PHOSPHORUS–NITROGEN COMPOUNDS. PART 58.[1] THE REACTIONS OF HEXACHLOROCYCLOTRIPHOSPHAZATRIENE WITH ETHANE–, 1,3-PROPANE– AND 1,4-BUTANE–DIOLS. SPIRO, ANSA, BRIDGED AND DANGLING DERIVATIVES AND THEIR ^{31}P AND ^{1}H NUCLEAR MAGNETIC RESONANCE SPECTRA‡

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Abstract–The reactions of hexachlorocyclotriphosphazatriene with ethane–, 1,3-propane– and 1,4-butanediols give the following derivatives: (1) spiro $N_3P_3[O(CH_2)_nO]_xCl_{6-2x}$ (x = 1,2 and 3; n = 2,3 and 4), ansa $N_3P_3[O(CH_2)_3O]Cl_4$, spiro-ansa $N_3P_3[O(CH_2)_3O]_2Cl_2$, bridged $N_3P_3Cl_5[O(CH_2)_nO]N_3P_3Cl_5$ (n = 3 and 4) and dangling $N_3P_3[O(CH_2)_nOH]Cl_5$ (n = 3 and 4). The ^{31}P and ^{1}H nmr spectra of the above compounds were investigated.

INTRODUCTION

The reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, (1), with monofunctional reagents, have received a great deal of attention.[2] By contrast, those of difunctional reagents have been until recently comparatively neglected. The products of the reactions with aliphatic primary diamines were initially ascribed erroneous ansa-structures.[3] A subsequent reinvestigation showed that the compounds were, in fact, spiro derivatives;[4] this was confirmed by X-ray crystallography[5–7]. Much of the other work with difunctional reagents has been summarised elsewhere.[8]

Some mono- and tris-spiro compounds were reported with aliphatic diols, however, with only very limited spectroscopic and no crystallographic data.[9–19] Our earlier investigations[20,21] of the hexachloride, $N_3P_3Cl_6$ (1) and the octachloride, $N_4P_4Cl_8$, with monofunctional alcohols had shown that unless moisture was rigorously excluded during the synthesis of the alkoxyphosphazenes, the properties of the resultant products showed little resemblance to those of the pure compounds.

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‡ Dedicated in friendship and admiration to Derek Barton on the occassion of his 70th Birthday.

DISCUSSION

Difunctional reagents can give rise in principle to four structural types: (i) spiro, (ii) ansa, (iii) bridged and (iv) dangling.[8] With diols the only products reported had been mono- and tris-derivatives of the first type. The other three, especially ansa, were of considerable chemical interest; in addition, the bis-spiro derivatives had the most complex and interesting ^{1}H nmr spectra.

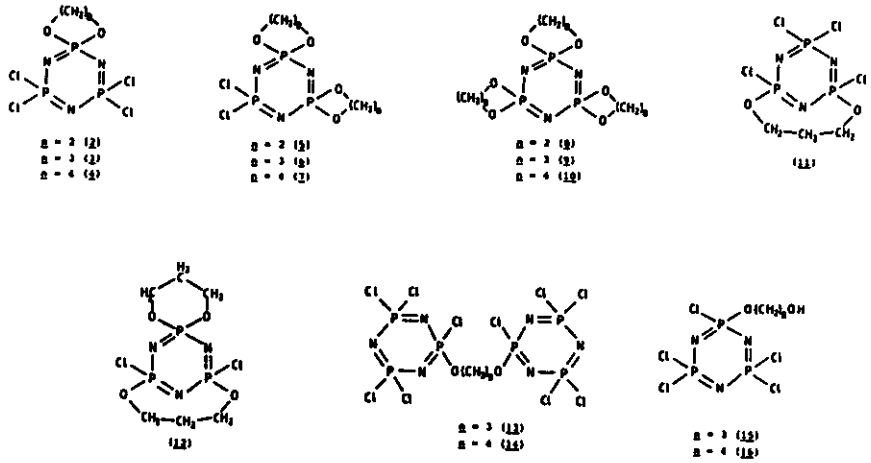
We therefore subjected the reactions of the hexachloride, $N_3P_3Cl_6$ (1) to a systematic investigation with ethane-, 1,3-propane- and 1,4-butanediols. Preliminary reports of this work have appeared.[22]

We noted during our synthetic work that traces of moisture caused the following complications: (i) a greater number of products; (ii) an apparent retardation of the rate of formation of the desired products; (iii) difficulties in purification by recrystallisation, in particular the inability to grow crystals suitable for X-ray crystallography. A combination of rigorous drying of reagents and solvents, chromatography, sublimation and recrystallisation, gave eventually pure products suitable for spectroscopic and crystallographic studies. The compounds are rather less soluble than analogous compounds based on diamines or amino alcohols and hence present greater difficulties in purification. This pertains particularly to the bis- and tris-spiro derivatives.

