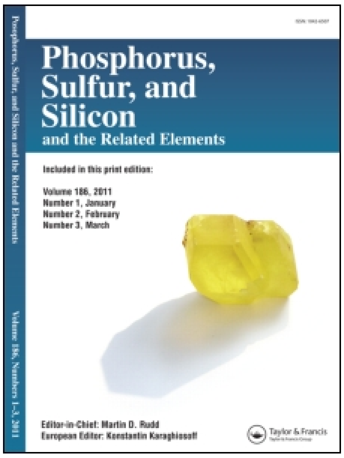

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THE REACTIONS OF GEMINAL $N_3P_3Ph_2Cl_4$ AND $N_3P_3(NHBu^t)_2Cl_4$ WITH DIFUNCTIONAL REAGENTS. X-RAY CRYSTALLOGRAPHY, NMR SPECTROSCOPY AND BASICITY OF THE PRODUCTS

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THE REACTIONS OF GEMINAL $N_3P_3Ph_2Cl_4$ AND $N_3P_3(NHBu^t)_2Cl_4$ WITH DIFUNCTIONAL REAGENTS. X-RAY CRYSTALLOGRAPHY, NMR SPECTROSCOPY AND BASICITY OF THE PRODUCTS

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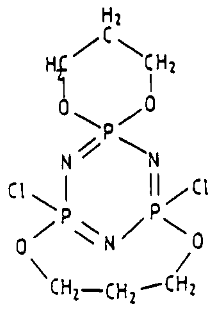
The reactions of geminal $N_3P_3Ph_2Cl_4$ and $N_3P_3(NHBu^t)_2Cl_4$ with difunctional reagents have been investigated. The N.M.R. spectra of the derivatives are reported. The basicity of these products in nitrobenzene solution is reported and the basicity substituent constants evaluated. X-ray crystallographic data are presented.

In the reactions of $N_3P_3Cl_6$ with 1,3-dihydroxypropane, $HO(CH_2)_3OH$, we have observed spiro-ansa (**1**) dispiro (**2**) isomerism for the compounds $N_3P_3Cl_2[O(CH_2)_3O]_2$.[1,2]



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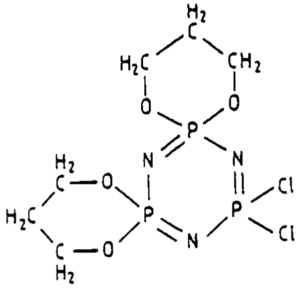

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We have therefore investigated the reactions of geminal $N_3P_3Ph_2Cl_4$ and $N_3P_3(NHBu^t)_2Cl_4$ with difunctional reagents to discover whether we obtain spiro (**3**), ansa (**4**), bridging (**5**) or monofunctional (dangling) (**6**) structures.[3-18]

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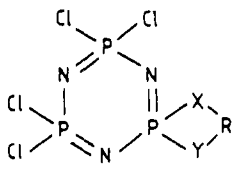

SPIRO

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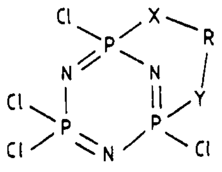

ANSA

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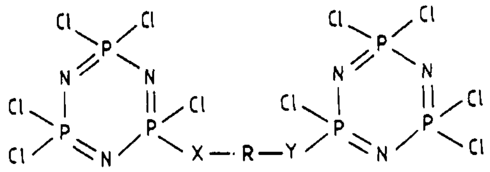
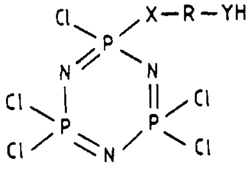


BRIDGING

5

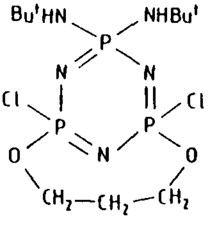


OPEN CHAIN
(DANGLING)

6

In our present study we find that spiro structures predominate; we have also observed bridging and dangling structural types. Generally the reactions of $N_3P_3(NHBu^t)_2Cl_4$ proceeded slower than those of $N_3P_3Ph_2Cl_4$ with corresponding reagents, in line with the greater electron supply of the $NHBu^t$ group compared with that of the Ph group, and thus a corresponding deactivation of the remaining P–Cl bonds towards bimolecular nucleophilic attack.

