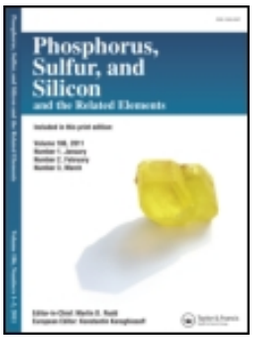

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Phosphorus, Sulfur, and Silicon and the Related Elements

ISSN: 1042-6507 (Print) 1563-5325 (Online) Journal homepage: www.tandfonline.com/journals/gpss20

Synthesis and Structural Characterization of Singly, Doubly, and Triply Bridged Derivatives of Hexachlorocyclotriphosphazene with Bis(2-hydroxyethyl) Ether and 2,2-dimethylpropane-1,3-diol

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To cite this article: Hulya Silah & Sedat Ture (2014) Synthesis and Structural Characterization of Singly, Doubly, and Triply Bridged Derivatives of Hexachlorocyclotriphosphazene with Bis(2-hydroxyethyl) Ether and 2,2-dimethylpropane-1,3-diol, Phosphorus, Sulfur, and Silicon and the Related Elements, 189:2, 198-214, DOI: 10.1080/10426507.2013.807255

To link to this article: https://doi.org/10.1080/10426507.2013.807255

Published online: 03 Dec 2013.

Phosphorus, Sulfur, and Silicon, 189:198–214, 2014

ISSN: 1042-6507 print / 1563-5325 online
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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF SINGLY, DOUBLY, AND TRIPLY BRIDGED DERIVATIVES OF HEXACHLOROCYCLOTRIPHOSPHAZENE WITH BIS(2-HYDROXYETHYL) ETHER AND 2,2-DIMETHYLPROPANE-1,3-DIOL

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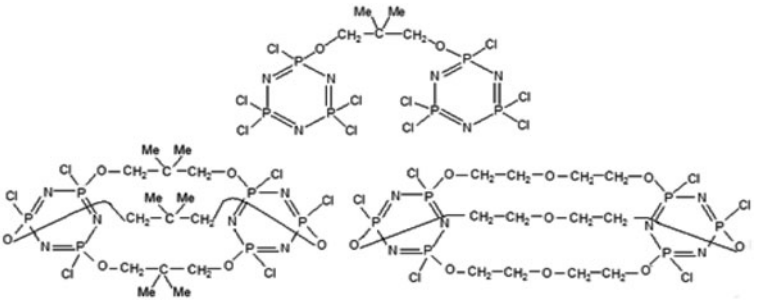
GRAPHICAL ABSTRACT



Abstract *The reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**1**), with 2,2-dimethylpropane-1,3-diol (**2**), and bis(2-hydroxyethyl) ether (**3**) have been previously reported. Although both reactions gave the expected spiro, ansa, and bridged type products, open-chain and triply bridged derivatives from both systems and singly bridged derivatives from 2,2-dimethylpropane-1,3-diol (**2**) were not isolated, and doubly bridged compounds were only detected in trace amounts in both systems. However, in a subsequent reinvestigation in tetrahydrofuran (THF) solution, the reaction of **1** with the diols **2** and **3** gave the open chain compounds $N_3P_3Cl_5[O(CH_2)_2CMe_2OH]$ (**4**) and $N_3P_3Cl_5[(OCH_2CH_2)_2OH]$ (**5**), the singly bridged compound $N_3P_3Cl_5[(OCH_2)_2\text{-}CMe_2]N_3P_3Cl_5$ (**6**), the doubly bridged compounds $N_3P_3Cl_4[(OCH_2)_2CMe_2]_2N_3P_3Cl_4$ (**8**) and $N_3P_3Cl_4[(OCH_2CH_2)_2O]_2N_3P_3Cl_4$ (**9**), and the triply bridged compounds $N_3P_3Cl_3[(OCH_2)_2\text{-}CMe_2]_3N_3P_3Cl_3$ (**10**) and $N_3P_3Cl_3[(OCH_2CH_2)_2O]_3N_3P_3Cl_3$ (**11**).*

Received 31 October 2012; accepted 3 May 2013.

The authors would like to thank the Shin Nisso Co. Ltd. for gifts of $N_3P_3Cl_6$ (**1**), the University College, London, UK, and King's College, London, UK, for NMR measurements, and the School of Pharmacy for mass spectrometric data, all these being carried out by the auspices of the University of London Intercollegiate Research Services. They would like to thank Mr. Don Ship and Dr. H. G. Parkes for obtaining the NMR data. Sedat Ture also would like to thank Prof. Dr. D. B. Davies for his financial support and providing a research placement at UCL during the postdoctoral studies.

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The doubly bridged derivatives were also isolated in better yields relative to earlier reports. The substituted cyclotriphosphazenes have been characterized by elemental analysis, mass spectrometry, as well as by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy. It is found that with variation of the solvent there is a decrease in the product formed by intramolecular reactions (spiro and ansa derivatives) and a concomitant increase in the amount of products formed by intermolecular reactions (singly, doubly, and triply bridged derivatives) of cyclophosphazene.

Keywords Chlorocyclophosphazene; bis(2-hydroxyethyl) ether; 2,2-dimethylpropane-1,3-diol; open-chain; bridged compounds; NMR studies

INTRODUCTION

The nucleophilic substitution reactions of hexachlorocylotriphosphazene, $N_3P_3Cl_6$ (**1**) with difunctional reagents have received a great deal of attention. Reactions particularly of difunctional alcohols and amines with halogenated cyclophosphazenes have been of considerable interest,[1–44] because these reactions may lead to the formation of different types of products: *spiro*, *ansa*, bridged, or open-chain compounds or mixtures thereof. General structures of the possible types of products are presented in Figure 1.

It has been reported that diols like ethane-1,2-, propane-1,3-, and butane-1,4-diol[3,5] react with hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**1**), to give the *spiro* derivatives as the most prevalent products, whereas no doubly and triply bridged derivatives were isolated from these systems.

The formation of phosphazene derivatives depends on many factors such as solvent, base, temperature variation, the dinucleophile, and the size of the cyclophosphazene ring. As observed in earlier investigations, the solvent has a great influence on the type of products formed and on the relative yields of cyclophosphazenes.[1–5,17,18] For example, when we use pyridine as the base in dioxane or diethyl ether solution, reactions of hexachlorocyclotriphosphazene **1** with 2,2-dimethylpropane-1,3-diol predominantly gave the *spiro* derivative (29%) and no *ansa* derivative.[1] On the other hand, when the same reaction was carried out in dichloromethane predominantly the *ansa* derivative was formed (36%).[1] However, in the present study, reactions of **1** with 2,2-dimethylpropane-1,3-diol and bis(2-hydroxyethyl)ether in tetrahydrofuran (THF) solution give both *spiro* (24.5%, 22.7%) and

