isolation of $N_3P_3(NHBu^t)_2[O(CH_2)_3OH]Cl_3$ and conversion to $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$

In following the reaction of geminal $N_3P_3(NHBu^t)_2Cl_4$ with propane-1,3-diol by $^{31}P\{^1H\}$ n.m.r. spectrometry, peaks in the reaction mixture could be assigned to an intermediate with an ABX type appearance. The compound was subsequently isolated and characterised as the monodentate structure (**3**).

The ^{31}P n.m.r. spectrum was measured with and without proton coupling and this allowed identification of lines arising from the $\equiv PCl_2$, $\equiv PCl[O(CH_2)_3OH]$ and $\equiv P(NHBu^t)_2$ groups. Lines of the ab subspectra of the AB basic multiplet were readily assigned and the coupling constants and chemical shifts of the phosphorus nuclei could be calculated. $\delta P Cl_2$, 22.2; $\delta P[O(CH_2)_3OH]$, 18.95; $\delta P(NHBu^t)_2$, 4.1 p.p.m.; $J\{PCl_2\text{–}P[O(CH_2)_3OH]\}$, 69.7; $J[PCl_2\text{–}P(NHBu^t)_2]$, 45.1; $J\{P[O(CH_2)_3OH]\text{–}P(NHBu^t)_2\} = 57.8$ Hz.

Further ^{31}P n.m.r. spectra (again with and without proton coupling) were obtained after the sample, dissolved in $CDCl_3$, had been treated with D_2O. If the $^{31}P\{^1H\}$ n.m.r. spectra are examined it can be observed that the splitting of the X part of the spectrum is greatly diminished after the "D_2O exchange" whereas the A part remains unsplit and the B part remains collapsed. This is consistent with the assignment of the X part of the spectrum to the $\equiv P(NHBu^t)_2$ group, since deuterium will selectively replace the NH (and OH) proton and hence diminish coupling of this group in the ^{31}P-H n.m.r. spectrum.

The monodentate compound, $N_3P_3(NHBu^t)_2[O(CH_2)_3OH]Cl_3$ (**3**) was conclusively shown to be the precursor of the major product of the reaction,

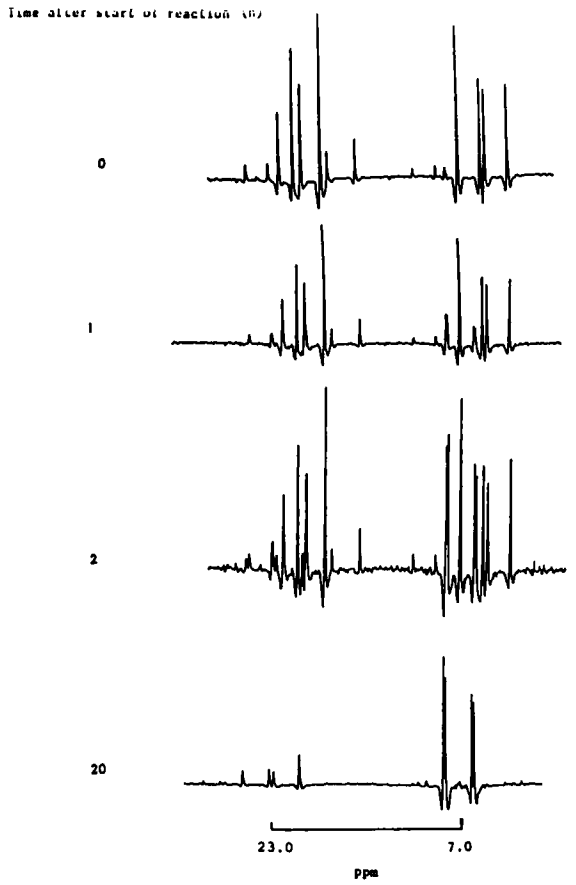


FIGURE 5 The intramolecular reaction of $N_3P_3(NHBu^t)_2[O(CH_2)_3OH]Cl_3$ (**3**) with pyridine as followed by $^{31}P\{^1H\}$ n.m.r. spectroscopy at 24.15 MHz in $CDCl_3$ at room temperature.

$N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ (**2**) by addition of pyridine. the intermolecular conversion of the monodentate compound (**3**) to the spiro compound (**2**) could be conveniently followed by $^{31}P\{^1H\}$ n.m.r. spectroscopy and is shown in Figure 5. $^{31}P\{^1H\}$ n.m.r. spectroscopy indicates that there is an almost total conversion of the precursor (**3**) into the product (**2**).