In the reaction of $N_3P_3(NHBu^t)_2Cl_4$ with 1,3-dihydroxypropane, we obtained a compound of composition $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$. Five structures (**1**–**5**) would agree with this composition and molecular weight.



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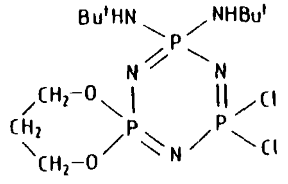

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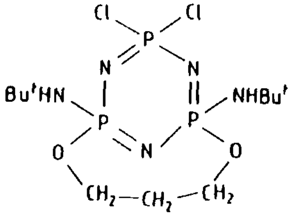
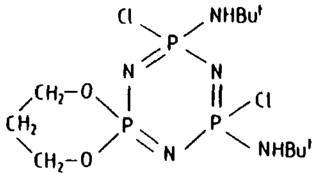
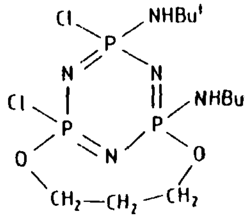






11 (cis, trans)

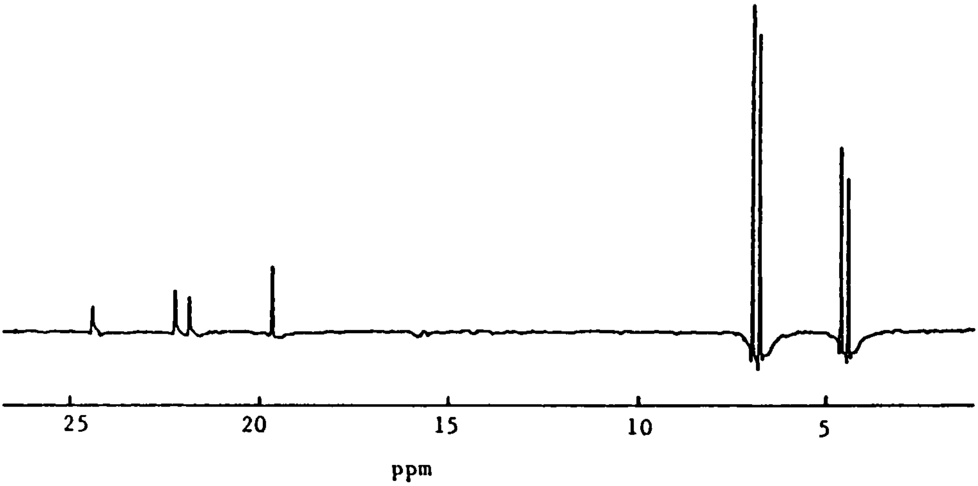


FIGURE 1 The ^{31}P {^1H} N.M.R. spectrum of $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ at 24.15 MHz at −50°C (resolution enhanced).