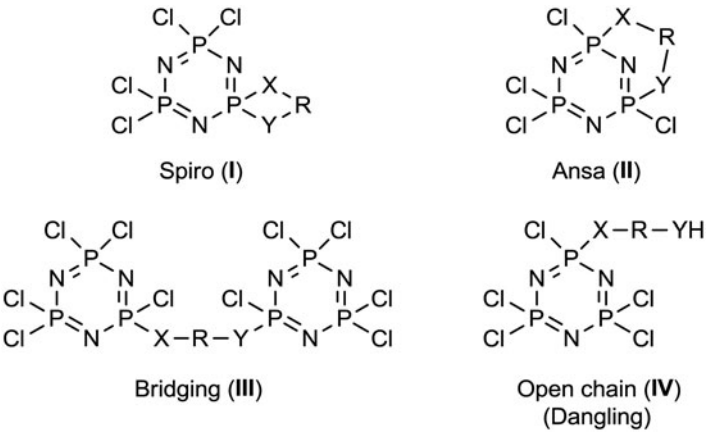
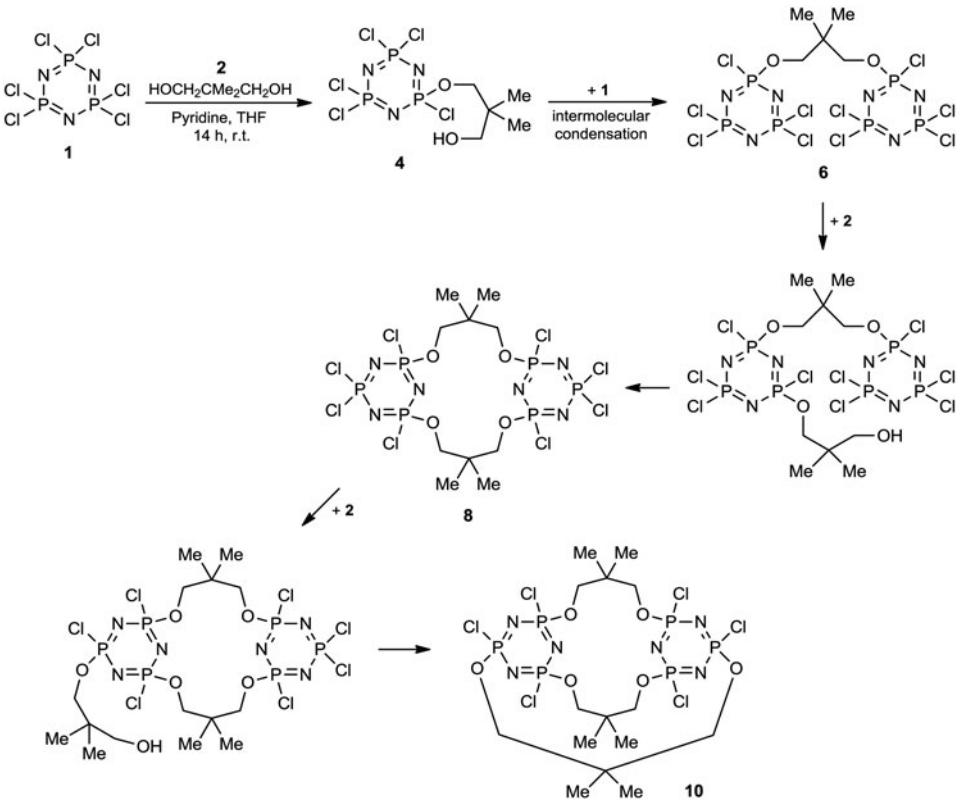


Figure 1 Structures of possible products resulting from the substitution in hexachlorocyclotriphosphazene.

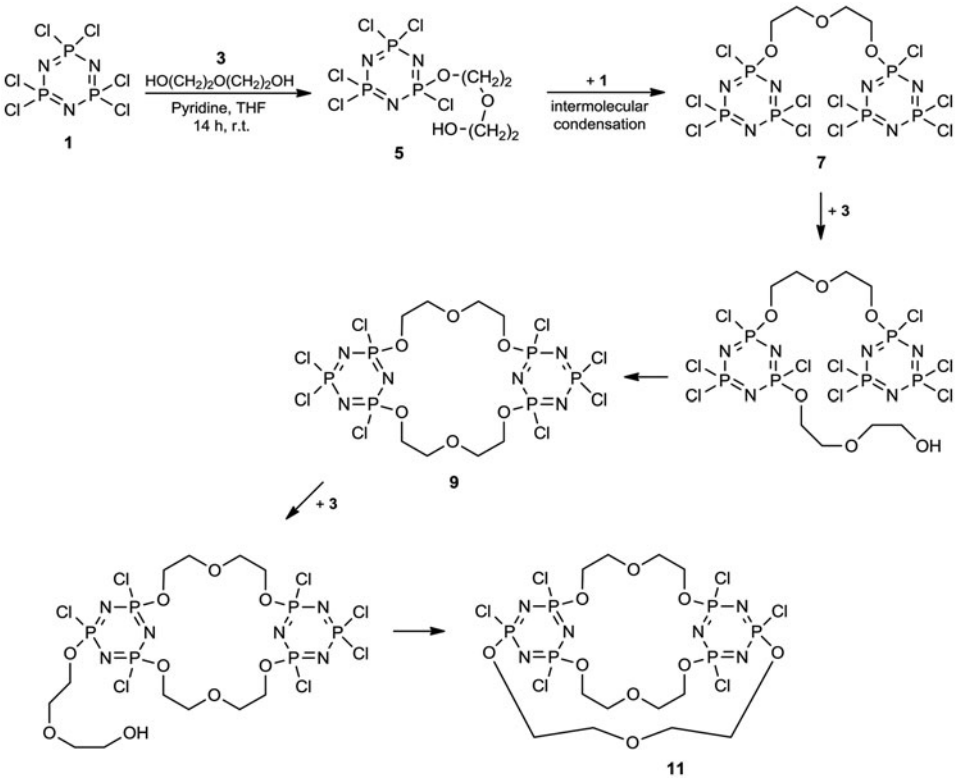
ansa (25.2%, 23.1%) products in considerably lower amounts, together with the open chain (**4**, 9.2%, **5**, 6.9%) and triply bridged (**10**, 8.9%, **11**, 7.7%) derivatives, forming the singly (**6**, 35.4%, **7**, 37.5%) and doubly bridged (**8**, 16.6%, **9**, 15.5%) derivatives in better yields.

Similarly, reaction of cyclotriphosphazene, $N_3P_3Cl_6$ (**1**), with ethane-, 1,3-propane-, and 1,4-butane-diols[3,5] and with amino-alcohols, diamines, and NMe derivatives, in dichloromethane or diethyl ether, showed a preference for the formation of *spiro* derivatives, when the linking $-(CH_2)_n-$ group of the reagent consisted of $n = 2$, 3, and 4 moieties.[39] Similar results were also obtained from the reaction of **1** with 1,4-butane-, 1,5-pentane and 1,6-hexane fluorinated diols.[20,27,30] Bridged compounds were obtained in better yields and assumed significant importance for reaction of **1** with diamines of increasing chain lengths and for the diols having the linking $-(CH_2)_n-$ group with $n = 5$, 6, 8, and 10, respectively.[28]

We have previously reported that the reaction of hexachlorocyclotriphosphazene **1** with 2,2-dimethylpropane-1,3-diol[1] and bis(2-hydroxyethyl) ether[2] leads, in general, to the formation predominantly of *spiro* and *ansa* structures (Schemes 1 and 2). Although doubly bridged derivatives $N_3P_3Cl_4(OCH_2CMe_2CH_2O)_2N_3P_3Cl_4$ and $N_3P_3Cl_4[(OCH_2CH_2)_2O]_2N_3P_3Cl_4$ were obtained from both reactions, these were formed only in trace amounts and the reaction of 2,2-di-methylpropane-1,3-diol did not give also the singly bridged product. We therefore reinvestigated both reactions to examine the



Scheme 1 The reaction of cyclotriphosphazene **1** with 2,2-dimethylpropane-1,3-diol **2**.



Scheme 2 The reaction of cyclotriphosphazene **1** with bis(2-hydroxyethyl) ether **3**.

effects, if any, of the above structural changes of the diol on the type and the quantity of the products produced under different reaction conditions.

RESULTS AND DISCUSSION

From the reaction of 2,2-dimethylpropane-1,3-diol (**2**) and bis(2-hydroxethyl) ether (**3**) with the hexachloride $N_3P_3Cl_6$ (**1**), we isolated a total of 8 compounds. Preliminary reports of these investigations have appeared.[1,2] Here, we report the following new compounds: two open-chain (dangling) derivatives (**4**, 9.2%) and (**5**, 6.9%), one singly bridged derivative (**6**, 35.4%), two doubly bridged derivatives (**8**, 16.6%) and (**9**, 15.5%) as well as two triply bridged derivatives (**10**, 8.9%) and (**11**, 7.7%) (see Schemes 1 and 2).