The ^1H n.m.r. spectrum of the acyclic intermediate (**3**) is shown in Figure 6.

The $POCH_2$ group gives rise to a highly complex multiplet structure at 4–5 p.p.m. The complexity of this multiplet can be understood in terms of the intrinsic non-equivalence of the $POCH_2$ protons.

No conformation exists in which the two $POCH_2$ protons can exist in identical chemical environments as indicated by the Newman projections. The two protons of the $POCH_2$ moiety therefore give rise to an AB quartet. Further coupling with the neighbouring CCH_2 protons and the phosphoruc nucleus would give rise to a large number of lines of which at least 14 are discernable.

Homonuclear decoupling of the CCH_2 protons results in simplification of the OCH_2 multiplet to six lines. Theoretically eight lines due to splitting of the AB

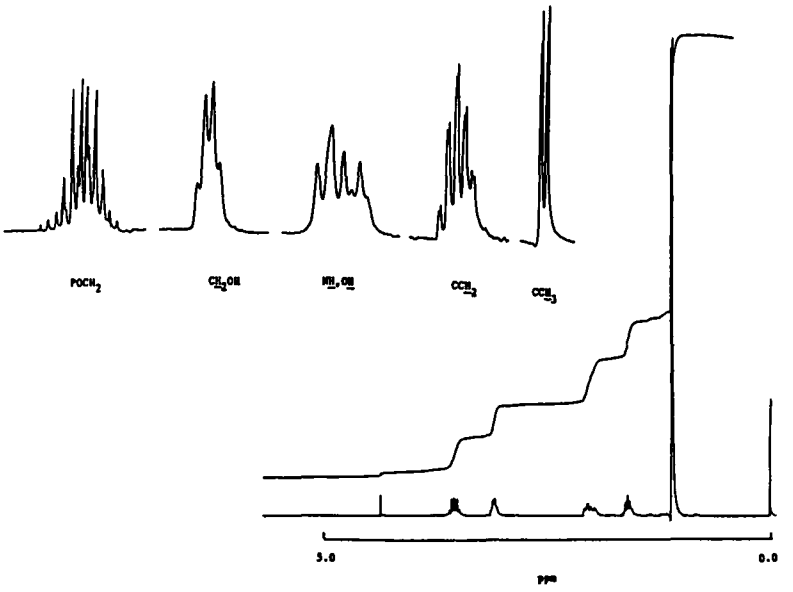


FIGURE 6 ^{1}H n.m.r. spectrum of $N_3P_3(NHBu^t)_2[O(CH_2)_3OH]Cl_3$ (3) at 199.5 MHz in $CDCl_3$ at room temperature.

quartet by phosphorus would be anticipated. A similar case of intrinsic asymmetry of the OCH_2 protons has been observed in the 2-*trans*-4-diamino-2,4,6,6-tetra-n-propoxycyclotriphosphazatriene.[31,32] A quintet structure corresponding to the CCH_2 protons is observed.

Homonuclear decoupling either of the CH_2OH and or of the $POCH_2$ protons, respectively, results in simplification of the CCH_2 peaks to a triplet. In addition a four-bond coupling of the CCH_2 protons to phosphorus, of the order of 1.5 Hz, is observed. A multiplet structure at 3.8 p.p.m. corresponds to the CCH_2OH protons. Decoupling of the CCH_2 protons results in simplification of the multiplet to a broad doublet, which arises from coupling with the O*H* proton.

Broad overlapping bands near 2.5 p.p.m. due to the O*H* and N*H* protons are observed. Treatment of the sample with D_2O results in the disappearance of these peaks. Simplification of the CCH_2OH to a triplet is also observed.

Two singlets are observed at 1.2 p.p.m. associated with the CH_3 protons. These arise, because the t-butylamino groups are in different environments, above and below the plane of the phosphazene ring. Furthermore each line is split into a doublet due to long range coupling with phosphorus [$^4J(PH) = \sim 1$ Hz].

The ^{1}H n.m.r. spectra of the spiro derivatives

The ^{1}H n.m.r. spectra of mono spiro derivatives of geminal $N_3P_3Ph_2Cl_4$ have been reported earlier by us[19] and it was noted that in a number of cases non-equivalence of methylene protons could be readily observed. A similar situation occurs in the case of mono spiro derivatives of geminal $N_3P_3(NHBu^t)_2Cl_4$ (1) since the methylene protons may observe preferentially the $\equiv P(NHBu^t)_2$ or the $\equiv PCl_2$ group. ^{1}H n.m.r. data is given in Table IV.