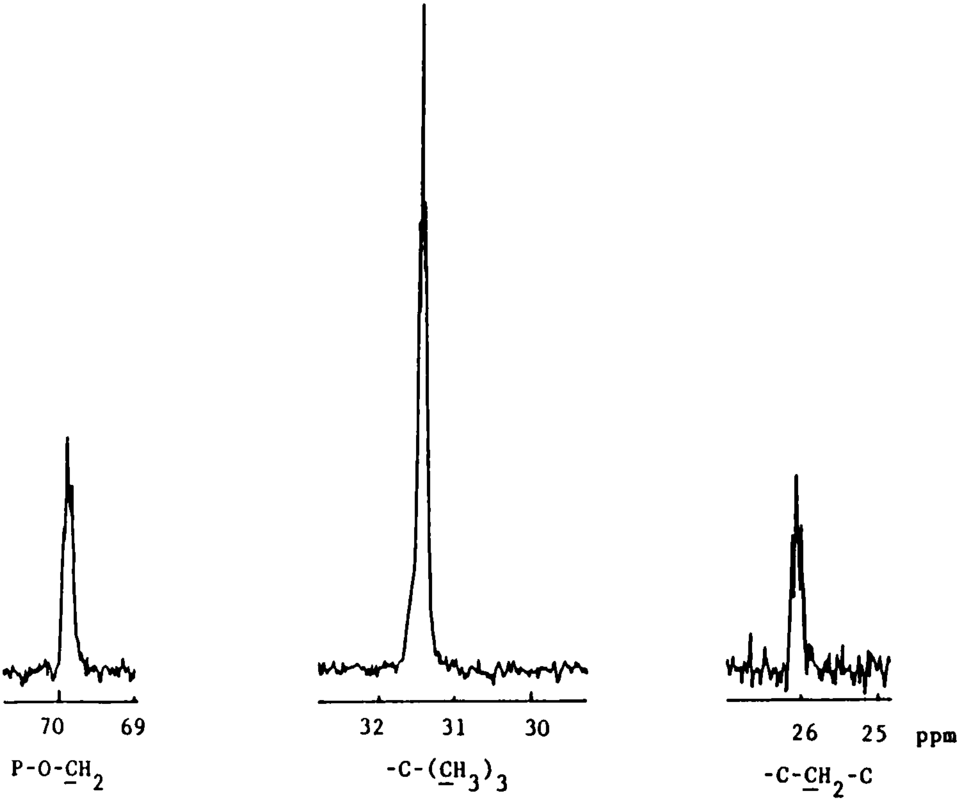
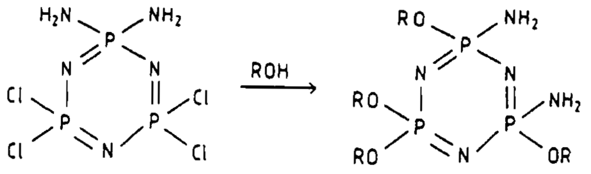


FIGURE 2 The ^{13}C {^1H} N.M.R. spectrum of $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ at 50.10 MHz at room temperature.

The ^{31}P N.M.R. spectrum at 24.15 MHz (Figure 1) and at 161 MHz had an AB_2 appearance. This seemed to rule out structures (**8**) and (**11**).

The ^{13}C N.M.R. spectrum at 50.10 MHz showed triplets due to virtual coupling of the $O\underline{C}H_2$, $C\underline{C}H_2$ and $NC\underline{C}H_3$ carbon nuclei with two phosphorus nuclei. This seemed to favour strongly structure (**9**).

Basicity measurements in nitrobenzene[19] gave a pK_a' value of -0.8, excluding structures (**7**, **10** and **11**). This too appeared to point to the ansa-structure (**9**) with a geminal → nongeminal rearrangement of amino groups during the alcoholysis. We have observed such a rearrangement in the alcoholysis of geminal $N_3P_3(NH_2)_2Cl_4$, (**12** → **13**).[20,21]



12 **13**

We therefore undertook a single crystal X-ray structure analysis of this compound, which to our surprise, revealed it to have the spiro structure (**8**) (Figure 3).