^{31}P NMR Studies

Structural assignments of the products are mainly based on the respective mass spectrometric (MS) investigations and ^{31}P NMR spectra. All assignments are supported by ^{1}H and ^{13}C NMR spectroscopic and elemental analysis data. It has been found that ^{31}P NMR spectroscopy is a reliable tool for determining molecular structures in cyclophosphazenes. The molecular structures of the compounds have been deduced by comparison of the proton-coupled and proton-decoupled ^{31}P NMR spectra, which enable assignment of phosphorus

Table 1 ^{31}P NMR data for compounds **1**, **4–11**[a]

	δ^{31}P (PCl$_2$)[b]	δ^{31}P (P(OR)Cl)[b]	^2J[P(OR)Cl–PCl$_2$][c]
1	19.9		
4	22.5	15.2	67.2
5	25.1	13.2	66.7
6	24.1	16.2	67.4
7	25.8	23.5	49.3
8	27.4	26.4	57.6
9	25.8	25.1	71.5
10		22.4	
11		22.6	

[a]In CDCl$_3$ (referenced to external 85% H$_3$PO$_4$) at 162.0 MHz (room temperature).
[b]In ppm.
[c]In Hz.

nuclei carrying aliphatic substituents. All ^{31}P NMR data for the respective series of the derivatives (**4** and **5**), (**6** and **7**), (**8** and **9**), and (**10** and **11**) are consistent with the proposed structures; a remarkable similarity of the spectra within the particular series has also been observed.

Except for the triply bridged compounds **10** and **11**, all cyclotriphosphazene derivatives contain both PCl(OR) and PCl$_2$ groups and the ^{31}P NMR spectra are observed as A$_2$X (or A$_2$B) spin systems, which can be readily assigned by consideration of signal intensities, chemical shifts, and coupling patterns. The triply bridged cyclophosphazene derivatives **10** and **11** contain only PCl(OR) groups and the respective ^{31}P NMR spectra consist of a single line. The ^{31}P NMR chemical shifts and the values of the $^2J_{PP}$ coupling constants of the compounds are summarized in Table 1.

In the open-chain compounds **4** and **5**, only one functional group is attached to the phosphorus atom, the other is free. Both types are known in the case of ethane-, propane-1,3-, and butane-1,4- diols.[3–5] The ^{31}P NMR spectra of these compounds are deceptively simple and give rise to an A$_2$B spin system with a downfield position of the triplet signal. The spectra indicate the presence of two phosphorus nuclei in the same environment and with identical chemical shift, different from the third phosphorus nucleus. Proton coupled ^{31}P NMR spectra show that the unchanged doublet signals (A$_2$) arise from the ≡PCl$_2$ groups, whereas the triplet signals feel the coupling to protons, indicating that these signals are associated with the ≡P(OR)Cl moieties. Together with elemental analysis and mass spectrometric data, we assigned them to the dangling derivatives. The yields of these two compounds (**4**, 9.2% and **5**, 6.9%) are comparable with those from propane-1,3-diol (12%) and butane-1,4-diol (11%).[3]

Unlike the bridging compound **3**, where the magnetic interaction between the phosphazene rings is well pronounced giving rise to an ^{31}P NMR spectrum of [A$_2$B]$_2$ type as the result of the special proximity of the two phosphazene rings, in our singly bridged compounds this spin system does not appear due to the relatively large separation between the phosphazene rings, caused by the aliphatic chain. Therefore, the ^{31}P NMR spectra of the singly bridged compounds were found to be similar to those of the open-chain derivatives, and we observed A$_2$B type spectra for compounds **6** and **7**. Thereby, the A$_2$ part is associated with the ≡PCl$_2$ groups and the B part, which is splitted into three lines by the A$_2$ nuclei, is associated with the ≡P(OR)Cl groups. As in the case of the dangling derivatives,

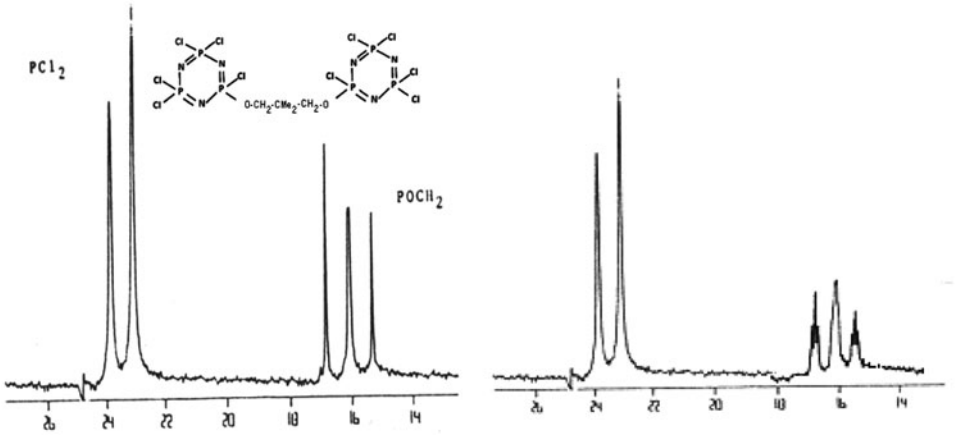


Figure 2 ^{31}P NMR spectra of compound **6**: (a) proton decoupled spectrum, (b) proton coupled spectrum, in $CDCl_3$ at 161.83 MHz, (room temperature), referenced to external 85% H_3PO_4.

proton coupled ^{31}P NMR spectra confirmed the $A_2/{\equiv}PCl_2$ assignment, by leaving the A_2 part (two lines), unaffected. The extra methylene group ($-CH_2-$) in the bridging skeleton does not significantly affect the overall electron release to the phosphazene rings and hence the chemical shifts of the A and B parts. In contrast to the ethane- and propane-1,3-diols[3] here the yield of singly bridged compounds is larger. Proton coupled and decoupled spectra of compound **6** are shown in Figure 2.

The doubly bridged compounds **8** and **9** display A_2B type spectra. The A_2 parts show fine splitting due to proton coupling. The ^{31}P spectra show that in the doubly bridged derivatives the signals of the ${\equiv}PCl_2$ and ${\equiv}PCl(OR)$ units are extremely close. However, the resolution of the spectra is good enough for a distinction between ${\equiv}PCl_2$ and ${\equiv}PCl(OR)$ chemical shifts. Proton coupling experiments as well as comparison with the derivatives of analogous pentane-1,5-, hexane-1,6-, and octane-1,8-diols allow unambiguous assignment of the structures.

It is known that there are two configurational isomers for the doubly bridged compounds from diamino, pentane-, hexane-, and octane-diols.[27,34] There are two different *meso* forms—one has a center of symmetry and the other has a plane of symmetry—which are formed with equal probability as mixture of diastereoisomers. In this case, two sets of closely spaced NMR signals of equal intensity should be expected for the mixture of diastereoisomers (which would indeed result in a doubling of the NMR signals for both the P(OR)Cl and PCl groups). By resemblance, the doubly bridged diol compounds **8** and **9** should also exhibit two configurational isomers. However, as explained above, the ^{31}P NMR spectra of the isolated doubly bridged compounds **8** and **9** display only one set of closely spaced NMR signals, which are shown in Figures 3a–c. Based on the ^{31}P NMR chemical shifts, comparison with data of our and other groups and in conjunction with the ^{1}H NMR data the signals observed can be assigned to the compounds with a doubly bridged structure **8** and **9**.