TABLE IV

^{1}H n.m.r. Data (199.5 Mhz) for spiro Derivatives of Geninal $N_{13}P_3(NHBu^t)_2Cl_4$ in $CDCl_3$ at temperature

Compound	δOCH_2 p.p.m.	δNCH_2 p.p.m.	δCCH_2 p.p.m.	δNCH_3 p.p.m.	$\delta NHBu^t$ p.p.m.	$\delta NHCH_2$ p.p.m.	δNCH_3 p.p.m.	$^3J(POCH_2)$ Hz	$^3J(PNCH_2)$ Hz	$^3J(PNCH_3)$ Hz
$N_3P_3(NHBu^t)_2[O[CH_2)_3O]Cl_2$ (**2**)	4.4*		1.68		2.4		1.25	*		
			2.08							
$N_3P_3(NHBu^t)_2[O(CH_2)_3NH]Cl_2$ (**5**)	4.4*	3.2*	1.7		2.4	2.5	1.25	*	*	
			2.0							
$N_3P_3(NHBu^t)_2[HN(CH_2)_3NH]Cl_2$ (**6**)		3.24	1.65		2.4	2.4	1.25		15.3	
		3.31	1.78							
$N_3P_3(NHBu^t)_2[HN(CH_2)_3NMe]Cl_2$ (**7**)		3.1*	1.8*	2.55	2.4	2.4	1.26		*	14.1
$N_3P_3(NHBu^t)_2[MeN(CH_2)_3NMe]Cl_2$ (**8**)		3.1*	1.77	2.59	2.4		1.25		*	14.2
			1.96				1.25			
$N_3P_3(NHBu^t)_2[O(CH_2)_2O]Cl_2$ (**9**)	4.42				2.4		1.25	11.4		
$N_3P_3(NHBu^t)_2[O(CH_2)_2NH]Cl_2$ (**10**)	4.3*	3.5*			2.4	2.6	1.26	*		
$N_3P_3(NHBu^t)_2[HN(CH_2)_2NH]Cl_2$ (**11**)		3.37			2.5	2.5	1.25		9.4	
$N_3P_3(NHBu^t)_2[HN(CH_2)_2NMe]Cl_2$ (**12**)		3.4*		2.56	2.4	2.4	1.27		*	~14[a]
		3.2*					1.28			
$N_3P_3(NHBu^t)_2[MeN(CH_2)_2NMe]Cl_2$ (**13**)		3.2*		2.56	2.4		1.25			
$N_3P_3(NHBu^t)_2[O(CH_2)_2NMe]Cl_2$ (**14**)	4.2*	3.2*		2.56	2.4		1.25	*	*	14.3
$N_3P_3(NHBu^t)_2[O(CH_2)_4O]Cl_2$ (**15**)	4.15		1.83		2.4			14.2		
$N_3P_3(NHBu^t)_2[O(CH_2)_4NH]Cl_2$ (**16**)		3.2	1.7*		2.4	2.9		*	*	
			1.8*				1.28			
$N_3P_3(NHBu^t)_2[HN(CH_2)_4NH]Cl_2$ (**17**)		3.23	1.72		2.5	2.9	~1.2[a]		12.3	
$N_3P_3(NHBu^t)_2[O(CH_2)_3O]_2$ (**18**)	4.37		1.82		2.4		*			
$N_3P_3(NHBu^t)_2[O(CH_2)_4O]_2$ (**19**)	4.4*		1.85		2.4					

* Complex overlap of lines. [a] Second order coupling effects.

The six-membered spiro derivatives of geminal $N_3P_3(NHBu^t)_2Cl_4$ (**1**) give rise to highly complex proton n.m.r. spectra, similar in appearance to those described for the analagous diphenyl derivatives. In both groups of compounds the methylene protons are clearly non-equivalent and give rise to AB quartet structures, which are further split by coupling with the adjacent methylene protons and with phosphorus.