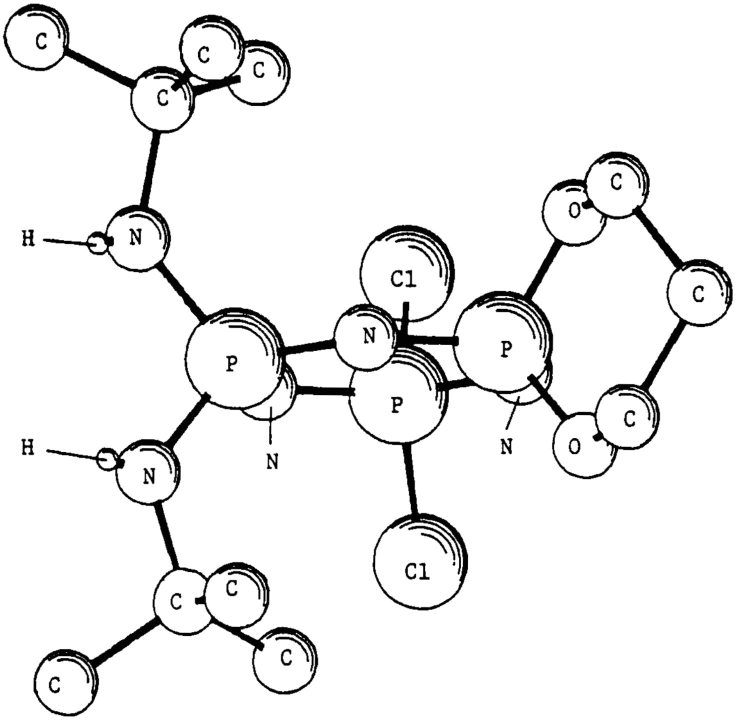


FIGURE 3 Molecular diagram of $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$.

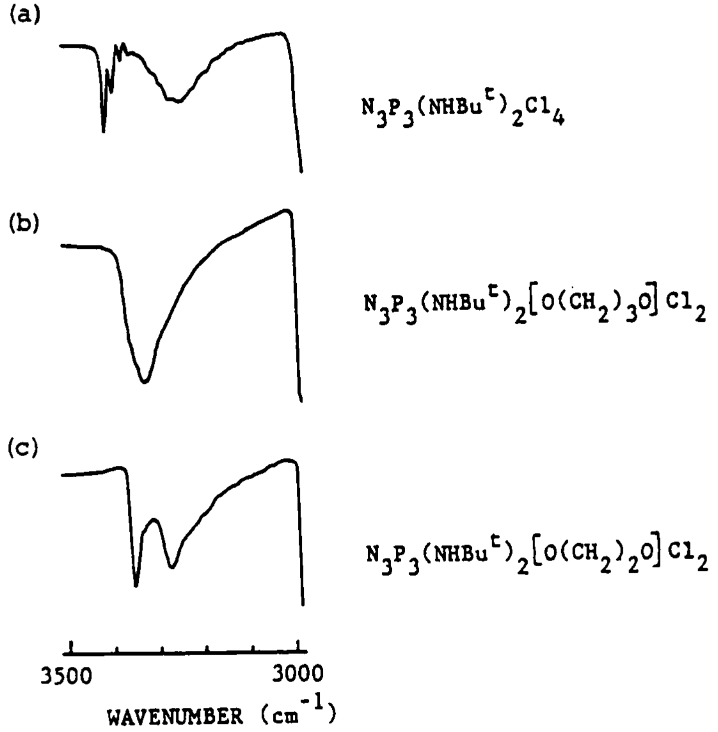


FIGURE 4 The I.R. spectra, NH stretching region, of $N_3P_3(NHBu^t)_2X_2Cl_2$ derivatives. (a) $X_2 = Cl_2$, (b) $X_2 = O(CH_2)_3O$, (c) $X_2 = O(CH_2)_2O$.