In the case of the triply bridged compounds **10** and **11**, the ^{31}P NMR spectra are of A_3 type. At low- or high-field strengths, the triply bridged structures give rise to A_3 spin systems, tending to a singlet in the ^{31}P NMR spectrum. The ${\equiv}P(OR)Cl$ groups are in identical environments and linked to similar groups; therefore, single lines are observed at

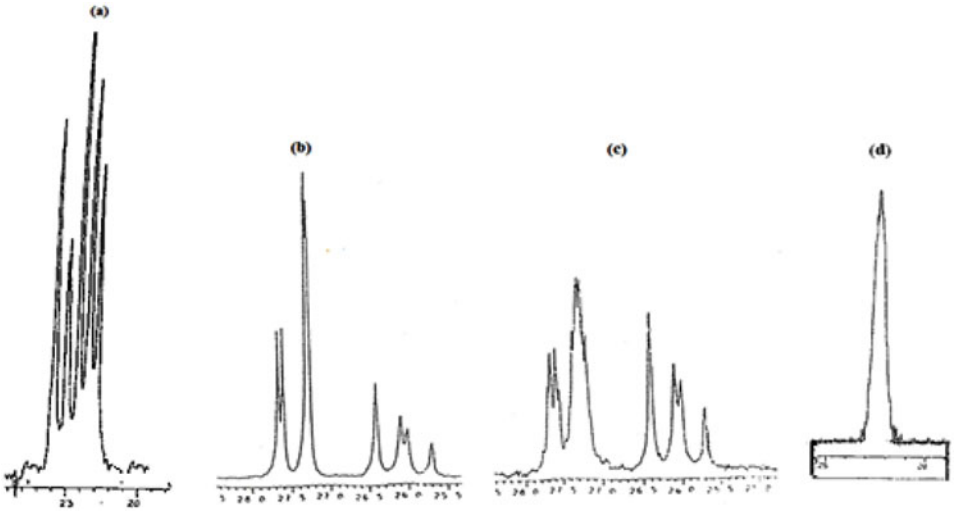


Figure 3 ^{31}P NMR spectra of doubly and triply bridged derivatives: (a) proton decoupled spectrum of compound **9**, (b) proton decoupled and (c) proton coupled spectra of compound **8**, (d) proton decoupled spectrum of compound **11**; all spectra in $CDCl_3$ at 161.83 MHz, (room temperature), referenced to external 85% H_3PO_4.

22.4 and 22.6 ppm for these compounds. ^{31}P NMR spectra of compounds **8**, **9**, and **11** are presented in Figure 3 (see also Table 4).

^{1}H NMR Spectra

^{1}H NMR spectroscopy provides additional information for the structural characterization of the isolated products. The recorded spectra are greatly simplified compared with those of the previously reported diol derivatives.[1–3,42] The OCH_2 protons are by about 0.5 ppm more shielded than those of the corresponding propane-1,3-diol derivatives.[3] The expected small shielding on passing from mono to tris derivatives is observed for the OCH_2 protons and to a lesser extent for the CH_3 protons of the 2,2-dimethylpropane-1,3-diol derivatives. It was shown earlier that alkoxyphosphazenes can show virtual coupling effects.[38,39] The OCH_2 protons of the alkanedioxy groups appeared to be very suitable to demonstrate virtual coupling. It is expected that the bis and tris substituted derivatives show multiplicities arising from virtual coupling by two, respectively, by three, phosphorus nuclei. This was observed for the 1,3-propane- and 1,4-butane-dioxy derivatives,[3] which displayed considerable chemical shift differences between the signals of the $\equiv PCl_2$ and $\equiv P$ *spiro* phosphorus atoms.

The monospiro-2,2-dimethylpropane-1,3-diol and monospiro-bis(2-hydroxyethyl) ether compounds have relatively simple proton NMR spectra with some four bond coupling, $^4J_{PH}$, observable. In a number of these spectra the OCH_2 protons, and where appropriate, the CCH_2 protons were in different chemical environments. Differences in chemical shifts of these methylene protons were only pronounced in the 6-membered phosphate rings,[3] and these proved most useful for structural assignments of the derivatives from pentane-1,5,[42] 2,2-dimethylpropane-1,3-diol (2), and bis(2-hydroxyethyl) ether (3).

The ^{1}H NMR spectra of the bis-spiro derivatives are by far the most complex and also the most interesting. The protons of the OCH_2 and the CCH_2 methylene groups are

nonequivalent due to the fact that they are part of a cyclic moiety, and therefore, the two protons of each methylene group see different environment. Thus, each methylene group displays a spectrum of AB type.

The $POCH_2$ protons for the open-chain (dangling) derivative (**5**) show a doublet of triplets centered at 4.4 ppm. Coupling with the phosphorus nucleus gives rise to a doublet structure, which further splits into two triplets due to coupling with the adjacent methylene protons. For the $POCCH_2$ protons, a symmetrical quintet arising from coupling to the equivalent $POCH_2$ and $POCC{-}O{-}CH_2$ protons would be expected, which would further split into 10 lines by long range $^4J_{PH}$ coupling. However, the signal for the $POCCH_2O$– protons remains unresolved even at higher field (400 MHz spectrometer) and overlaps with the signal of the $POCC{-}O{-}CH_2C$ protons at 3.6 ppm. The $-CH_2$-OH protons would be expected to give a triplet arising from coupling with the $C{-}CH_2$-C protons, and this triplet would further split into doublets due to coupling with −OH proton. The ^{1}H NMR spectrum of this compound was obtained at 400 MHz and we only observed a triplet structure.

In the case of the singly bridged derivative, the number of protons in each environment would be equal, giving rise to similar intensity and integration to be observed. The $POCH_2$ protons are equivalent and give rise to a six line pattern located at 4.0 ppm, three lines from coupling with the adjacent CCH_2 protons and further splitting into six lines from coupling with the phosphorus nucleus. When selective decoupling with the $POCCH_2$ proton frequency was applied the $POCH_2$ multiplet was reduced to a doublet. The $POCCH_2$ protons in compound **7** show also a six-line multiplet centered at 3.7 ppm arising from coupling with the magnetically and chemically equivalent neighboring $POCH_2$ protons.

The proton NMR spectrum of the doubly bridged derivative **8** exhibits two complex signals in the upfield region of the spectrum. Two similar multiplets for the OCH_2 protons were observed at 4.3 and 3.9 ppm, respectively, which indicate the presence of two types of methylene protons having different chemical environments. It demonstrates that between two phosphazene rings four of the eight bridging protons facing each other are equivalent and the other four pointing out in the opposite directions are also identical but different from the former. The protons facing each other (inner) are likely to be more shielded as compared with the protons pointing to opposite directions (outer) so the outer protons are expected at lower field than the inner protons. Nonequivalence of these OCH_2 protons would give rise to an AB spectrum with each line being split into three by coupling to two adjacent equivalent phosphorus nuclei leading to a spectrum with 12 lines. Further ^{1}H NMR spectra were recorded at different temperatures and show that only the multiplet at 4.3 ppm is affected by temperature, whereas the outer multiplet remains relatively unchanged. This explains the presence of two different types of protons as indicated above. Temperature effect is obvious on the multiplet at lower field. It seems reasonable to suggest that temperature affects the outer protons, not the inner protons. The effect is more pronounced at temperatures between −50 and +80°C. The ^{1}H NMR spectrum of compound **8** is presented in Figure 4.

The ^{1}H NMR signals of the methyl groups of this series were observed either as a sharp singlet or as two singlets depending on their chemical environment. The methyl groups of the monospiro compound exhibit only one singlet due to their identical environment, whereas the dispiro and doubly bridged derivatives display two distinct singlets for the CH_3 protons, showing that the methyl groups are not identical. The singly (**7**), doubly (**9**), and triply bridged (**11**) derivatives show remarkable similarity in the OCH_2 and $COCH_2$ chemical shifts. The ^{1}H NMR spectra of the bis(2-hydroxyethyl) ether derivatives were very complex, and no analysis to evaluate the $^3J_{PH}$ coupling constants was attempted. Chemical shift and values of $^3J_{PH}$ are presented in Tables 2 and 3.