Homonuclear decoupling of the XCH_2 (YCH_2) protons (where X = Y = O, NH, NMe) of the spiro derivatives (containing a symmetric six-membered spiro group) results in simplification of the CCH_2 signals to quartet structures. Simplification of the XCH_2 (YCH_2) resonances is also observed on homonuclear decoupling of the CCH_2 protons, although the AB quartet structure is further split by phosphorus. Chemical shift differences between the two CH_2 protons is of a similar magnitude in both the six-membered spiro derivatives of gem $N_3P_3Ph_2Cl_4$ and gem $N_3P_3(NHBu^t)_2Cl_4$ (**1**).

The ^1H n.m.r. spectrum of $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ (**2**) closely resembles that of $N_3P_3Ph_2[O(CH_2)_3O]Cl_2$[19] since the conformation of the spiro ring in the two systems are likely to be similar. The CCH_2 region of the spectrum is distinctly asymmetric due to different coupling parameters of the CCH_2 protons with the OCH_2 protons. The resonances due to the two OCH_2 protons are much closer than for the CCH_2 protons and multiplet structures clearly overlap (Figure 7a).

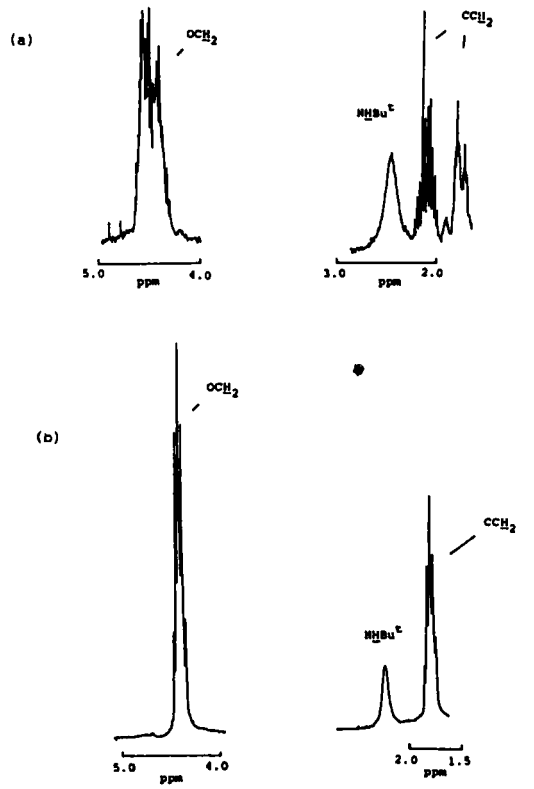


FIGURE 7 ^1H n.m.r. spectra in $CDCl_3$ at 199.50 MHz (room temperature) (*a*) $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ (**2**) (*b*) $N_3P_3(NHBu^t)_2[O(CH_2)_3O]_2$ (**4**).

By contrast a relatively simple spectrum is observed for the dispiro derivative $N_3P_3(NHBu^t)_2[O(CH_2)_3O]_2$ (**4**) as shown in Figure 7b. A symmetrical quintet structure is observed for the CCH_2 protons arising from coupling with four neighbouring OCH_2 protons. The quintet structure of the OCH_2 protons may arise from coupling with the neighbouring CCH_2 protons to give a triplet structure, which is further split by coupling with a neighbouring phosphorus and by second order effects due to the magnetic and chemical equivalence of the two ≡Pspiro nuclei. This is confirmed from homonuclear decoupling experiments of the CCH_2 protons, which results in simplification of the multiplet to a triplet.

Comparison of the ^{1}H n.m.r. spectrum of $N_3P_3(NHBu^t)_2[O(CH_2)_3O]_2$ (**4**) with that of $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ (**2**) and the dispiro compound, $N_3P_3[O(CH_2)_3O]_2Cl_2$, therefore indicates that two distinct chemical environments of the methylene protons (OCH_2 and CCH_2, respectively) are resolved, when the molecule contains the $\equiv PCl_2$ and either the $\equiv P(NHBu^t)_2$ or the ≡Pspiro groups, but not when the molecule contains the $\equiv P(NHBu^t)_2$ and ≡Pspiro moieties.

In the case of $N_3P_3(NHBu^t)_2[HN(CH_2)_3NH]Cl_2$ (**6**) and $N_3P_3(NHBu^t)_2$-$[MeN(CH_2)_3NMe]Cl_2$ (**8**) complex multiplet structures corresponding to the $NHCH_2$ and CCH_2 protons are observed. $\delta(H_A)-\delta(B_B)$ is significantly smaller in the primary amino derivative (**6**) than in the corresponding secondary amino-derivative (**8**), being 0.06 p.p.m. and 0.20 p.p.m., respectively.