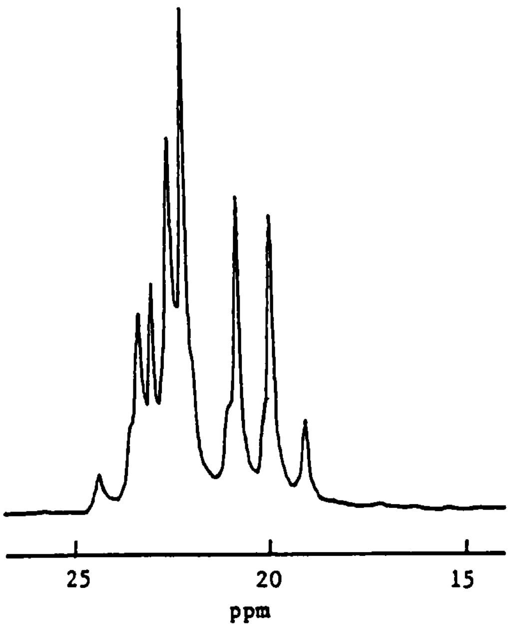


FIGURE 5 The $^{31}P\ \{^1H\}$ N.M.R. spectrum of $N_3P_3Ph_2[NMe(CH_2)_2NMe]Cl_2$ at 24.15 MHz at room temperature.

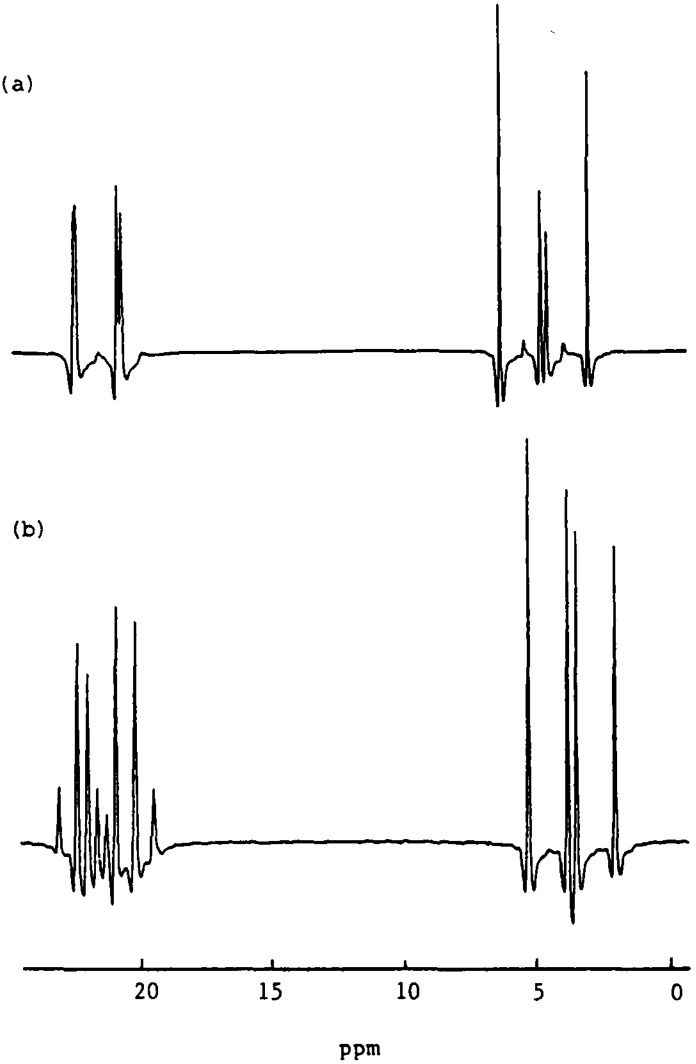


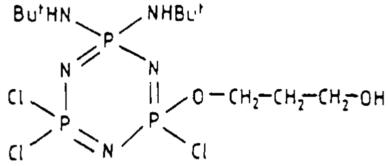
FIGURE 6 The ^{31}P {^{1}H} N.M.R. spectra of $N_3P_3Ph_2[O(CH_2)_3O]Cl_2$ at 24.15 MHz. (a) at room temperature; (b) at − 50 °C (both resolution enhanced).

We have therefore a rather unique case of accidentally isochronous chemical shifts of the $\underline{P}(NHBu^t)_2$ and $\underline{P}[O(CH_2)_3O]$ nuclei which explains the AB_2 ^{31}P spectrum, even at the highest magnetic field available to us and the virtual coupling effect in the ^{13}C N.M.R. spectrum of this compound.