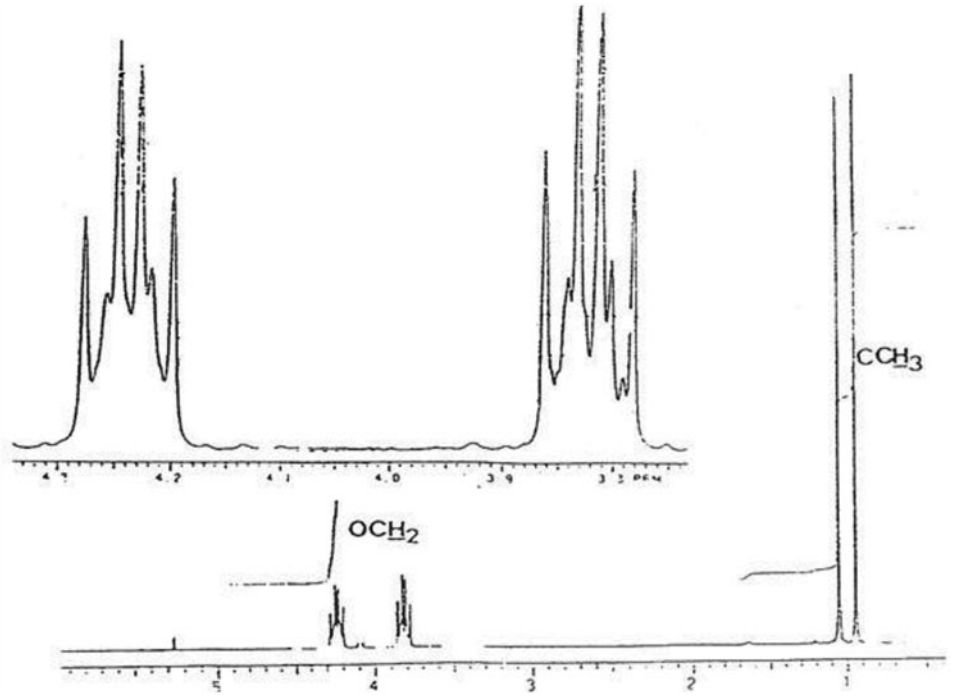


Figure 4 ^{1}H NMR spectrum of compound **8** in $CDCl_3$ at 399.95 MHz and at room temperature, TMS was used as internal reference.

^{13}C NMR Spectra

In general, three environments are observed for the carbon atoms in the 2,2-dimethylpropane-1,3-diol derivatives, except for the *spiro-ansa* compound, where separate carbon resonances are observed for the *spiro* and *ansa* moieties.

The ^{13}C NMR spectra of the open-chain (dangling) derivatives show four different chemical environments in the case of the bis(2-hydroxyethyl) ether derivative. The doublets at low field are observed at around 73.2 and 68.1 ppm corresponding to the α and β methylene carbon atoms, which are attached to the phosphazene ring through the dioxy linkage. Coupling of phosphorus with the other methylene carbon atoms (CCOCC) is not observed.

The ^{13}C NMR signal of the $POCH_2$ moiety splits to a doublet in the case of the monospiro compound due to coupling with the phosphorus nucleus. Virtual coupling effects are observed for the ^{13}C nuclei in $POCH_2$ of the bis-spiro compounds resulting in a triplet structure of the ^{13}C NMR signal. The $POCH_2$ spectrum of the *spiro-ansa* compound also shows virtual coupling for the *ansa* ring. The signal showing a triplet structure is assigned to the α methylene carbon atom in the *ansa* ring and the two doublets, which are observed at 76.0 and 74.5 ppm, belong to the *spiro* ring.

Doublets are also observed for the quarterly carbon atoms ($POCH_2C$) of the mono*spiro* and the *spiro* ring of the *spiro-ansa* compounds due to coupling with the phosphorus nucleus. The signals of the carbon atoms in the POCC fragments of the bis-*spiro* and *ansa* ring of the *spiro-ansa* compound give rise to triplets due to virtual coupling.

Table 2 Selected ^{1}H NMR data for compounds **4–11**[a]

	δ (P–OCH_2-)[b]	δ (C–CH_3)[b]	δ (O–CH$_2$CH_2-)[b]	$^3J_{PH}$[c]
4	4.1	1.3		12.6
5	4.4		3.3	10.8
6	4.3	1.2		9.9
	3.9	1.1		7.4
7	4.0		3.7	9.5
8	4.3	1.2		7.8
	3.9	1.0		8.8
9	4.2		3.7	
10	4.0	1.1		8.6
	4.0	1.1		10.0
11	4.2		3.9	

[a]In $CDCl_3$ (TMS internal reference), at 199.5 and 399.95 MHz (room temperature).
[b]In ppm.
[c]In Hz.

The ^{13}C NMR signals of the two methyl groups appear as two sharp singlets in the case of the bis-*spiro* and *ansa* part of the *spiro-ansa* compounds, since these groups are not in identical chemical environments, whereas the absorptions for the same nuclei in the mono-*spiro* and *spiro* ring of the *spiro-ansa* compounds give rise to single lines owing to the identity of the methyl group environments in these molecules.

In the case of the doubly (**8**) and triply bridged (**10**) compounds the expected triplets for the ^{13}C nuclei in the $POCH_2$ groups are observed. These triplets are arising from the virtual coupling with two chemically equivalent phosphorus nuclei. Also the signals of the central carbon atoms are expected to give quintets, since these nuclei are linked to four equivalent phosphorus atoms. Coupling over two bonds to the phosphorus nuclei is likely, though the interaction over three bonds according to the Karplus[7,8] relationship might reduce the couplings so to be nonobservable. The ^{13}C absorption of the POCC nuclei was observed as single lines. However, the resolution enhanced spectrum at the same field strength displayed a five-line spectrum for these nuclei. 13C NMR spectra of the double-bridged derivative (8) are presented in Figure 5.

The ^{13}C NMR chemical shifts of the ethylene carbon atoms adjacent to the oxygen atoms are deshielded relative to the chemical shifts of (OC-C-C) carbon atoms. The deshielding is more pronounced for the $POCH_2$ carbon atoms than for the $POCH_2$-CCOH carbon atoms depending on the neighboring atom or group to which it is attached. In the case of the CH_2-OH groups, however, the deshielding is limited to the effect of the oxygen atom. When we consider the ^{13}C NMR data of the cyclic derivatives, marginal differences in chemical shift values are observed. The chemical shift values for the $POCH_2$ carbon atom are slightly increased by adding an extra methylene group to the aliphatic chain or aliphatic bridge of the diol moiety. Similar applies for the chemical shifts of CH_2-CH_2OH carbon atoms. However, a decrease in the chemical shift value of POCC is observed for the dangling and bridge derivatives.

It has been reported[40,41] that the values of the three-bond coupling constants ^3J(PXCC) (X = NH or O) are depended on many factors such as the P—N (or P—O) bond length, the hybridization of the nitrogen atom, as well as the dihedral angle PXCC of the compounds. Crystallographic data of six- and seven-membered *spiro* ring of compounds

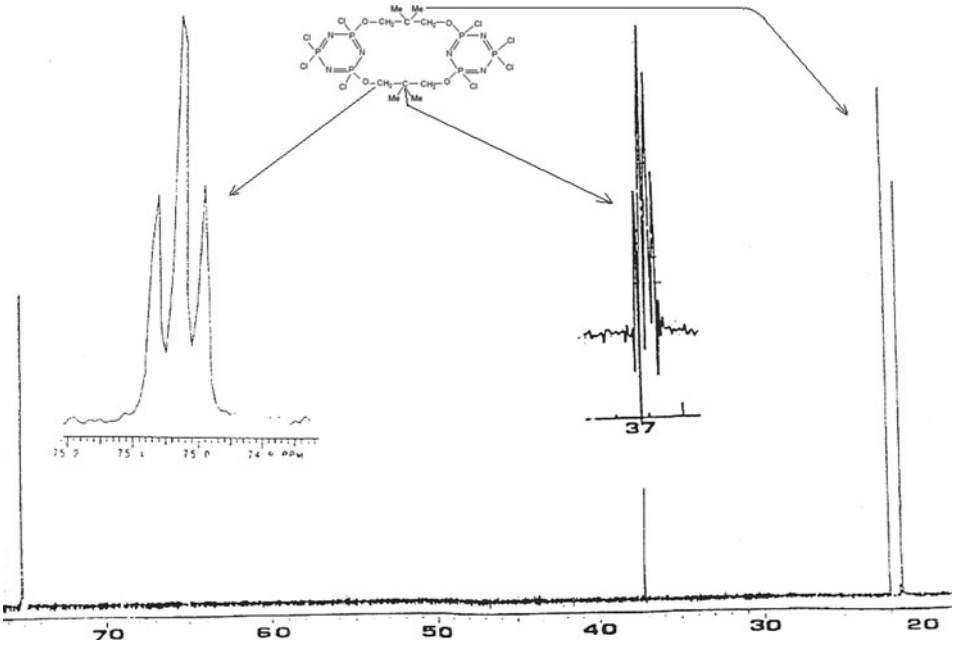


Figure 5 ^{13}C NMR spectrum (50.1 MHz) of compound **8** at room temperature, in $CDCl_3$.