Multiplet structures arising due to NCH_2, OCH_2 and CCH_2 protons of $N_3P_3(NHBu^t)_2[O(CH_2)_3NH]Cl_2$ (**5**) are shown in Figure 8. The multiplet structure of the CCH_2 protons shows a similarity to that obtained for $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ (**2**) suggesting that the conformation of the CCH_2 protons are similar in these two compounds.

The $NHCH_2$ signals of the ≡Pspiro ring of compound (**5**) are clearly distinguishable from signals due to the $NHBu^t$ protons. The $NHBu^t$ protons give

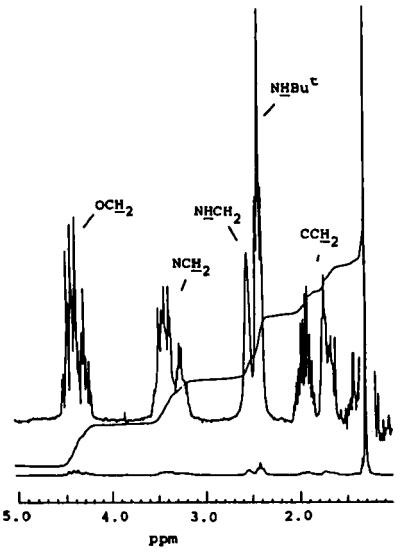


FIGURE 8 ^{1}H n.m.r. spectrum in $CDCl_3$ at 199.5 MHz (room temperature) $N_3P_3(NHBu^t)_2[O(CH_2)_3NH]Cl_2$ (**5**).

rise to an apparent triplet, which presumably arises from the overlap of two doublets. This may be rationalised if it is considered that the N*H*Bu^t protons observe different chemical environments due to the asymmetry of the spiro ring and hence give rise to two signals which are further split by coupling with phosphorus.

The ^{1}H n.m.r. spectrum of $N_3P_3(NHBu^t)_2[HN(CH_2)_3NMe]Cl_2$ (**7**) shows considerable overlap of multiplet structures arising from the NHC*H*$_2$ and NMeC*H*$_2$ resonances. A complex multiplet structure is also observed for the CC*H*$_2$ protons due to further splitting of the AB quartet by the neighbouring NHCH$_2$ and NMeC*H*$_2$ protons.

The sharpness and resolution of the N*H*Bu^t protons in these six-membered spiro derivatives is noteworthy since the N*H* resonances in most primary amino derivatives (including t-butylamino derivatives of $N_3P_3Cl_6$) appear as unresolved humps.

The ^{1}H n.m.r. spectra of $N_3P_3(NHBu^t)_2[O(CH_2)_2O]Cl_2$ (**9**) and $N_3P_3(NHBu^t)_2[HN(CH_2)_2NH]Cl_2$ (**11**) give rise to doublet structures in the OC*H*$_2$ and NC*H*$_2$ regions of the spectrum. The simplicity of these spectra arise from the apparent equivalence or near chemical equivalence of the C*H*$_2$ protons. The spectra of these compounds (**9**) and (**11**) resemble those of their diphenyl analogues.[19] (This may be contrasted with the six-membered spiro ring analogues where the non-equivalence of the OC*H*$_2$ and NC*H*$_2$ protons is clearly apparent). A much more complex multiplet structure is observed for the NC*H*$_2$ protons of $N_3P_3(NHBu^t)_2[MeN(CH_2)_2NMe]Cl_2$ (**13**). This increased complexity arises from the greater chemical non-equivalence of methylene protons compared with those of its non-methylated analogue (**11**).

$N_3P_3(NHBu^t)_2[HN(CH_2)_2NMe]Cl_2$ (**12**) shows broad multiplet structures assignable to the NHC*H*$_2$ and NMeC*H*$_2$ protons. The NC*H*$_3$ group shows a fairly sharp peak in the centre of the anticipated doublet. This feature arises from second order effects due to the accidental isochrony of the ≡Pspiro and the ≡PCl$_2$ groups. Similar effects have been observed in dimethylaminophosphazene derivatives.[42,43]

The ^{1}H n.m.r. spectra of the seven-membered mono spiro derivatives $N_3P_3(NHBu^t)_2[X(CH_2)_4Y]Cl_2$(X = Y = O, NH) (**15**), (**18**) give rise to a broad peak due to the CC*H*$_2$ protons and to two broad peaks due to the OCH$_2$ and NCH$_2$ protons, respectively.