Other six-membered spiro structural units also absorb near the region of the $\underline{P}(NHBu^t)_2$ group, but do not give rise to deceptively simple spectra.

In the infrared spectra of the bis-tertiary-butylamino-derivatives, we have so far observed at least three different patterns in the NH stretching region (Figure 4). For $N_3P_3(NHBu^t)_2Cl_4$ there are two sharp bands at 3420 and 3400 cm^{-1} and one very broad absorption at ~ 3260 cm.$^{-1}$ (Figure 4a); $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ has one fairly broad absorption at 3340 cm^{-1} (Figure 4b), whilst its five-membered ring analogue, $N_3P_3(NHBu^t)_2[O(CH_2)_2O]Cl_2$, has one sharp band at 3360 cm^{-1} and a somewhat more broad one at 3270 cm^{-1} (Figure 4c). From crystallographic studies we know that the pattern of (Figure 4a) is associated with hydrogen-bonded dimers, only one $NHBu^t$ group of each monomer being involved in a hydrogen bond to the ring nitrogen atom of the other. This results in an eight-membered hydrogen-bonded ring. The pattern of (Figure 4b) arises from infinite chains, both $NHBu^t$ groups donating a hydrogen bond each to the same ring nitrogen atom of another molecule, this resulting in six-membered hydrogen-bonded rings.

In following the above reactions by N.M.R. spectroscopy, we observed an intermediate with an ABX ^{31}P spectra. We isolated this and characterised it as the dangling precursor (**14**) of the spiro compound (**8**).



14

The N.M.R. spectroscopic analyses of the $N_3P_3Ph_2Cl_4$ derivatives were complicated by the closeness of the chemical shifts of $\underline{P}Cl_2$ and $\underline{P}Ph_2$ nuclei, sometimes giving rise to isochrony. The analysis of the ^{31}P spectra was further complicated in the presence of five-membered spiro rings, *e.g.*, $N_3P_3Ph_2[NMe(CH_2)_2NMe]Cl_2$ (Figure 5) with all three different ^{31}P nuclei having very similar chemical shifts.

We found the temperature dependance of the ^{31}P spectra of the $N_3P_3Ph_2Cl_4$ derivatives very useful. $\underline{P}Cl_2$ and $\underline{P}Ph_2$ chemical shifts, which sometimes showed

TABLE I

Selected values of basicity substituent constants for spirocyclic and acyclic substituents

Substituent	Substituent constants α_R for acyclic, $\alpha_{\frac{1}{2}R}$ for spirocyclic } substituents
OMe	3.6
OEt	3.9
OPr^i	4.2
$O(CH_2)_2O$	3.6
$O(CH_2)_3O$	3.7
$O(CH_2)_4O$	3.6
NHMe	5.8
NHEt	5.8
$NH(CH_2)_3NH$	6.1
$NH(CH_2)_4NH$	6.2
$NH(CH_2)_3O$	4.8
NMe_2	5.6
$NMe(CH_2)_3NMe$	5.8

little or no chemical-shift differences at room temperature, even at fairly high magnetic fields, frequently gave readily analysable spectra on lowering the temperature even at moderate field strength. We exemplify this with $N_3P_3Ph_2[O(CH_2)_3O]Cl_2$ at room temperature (Figure 6a) and at -50 C (Figure 6b) both at 24.15 MHz.

We further note the inversion of chemical shifts of the $\underline{P}Cl_2$ and $\underline{P}Ph_2$ nuclei. In acyclic and many six-membered spiro-ring derivatives the absorption of the $\underline{P}Ph_2$ group occurs at lower field than that of the $\underline{P}Cl_2$ group, whilst in many five- and seven-membered spiro structures the reverse is the case.

Finally, we have done a preliminary evaluation of the basicity substituent constants[23] of spiro groups and compared these with related acyclic substituents (Table I). We needed this data for a relationship, which we had observed, with endocyclic bond angles in N_3P_3 derivatives, which will be demonstrated elsewhere in this Symposium.[24]

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