$N_3P_3Cl_4[O(CH_2)_3O]$ and $N_3P_3Cl_4[O(CH_2)_4O]$ are available.[36–38] In the seven-membered systems, the ^{13}C chemical shifts of the PXCC moieties were slightly different from those in the six-membered ring systems. The three-bond coupling constants ^3J(POCC) display much larger differences than the chemical shifts. Comparing six- and seven-membered *spiro* rings the values of ^3J(POCC) for the seven-membered rings are around zero, whereas for the six-membered rings the corresponding values are approximately 6.4 Hz. The crystal structure of $N_3P_3Cl_4[O(CH_2)_4O]$ has revealed that the POCC dihedral angles are near 90°.[36] Therefore, the value of ^3J(POCC) is anticipated to be zero or near to zero Hz according to the Karplus relationship.[7,8]

The coupling constants ^2J(POC) and ^3J(POCC) are similar in both the dangling and bridge structures; the extra methylene group (–CH_2-) has not much effect on the coupling constants. Relevant ^{13}C NMR chemical shifts and coupling constants are presented in Table 3.Table 4 Table 5

EXPERIMENTAL

Materials

Reagent grade solvents were used throughout this work: THF, benzene, light petroleum (bp 40–60°C), anhydrous diethyl ether (May and Baker Ltd., London), 1,4-dioxane (Fisons Scientific Apparatus, London), deuterated solvents for NMR spectroscopy, 2,2-dimethylpropane-1,3-diol, and bis(2-hydroxyethyl)ether (Aldrich Chem. Co. Ltd., Gillingham, England), pyridine, dichloromethane (B.D.H. Chemical Co. Ltd., East Yorkshire, England), hexachlorocyclotriphosphazene (Shin Nisso Kako Co. Ltd., Tokyo). Solvents were dried by conventional methods.

Table 3 Selected ^{13}C NMR data for compounds **4–11** (50.1 MHz, in $CDCl_3$, referred to internal TMS, room temperature, coupling constants J in Hz)

	$\delta(POCH_2)$	$\delta(POCH_2C)$	$\delta(CH_3)$	$^2J(POCH_2)$	$^3J(POCC)$
4	75.6	31.5	22.4	6.9	5.8
5	73.2	60.1		0.0	7.9
6	76.8	32.1	21.9	7.0	5.8
			21.0		
7	71.0	69.0		0.0	7.3
8	75.0	37.1	21.9	6.9	5.7
			21.2		
9	70.5	69.5		0.0	9.6
10	75.0	32.9	21.9	6.6	5.5
			21.7		
11	68.2	65.2		0.0	6.2

Methods

All reactions were monitored by using Kieselgel 60° 254 (silica gel) precoated TLC plates and sprayed with ninhydridine (0.5% w/v) in butanol solution, and developed at approximately 130°C. Separations of products were carried out by flash column chromatography using Kieselgel 60. Melting points were determined with a Reichart–Kofler micro heating stage and a Mettler FB 82 hot stage connected to an FP 800 central processor both fitted using a polarizing microscope. ^1H NMR spectra were recorded using a JEOL FX-200 spectrometer operating at 199.5 MHz, a Bruker WH 250 spectrometer operating at 250.48 MHz (King's College, London) and a Varian XL-400 spectrometer operating at 399.5 MHz (King's College, London). Samples were dissolved in $CDCl_3$ and placed in 5-mm NMR tubes. Measurements were carried out using $CDCl_3$ lock, tetramethylsilane (TMS) as internal reference and sample concentrations of 15–20 mg cm^3. ^{31}P NMR spectra were recorded using a Varian XL-200 spectrometer operating at 80.96 MHz (King's College London) and a Varian 400 spectrometer operating at 162.0 MHz (King's College, London); 85% H_3PO_4 was used as external reference. ^{13}C NMR spectra were recorded using a JEOL FX-200 spectrometer operating at 50.10 MHz and a Varian VXR 400 spectrometer operating at 100.577 MHz (King's College, London). TMS was used as internal reference. The mass spectra were recorded using a VG 7070 H mass spectrometer with Finingan INCOS Data System at King's College, London, and a VG 2AB IF mass spectrometer at the School of Pharmacy. Microanalyses were carried out by King's College, London microanalytic service.

Reaction of Trichlorocyclotriphosphazene $N_3P_3Cl_6$ (1) with 2,3-Dimethylpropane-1,3-diol, $[(HOCH_2)_2\text{-}CMe_2]$

One Equivalent of Compound 2. $N_3P_3Cl_6$ (**1**) (9 g, 25.86 mmol) and 2,2-dimethylpropane-1,3-diol (2.7 g, 25.92 mmol) were placed in 150 mL of dry THF in a 300-mL three-necked round-bottom flask, and the solution was stirred at room temperature for 2 h. The reaction mixture was cooled in an ice-bath and anhydrous pyridine (4.1 g, 51.83 mmol) in 30 mL of dry THF was added dropwise as hydrogen chloride acceptor. The solution was heated for 14 h under reflux. The course of the reaction was followed by TLC with silica gel plates using benzene/dichloromethane (1:5). Heating was stopped and

Table 4 Comparison of ^{31}P NMR data (80.95, 162.0, and 202.38 MHz) for singly, doubly, and triply bridged derivatives of cyclotriphosphazene **1** with relative diols (in $CDCl_3$, referred to external 85% H_3PO_4, at room temperature)