Homonuclear decoupling of the OC*H*$_2$ and NC*H*$_2$ protons of compounds (**15**) and (**18**) results in simplification in both cases of the CC*H*$_2$ signals to sharp singlet, and homonuclear decoupling of the CC*H*$_2$ signals results in simplification of the OC*H*$_2$ and the NC*H*$_2$ signal to a sharp doublet (due to splitting by the phosphorus nucleus). The homonuclear decoupling experiments therefore show the apparent equivalence of the methylene protons in contrast to the six-membered ring analogues in which two distinct environments are indicated from their ^{1}H n.m.r. spectra. In the case of the seven-membered diphenyl analogues[19] it was possible to observe small chemical shift differences for the OC*H*$_2$ and NC*H*$_2$ proton environments respectively, suggesting a greater degree of non-equivalence of the protons in the phenylated compounds.

A considerably more complex multiplet is observed due to the OCH_2 protons of $N_3P_3(NHBu^t)_2[O(CH_2)_4O]_2$ (**16**) in contrast to its mono spiro analogue (**15**), presumably as a result of second order effects. It is interesting to note that for the six-membered ring analogues a simpler spectrum was obtained for the bis than the mono derivative.

EXPERIMENTAL

Geminal $N_3P_3(NHBu^t)_2Cl_4$ (**1**) was obtained by a literature method.[44] Solvents and reagents were obtained as in Part 55.[19] Chromatographic procedures and instrumental methods were detailed earlier.[19] Three experiments are described. The rest are gathered in Table V. Analytical data are presented in Table VI.

(a) *The reaction of geminal $N_3P_3(NHBu^t)_2Cl_4$ (**1**) with one equivalent of propane-1,3-diol and two equivalents of pyridine.* Compound (**1**) (2 g, 4.75 mmol) was dissolved in dichloromethane (25 cm^3). To this solution one equivalent of propane-1,3-diol (0.36 g, 4.75 mmol) and two equivalents of pyridine (0.38 g, 9.5 mmol) were added. The reaction was observed to be initially slightly exothermic. Pyridine hydrochloride was precipitated as long thin needle like crystals after about 20 h. $^{31}P\{^1H\}$ n.m.r. spectroscopy and t.l.c. reveals essentially the formation of two major components in the reaction mixture. Peaks in the $^{31}P\{^1H\}$ n.m.r. spectrum of the reaction mixture could be assigned to the starting material (**1**), an intermediate, subsequently identified as $N_3P_3(NHBu^t)_2[O(CH_2)_3OH]Cl_2$, (**3**) and a major product identified as $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$, (**2**). Examination of the mixture by t.l.c. using a mixture of CH_2Cl_2 and ether (1:1) as eluent showed the presence of 3 major components in the reaction mixture, with the following R_f-values: (**1**) 0.90, (**2**) 0.76, (**3**) 0.58. The dispiro derivative $N_3P_3(NHBu^t)_2[O(CH_2)_3O]_2$ (**4**) was also observable in small amounts by t.l.c. (R_f 0.35).

T.l.c. and n.m.r. of the reaction mixture show that in the early stages of the reaction an increase in the relative proportion of the intermediate (**3**) in the reaction is observed. 3 h after the start of reaction the major product (**2**) is observed to be the largest component. Beyond this stage of reaction a decrease in the proportion of the intermediate in the reaction mixture is observable. 20 h after the start of reaction only minor quantities of starting material (**1**) and intermediate (**3**) are observable with the major product (**2**) present in high yield. An intense spot is observable on the base line of the t.l.c. plate and is presumably due to amine hydrochloride, polymeric materials and hydrolysis products. The pyridine hydrochloride formed from the reaction mixture was filtered off and the individual phosphazene derivatives separated by column chromatography using a mixture of CH_2Cl_2 and either (1:) as eluent. The dangler (**3**) was obtained in small yield from this reaction (0.11 g, 5%) [see (b) for details]. The mono spiro compound (**2**) was recrystallised from $CHCl_3$, m.p. 158–159°C, (0.99 g, 54%). The dispiro derivative (**4**) was recrystallised from benzene, m.p. 132–135°C, (0.08 g, 4.0%).