Compound	Type[a]	$\delta(PCl_2)$[b]	$\delta(P(OR)Cl)$[b]	$^2J_{PNP}$[c]	Ref.
$N_3P_3Cl_5[OCH_2C(Me)_2CH_2OH]$	Open-chain	22.5	15.2	67.2	4
$N_3P_3Cl_5[OCH_2C(Me)_2CH_2O]N_3P_3Cl_5$	Singly bridged	24.6	8.1	63.5	6
$N_3P_3Cl_4[OCH_2C(Me)_2CH_2O]_2N_3P_3Cl_4$	Doubly bridged	26.4	27.5	57.6	8
$N_3P_3Cl_3[OCH_2C(Me)_2CH_2O]_3N_3P_3Cl_3$	Triply bridged		25.2		10
$N_3P_3Cl_5[(OCH_2CH_2)_2OH]$	Open chain	25.1	13.2	66.7	5
$N_3P_3Cl_5[(OCH_2CH_2)_2O]N_3P_3Cl_5$	Singly bridged	23.5	25.8	49.3	7
$N_3P_3Cl_4[(OCH_2CH_2)_2O]_2N_3P_3Cl_4$	Doubly bridged	25.8	26.1	61.8	9
$N_3P_3Cl_3[(OCH_2CH_2)_2O]_3N_3P_3Cl_3$	Triply bridged		24.6		11
$N_3P_3Cl_5[O(CH_2)_3OH]$	Open-chain	23.5	16.1	61.7	3
$N_3P_3Cl_5[O(CH_2)_4OH]$	Open-chain	23.5	15.9	62.1	3
$N_3P_3Cl_5[O(CH_2)_3O]N_3P_3Cl_5$	Singly bridged	23.4	16.0	63.0	3
$N_3P_3Cl_5[O(CH_2)_4O]N_3P_3Cl_5$	Singly bridged	23.5	15.9	61.9	3
$N_3P_3Cl_5[OCH_2(CF_2)_4CH_2O]N_3P_3Cl_5$	Singly bridged	23.8	17.6	65.2	17
$N_3P_3Cl_4[OCH_2(CF_2)_4CH_2O]_2N_3P_3Cl_4$-*anti*	Doubly bridged	26.0	20.4	67.3	17
$N_3P_3Cl_4[OCH_2(CF_2)_4CH_2O]_2N_3P_3Cl_4$-*syn*	Doubly bridged	26.1	20.4	67.7	17
$N_3P_3Cl_3[OCH_2(CF_2)_4CH_2O]_3N_3P_3Cl_3$	Triply bridged		23.1		17
$N_3P_3Cl_5[O(CH_2)_5O]N_3P_3Cl_5$	Singly bridged	22.6	15.0	62.2	23
$N_3P_3Cl_4[O(CH_2)_5O]_2N_3P_3Cl_4$-*anti*	Doubly bridged	24.4	18.3	65.5	23
$N_3P_3Cl_4[O(CH_2)_5O]_2N_3P_3Cl_4$-*syn*	Doubly bridged	24.5	18.2	65.9	23
$N_3P_3Cl_3[O(CH_2)_5O]_3N_3P_3Cl_3$	Triply bridged		21.2		23
$N_3P_3Cl_5[O(CH_2)_6OH]N_3P_3Cl_5$	Open-chain	23.9	15.5	61.8	Unpubl.
$N_3P_3Cl_5[O(CH_2)_6O]N_3P_3Cl_5$	Singly bridged	23.7	16.1	62.1	23
$N_3P_3Cl_4[O(CH_2)_6O]_2N_3P_3Cl_4$-*anti*	Doubly bridged	26.0	19.4	67.0	23
$N_3P_3Cl_4[O(CH_2)_6O]_2N_3P_3Cl_4$-*syn*	Doubly bridged	26.0	19.3	67.5	23
$N_3P_3Cl_3[O(CH_2)_6O]_3N_3P_3Cl_3$	Triply bridged		22.1		23
$N_3P_3Cl_5[O(CH_2)_8O]N_3P_3Cl_5$	Singly bridged	23.6	16.2	62.1	23
$N_3P_3Cl_4[O(CH_2)_8O]_2N_3P_3Cl_4$-*anti*	Doubly bridged	25.9	19.3	66.9	23
$N_3P_3Cl_4[O(CH_2)_8O]_2N_3P_3Cl_4$-*syn*	Doubly bridged	25.9	19.3	67.3	23
$N_3P_3Cl_3[O(CH_2)_8O]_3N_3P_3Cl_3$	Triply bridged		22.3		23
$N_3P_3Cl_5[O(CH_2)_{10}O]N_3P_3Cl_5$	Singly bridged	22.3	14.8	62.2	23
$N_3P_3Cl_4[O(CH_2)_{10}O]_2N_3P_3Cl_4$-*anti*	Doubly bridged	24.7	18.2	67.1	23
$N_3P_3Cl_4[O(CH_2)_{10}O]_2N_3P_3Cl_4$-*syn*	Doubly bridged	24.8	18.2	67.2	23
$N_3P_3Cl_3[O(CH_2)_{10}O]_3N_3P_3Cl_3$	Triply bridged		21.3		23

the apparatus was cooled to room temperature. Then the bulk of the pyridine hydrochloride was filtered off and the remaining was removed by column chromatography using a mixture of CH_2Cl_2/Et_2O (3:1). For the separation of the individual phosphazenes the mixture was rechromatographed using benzene/dichloromethane (1:5) as eluent. Four main phosphazene fractions were obtained: (i) mono-*spiro* derivative (20.1%), (ii) mono-*ansa* (25.2%), (iii) bis-*spiro* (11.6%),[1] and (iv) the doubly bridged derivative $N_3P_3Cl_4[(OCH_2)_2$-$CMe_2]_2N_3P_3Cl_4$ (**8**), which was recrystallized from benzene containing a few drops of light petroleum (bp 40–60°C), mp 178–179°C, yield 0.63 g (16.6%). Found: C, 15.83; H, 2.7; N, 11.1%; M^+, 754. $C_{10}H_{20}O_4N_6P_6Cl_8$ requires C, 15.85; H, 2.7; N, 11.1%; M, 754). ^1H NMR ($CDCl_3$): $\delta = 4.3$ (d, $^3J_{PH} = 7.8$ Hz, 2H, $POCH_2$), 3.9 (d, $^3J_{PH} = 8.8$ Hz, 2H, $POCH_2$), 1.2 (s, 3H, CH_3), 1.0 (s, 3H, CH_3). ^{31}P NMR ($CDCl_3$): $\delta = 27.4$ (PCl_2), 26.4 (P_{spiro}), $^2J_{PP} = 57.6$ Hz. ^{13}C NMR ($CDCl_3$): $\delta = 74.9$ (d, $^2J_{PC} = 6.9$ Hz, PO*C*), 37.1 (d, $^3J_{PC} = 5.7$ Hz, POC*C*), 21.9 (s, *C*H_3), 21.2 (s, CH_3).

Table 5 Quantitative comparison of the relative proportions (%) of *spiro*, *ansa*, and bridged derivatives of cyclotriphosphazene **1** with diols

Compound	2,2-Dimethylpropane-1,3-diols				Bis(2-hydroxethyl) ether		
Mono-*spiro*		29[a]	24.5[b]	20.1[c]		27.5[b]	22.7[c]
Bis-*spiro*		25[a]	14.1[b]	11.6[c]		15[b]	10.8[c]
Tris-*spiro*		20[a]	—	7.3[c]		20.7[b]	8.2[c]
Mono-*ansa*		—	36.2[b]	25.2[c]		34.5[b]	23.1[c]
Spiro-*ansa*		8[a]	17.1[b]	6.8[c]		16.7[b]	9.3[c]
Open-chain		—	—	9.2[c]		—	6.9[c]
Singly bridged		—	—	35.4[c]		43.5[b]	37.5[c]
Doubly bridged		10[a]	6.3[b]	16.6[c]		trace[b]	15.5[c]
Triply bridged		—	—	8.9[c]		—	7.7[c]
Compound	1,2-diol[d]	1,3-diol[d]	1,4-diol[d]	1,5-diol[e]	1,6-diol[e]	1,8-diol[e]	1,10-diol[e]
Mono-*spiro*	25	41	35	22.9	Obsd. by NMR	Obsd. by NMR	
Bis-*spiro*	15	58	38	20.8			
Tris-*spiro*	20	45	25				
Mono-*ansa*	—	4	25	10	3	2	
Spiro-*ansa*	—	1	21				
Open-chain	—	12	11				
Singly bridged	—	18	32	14.2	1	4	Obsr. by NMR
Doubly bridged				43 *syn*+*anti*	*syn* 30, *anti* 20	58 *syn*+*anti*	50 *syn*+*anti*
Triply bridged				7.8	Obsd. by NMR	2	Obsd. by NMR
Compound	Tetraflorobutane-1,4-diol[f]			Hexafloropentane-1,5-diol[g]			Octoflorohexane-1,6-diol[h]
Mono-*spiro*	51			10			—
Bis-*spiro*	13			4			—
Tris-*spiro*	—			1			—
Mono-*ansa*	25			18			21
Spiro-*ansa*	7			3			—
Open-chain							
Singly bridged							27
Doubly bridged							4 *syn*; 9 *anti*
Triply bridged							2

[a]In dioxane (at room temp.).
[b]In dichloromethane (reflux).
[c]In THF(reflux).
[d][Ref. 3, in dichloromethane, at room temp.].
[e][Ref. 23, in THF, at room temp.].
[f][Ref. 20, in THF, at room temp.].
[g][Ref. 27, in THF, at room temp.].
[h][Ref. 30, in THF, at room temp.].