(b) *Reaction of one equivalent of geminal $N_3P_3(NHBu^t)_2Cl_4$ (**9**) with one equivalent of propane-1,3-diol and one equivalent of pyridine.* Compound (**1**) (2 g, 4.75 mmol) was dissolved in dichloromethane (40 cm^3). To this solution one equivalent of prpoane-1,3-diol (0.19 g, 4.75 mmol) and one equivalent of pyridine (0.18 g, 4.75 mmol) were added. A substantial amount of starting material (**1**), dangling intermediate (**3**) and mono spiro product (**2**) are observable by t.l.c. and n.m.r. spectroscopy 20 h after the start of reaction [the two products (**3**) and (**2**) being in a ration of approx.1:1]. No appreciable change in the proportion of these components was observed over the following 6 h. Under these conditions the intermediate (**3**) could be isolated in good yield by chromatography using CH_2Cl_2-ether (1:1 as eluent. It is obtained as a liquid at room temperature (0.83 g, 38%).

(c) *The intramolecular conversion of $N_3P_3(NHBu^t)_2[O(CH_2)_3OH]Cl_3$ (**3**) in the presence of pyridine to the spiro derivative* (**2**). Compound (**3**) (0.35 g, 0.11 mmol) was dissolved in $CDCl_3$ (1 cm^3). To this solution pyridine (0.15 g, 0.22 mmol) was added. The reaction was followed by $^{31}P\{^1H\}$ n.m.r. spectroscopy. Formation of the spiro product (**2**) is observed 20 mins after the start of reaction. An increase in the amount of product is observed throughout the reaction and eventually results in the total conversion of compound (**3**) into the product (**2**).

TABLE V

Experimental details of the reactions of geminal $N_3P_3(NHBu^t)_2Cl_4$ with difunctional reagents using dichloromethane as solvent

gem (f)	$N_3P_3(NHBu^t)_2Cl_4$ (mmol)	Difunctional reagent	Amount (g)	Amount (mmol)	Tertiary base	Amount (g)	Amount (mmol)	Solvent used for column chromatography	Product	Yield %	M.P.(°C) of product	M^+	M
2	4.75	$HO(CH_2)_2OH$	0.291	4.75	pyridine	0.752	9.51	CH_2Cl_2-ether(3:1)	**(9)**[a]	56	141	409	409
2	4.75	$HO(CH_2)_3OH$	0.362	4.75	pyridine	0.752	9.51	CH_2Cl_2-ether(1:1)	**(2)**[b]	54	158–159	423	423
								CH_2Cl_2-ether(1:1)	**(3)**	5	liq at RT	354	354
								CH_2Cl_2-ether(1:1)	**(4)**[a]	4	132–135	427	427
2	4.75	$HO(CH_2)_3OH$	0.362	4.75	pyridine	0.376	4.75		**(2)**	38	158–159	423	423
									(3)	30	liq at Rt	354	354
2	3.57	$HO(CH_2)_4OH$	0.429	4.75	pyridine	0.752	9.51	CH_2Cl_2-ether(1:1)	**(15)**[c]	48	137–138	437	437
	3.57							CH_2Cl_2-ether(1:1)	**(16)**[a]	8	164–166	455	455
1.5	3.57	$H_2N(CH_2)_2NH_2$	0.214	3.57	NEt_3	0.722	7.14	CH_2Cl_2-acetone(3:1)	**(11)**[d]	60	145	407	407
1.5	3.57	$H_2N(CH_2)_3NH_2$	0.265	3.57	NEt_2	0.722	7.14	CH_2Cl_2-CH_3CN(1:1)	**(6)**[b]	53	156–158	421	421
1.5	3.57	$H_2N(CH_2)_4NH_2$	0.315	3.57	NEt_3	0.722	7.14	CH_2Cl_2-ether(1:1)	**(18)**[c]	50	193	435	435
1.5	3.57	$HO(CH_2)_2NH_2$	0.218	3.57	pyridine	0.564	7.14	CH_2Cl_2-ether(3:1)	**(10)**[b]	53	136–137	408	408
1.5	3.57	$HO(CH_2)_3NH_2$	0.268	3.57	pyridine	0.564	7.14	CH_2Cl_2-ether(1:1)	**(5)**[c]	42	159–160	422	422
1.5	3.57	$HO(CH_2)_4NH_2$	0.218	3.57	pyridine	0.564	7.14	CH_2Cl_2-ether(1:1)	**(17)**[f]	40	164	436	436
1.5	3.57	$MeNH(CH_2)_2NHMe$	0.315	3.57	NET_3	0.722	7.14	CH_2Cl_2-ether(9:1)	**(13)**[g]	60	111	435	435
1.5	3.57	$MeNH(CH_2)_3NMHe$	0.365	3.57	NEt_3	0.722	7.14	CH_2Cl_2-ether(1:1)	**(8)**[a]	52	99–100	449	449
1.5	3.57	$MeNH(CH_2)_2NH_2$	0.264	3.57	NEt_3	0.722	7.14	CH_2Cl_2-ether(1:1)	**(12)**[b]	45	108–110	421	421
1.5		$MeNH(CH_2)_3NH_2$	0.314	3.57	NEt_3	0.722	7.14	CH_2Cl_2-ether(1:1)	**(7)**[a]	55	129–130	435	435
1.5		$HO(CH_2)_2NMeH$	0.268	3.57	pyridine	0.564	3.57	CH_2Cl_2-ether(1:1)	**(14)**[g]	43	142–144	408	408