Three Equivalents of Compound 2. The same procedure as described above was applied; refluxing time was 14 h. One known and three new products were separated by column chromatography using a mixture of dichloromethane/diethyl ether (3:1) as eluent. Products were recrystallized from benzene containing a few drops of light petroleum (bp 40–60°C). The first phosphazene derivative was identified as the open-chain compound **4**: mp 159°C, yield 0.33 g (9.2%). Found: C, 14.55; H, 2.70, N; 10.21%; M^+, 413. $C_5H_{11}O_2N_3P_3Cl_5$ requires C, 14.52; H, 2.66; N, 10.16%; M, 413. ^{1}H NMR ($CDCl_3$): $\delta =$ 4.13 (d, $^3J_{PH} = 12.6$ Hz, $POCH_2$), 1.3 (s, 3H, CH_3). ^{31}P NMR ($CDCl_3$): $\delta = 22.5$ (PCl_2),

15.2 (P(OR)Cl), $^2J_{PP}$ = 67.2 Hz. ^{13}C NMR ($CDCl_3$): δ = 75.6 (d, $^2J_{PC}$ = 6.9 Hz, PO*C*), 31.5 (d, $^3J_{PC}$ = 5.8 Hz, POCC), 22.4 (s, CH_3), 21.9 (s, CH_3).

The singly bridged compound **6** was obtained as an oily product, yield 1.6 g (35.4%). Found: C, 8.35; H, 1.39; N, 11.66%; M^+, 722. $C_5H_{10}O_2N_6P_6Cl_{10}$ requires C, 8.31; H, 1.38; N, 11.63%; M, 722. ^{1}H NMR ($CDCl_3$): δ = 4.3 (d, $^3J_{PH}$ = 9.9 Hz, 2H, $POCH_2$), 3.9 (d, $^3J_{PH}$ = 7.4 Hz, 2H, $POCH_2$), 1.2 (s, 3H, CH_3), 1.1 (s, 3H, CH_3). ^{31}P NMR ($CDCl_3$): δ = 24.1 (PCl_2), 16.2 (P(OR)Cl), $^2J_{PP}$ = 67.4 Hz. ^{13}C NMR ($CDCl_3$): δ = 76.8 (d, $^2J_{PC}$ = 7.0 Hz, POC), 32.1 (d, $^3J_{PC}$ = 5.8 Hz, POCC), 21.9 (s, CH_3), 21.1 (s, CH_3).

The *spiro-ansa* compound (6.8%) was identified by comparison with literature.[1]

The triply bridged compound **10**: mp 187°C, yield 0.28 g (8.9%). Found: C, 23.0; H, 3.87; N, 10.51%; M^+, 786. $C_{15}H_{30}O_6N_6P_6Cl_6$ requires C, 22.90: H, 3.81; N, 10.43%; M, 786. ^{1}H NMR ($CDCl_3$): δ = 4.3 (d, $^3J_{PH}$ = 8.6 Hz, 2H, $POCH_2$), 4.0 (d, $^3J_{PH}$ = 10.0 Hz, 2H, $POCH_2$), 1.2 (s, CH_3), 1.0 (s, CH_3). ^{31}P NMR ($CDCl_3$): δ = 22.4 (P(OR)Cl). ^{13}C NMR ($CDCl_3$): δ = : 75.0 (d, $^2J_{PC}$ = 6.6 Hz, PO*C*), 32.9 (d, $^3J_{PC}$ = 5.5 Hz, POC*C*), 21.9 (s, CH_3), 21.7 (s, CH_3).

Reaction of Compound 1 with Bis(2-hydroxyethyl) Ether (2)

One Equivalent of Compound 2. The hexachloride $N_3P_3Cl_6$ (4 g, 11.49 mmol) and liquid bis(2-hydroxyethyl) ether (1.21 g, 11.41 mmol) were dissolved in 150 mL of dry THF in a 250-mL three-necked round-bottom flask. The reaction mixture was cooled in an ice-bath and to this solution pyridine (1.8 g, 22.75 mmol) in 30 mL of dry THF was added dropwise while stirring. The reaction mixture was then allowed to reflux for 10 h. The bulk of the pyridine hydrochloride and other insoluble materials were filtered off approximately 14 h after the start of the reaction. The course of the reaction was followed by TLC with silica gel plates using dichloromethane/benzene (6:1) showing one new product and two previously reported products. The solvent was removed at reduced pressure and the resulting colorless oil was subjected to column chromatography using dichloromethane/benzene (6:1) as the mobile phase. The first product was the *mono-spiro* derivative (22.7%).[2] The second product was the singly bridged compound **7**, isolated as an oil, yield: 1.2 g (37.5%). Found: C, 6.76; H, 1.16; N, 11.63%; M^+, 724. $C_4H_8O_3N_6P_6Cl_{10}$ requires C, 6.71; H, 1.10; N, 11.61%; M, 724. ^{1}H NMR ($CDCl_3$): δ = 4.0 (d, $^3J_{PH}$ = 9.5 Hz, 2H, $POCH_2$), 3.7 (s, 2H, $OCCH_2$). ^{31}P NMR ($CDCl_3$): δ = 25.8 (PCl_2), 23.5 (P(OR)Cl), $^2J_{PP}$ = 49.3 Hz. ^{13}C NMR (CDCl3): δ = 71.0 (s, POC), 69.0 (d, $^3J_{PC}$ = 7.3 Hz, POC*C*). The third product was the mono-*ansa* derivative (23.1%).[2]

Three Equivalents of Compound 2. The reaction was carried out as described above, refluxing time was 14 h. Two new and three previously reported phosphazene derivatives were separated by column chromatography using a mixture of dichloromethane/hexane (3: 1) as eluent.

The open-chain compound **5**: mp 133–134°C, yield: 0.32 g (6.9%). Found: C, 11.55; H, 2.13; N, 10.17%; M^+, 415. $C_4H_9O_3N_3P_3Cl_5$ requires C, 11.56; H, 2.16; N, 10.12%; M, 415. ^{1}H NMR ($CDCl_3$): δ = 4.4 (d, $^3J_{PH}$ = 10.8 Hz, 2H, $POCH_2$), 3.3 (s, 2H, $OCCH_2$). ^{31}P NMR ($CDCl_3$): δ = 25.1 (PCl_2), 13.2 (P(OR)Cl), $^2J_{PP}$ = 66.7 Hz. ^{13}C NMR ($CDCl_3$): δ = 73.2 (s, POC), 69.1 (d, $^3J_{PC}$ = 7.9 Hz, POCC).

The bis-*spiro* compound (10.8%) and the spiro-*ansa* compound (9.3%) were identified according to the literature.[2]

The doubly bridged derivative **9**: mp 156.5°C, yield: 0.39 (15.5%). Found: C, 12.61; H, 2.14; N, 11.01%; M^+, 758. $C_8H_{16}O_6N_3P_3Cl_8$ requires C, 12.66; H, 2.11; N, 11.08%; M,

758. ^{1}H NMR ($CDCl_3$): $\delta = 4.2$ (2H, $POCH_2$), 3.7 (2H, $OCCH_2$). ^{31}P NMR ($CDCl_3$): $\delta =$ 25.8 (PCl_2), 25.1 (P(OR)Cl), $^{2}J_{PP} = 71.5$ Hz. ^{13}C NMR ($CDCl_3$): $\delta = 70.5$ (s, POC), 69.5 (d, $^{3}J_{PC} = 6.6$ Hz, POCC).

The triply bridged derivative **11**: mp 179°C, yield: 0.36 g (7.7%). Found: C, 18.13; H, 3.23; N, 10.6%; M^+, 792. $C_{12}H_{24}O_9N_3P_3Cl_6$ requires C, 18.18; H, 3.30; N, 10.6%; M, 792. Note: Products were recrystallized from the minimum quantity of benzene by adding few drops of light petroleum (bp 40–60°C). ^{1}H NMR ($CDCl_3$): $\delta = 4.2$ (2H, $POCH_2$), 3.9 (s, 2H, $OCCH_2$). ^{31}P NMR ($CDCl_3$): $\delta = 22.6$ (P(OR)Cl). ^{13}C NMR ($CDCl_3$): $\delta = 68.2$ (s, POC), 65.2 (d, $^{3}J_{PC} = 6.2$ Hz, POCC) (Table 5).

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