Recrystallised from : [a] PhH [b] $CHCl_3$ [c] pure from column.
[d] CH_2Cl_2 with a few drops of light petroleum (b.p. 60–80°C).
[e] Hexane/CH_2Cl_2 (4:1) [f] light petroleum (b.p. 60–80°C)/$CHcl_3$(9:1).
[g] Ethyl acetate.

TABLE VI

Analytical data (%)* of derivatives of geminal $N_3P_3(NHBu^t)_2Cl_4$

Compound	C %		H %		N %	
(9) $N_3P_3(NHBu^t)_2[O(CH_2)_2O]Cl_2$	29.5	(29.3)	6.0	(5.9)	17.4	(17.1)
(2) $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$	31.4	(31.1)	6.2	(6.2)	16.3	(16.5)
(3) $N_3P_3(NHBu^t)_2[O(CH_2)_3OH]Cl_3$	28.9	(28.7)	6.0	(5.9)	15.0	(15.2)
(4) $N_3P_3(NHBu^t)_2[O(CH_2)_3O]_2$	39.6	(39.3)	7.8	(7.6)	16.2	(16.4)
(15) $N_3P_3(NHBu^t)_2[O(CH_2)_4O]Cl_2$	32.8	(32.9)	6.4	(6.5)	16.1	(16.0)
(16) $N_3P_3(NHBu^t)_2[O(CH_2)_4O]_2$	42.4	(42.2)	7.7	(8.0)	15.1	(15.4)
(11) $N_3P_3(NHBu^t)_2[HN(CH_2)_2NH]Cl_2$	29.6	(29.4)	6.7	(6.4)	23.7	(24.0)
(6) $N_3P_3(NHBu^t)_2[HN(CH_2)_3NH]Cl_2$	31.5	(31.3)	6.8	(6.7)	23.1	(23.2)
(18) $N_3P_3(NHBu^t)_2[HN(CH_2)_4NH]Cl_2$	33.0	(33.0)	7.1	(6.9)	22.4	(22.5)
(10) $N_3P_3(NHBu^t)_2[O(CH_2)_2NH]Cl_2$	29.8	(29.3)	5.9	(6.2)	20.2	(20.5)
(5) $N_3P_3(NHBu^t)_2[O(CH_2)_3NH]Cl_2$	30.7	(31.2)	6.7	(6.4)	19.8	(19.9)
(17) $N_3P_3(NHBu^t)_2[O(CH_2)_4NH]Cl_2$	33.0	(32.9)	7.2	(6.8)	19.0	(19.2)
(13) $N_3P_3(NHBu^t)_2[MeN(CH_2)_2NMe]Cl_2$	33.3	(33.0)	6.9	(6.9)	22.9	(22.8)
(8) $N_3P_3(NHBu^t)_2[MeN(CH_2)_3NMe]Cl_2$	35.0	(34.7)	7.2	(7.2)	21.3	(21.8)
(12) $N_3P_3(NHBu^t)_2[NH(CH_2)_2NMe]Cl_2$	31.6	(31.3)	7.0	(6.7)	22.8	(23.2)
(7) $N_3P_3(NHBu^t)_2[NH(CH_2)_3NMe]Cl_2$	33.2	(33.0)	7.1	(6.9)	22.2	(22.5)
(14) $N_3P_3(NHBu^t)_2[O(CH_2)_2MeN]Cl_2$	31.2	(31.2)	6.5	(6.4)	19.7	(19.9)

* Calculated values are given in parentheses.

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