We isolated a total of 15 compounds, which included examples of all 4 structural types: 9 spiro, $N_3P_3[O(CH_2)_nO]_xCl_{6-x}$ (x = 1,2 and 3; n = 2,3 and 4)(2 - 10); 1 ansa, $N_3P_3[O(CH_2)_3O]Cl_4$ (11); 1 spiro-ansa, $N_3P_3[O(CH_2)_3O]_2Cl_2$ (12); 2 bridged, $N_3P_3Cl_5[O(CH_2)_nO]N_3P_3Cl_5$ (n = 3 and 4), (13, 14) and 2 dangling, $N_3P_3[O(CH_2)_nOH]Cl_5$ (n = 3 and 4) (15, 16). In addition, we observed, but did not isolate in a pure form, a bridge $N_3P_3Cl_5[O(CH_2)_2O]N_3P_3Cl_5$ and a dangling derivative, $N_3P_3[O(CH_2)_2OH]Cl_5$, based on ethylenediol. The spiro derivatives are by far the major products, especially for the ethylene- and propylenediols. Bridged derivatives assume significant importance with butylenediol. The spiro-ansa compound (12) is present in considerably smaller amounts than its dispiro isomer (6). The ansa derivative (11) is isolated in only trace amounts. Bridged compounds are obtained in better yields than danglers.

Crystal structures of 7 of these (2-4)[22b,23], (5)[24], (6)[22c], (10)[25], and (12)[22c,d] have been reported, as well as the ^{35}Cl nqr spectra of three of these (2-4)[26].

As with ethylenediamine and ethanolamine, the five-membered ring substituent, the ethylenedioxy group, differed markedly from the six- and seven-membered homologues and from related acyclic compounds.[4,27-30]



We had shown earlier that with ethylenediamine only a mono-, $N_3P_3[NH(CH_2)_2NH]Cl_4$, with ethanolamine, a mono-, $N_3P_3[O(CH_2)_2NH]Cl_4$ and traces of two isomeric bis-derivatives, $N_3P_3[O(CH_2)_2NH]_2Cl_2$ could be isolated. More forcing reaction conditions lead to resinous, polymeric glues.[4] We had suggested[8] that the structural moiety P-NH in a five-membered ring was responsible for the polymerisation reaction and this was borne out by subsequent studies with N,N'-dimethylethylenediamine[31] and N-methylethanolamine,[32] where mono-, bis- and tris-derivatives were characterised. Thus, the formation of the three spiro ethanedioxy derivatives follows the same predicted pattern. These three derivatives, especially the tris (8), appear to be unstable on storage, probably due to hydrolysis. The unique nature of five-membered ring phosphates has been recognised since the seminal work by Westheimer's group[37] on the kinetics of their hydrolysis.

By contrast, diamines[30,33] and amino alcohols[30,34] giving rise to six-membered spiro substituents, suffer much less from this side reaction, which leads to polymeric products. The next higher homologues give, in addition to spiro, also bridged derivatives,[35] which with the higher diamines, $H_2N(CH_2)_nNH_2$ ($n > 5$) become the exclusive products.[36]

^{31}P NMR SPECTRA

The chemical uniqueness of the five-membered phosphorus-containing rings is mirrored in their ^{31}P nmr chemical shifts. Attention to this in mononuclear phosphates was drawn some time ago.[27-29] In cyclotriphosphazatriene derivatives, the six- and seven-membered ring spiro-derivatives give well-resolved spectra.[31] By contrast, those of the ethylenediamine and

ethanolamine derivatives gave only a single broad line at medium magnetic field, because of the small chemical shift separation between the $\equiv PCl_2$ and the $\equiv P$spiro group.[4] We have now been able to analyse these spectra at high field. Similar remarks pertain to the mono- and particularly to the bis-ethylenedioxy derivatives. The ^{31}P nmr data of the 15 alkanedioxy derivatives, together with that of the starting material (1) are presented in Table 1. The ^{31}P chemical shifts for some of these compounds have been related to their exocyclic OPO bond angles.[23]

Table 1: ^{31}P nmr data[a] for the diol derivatives of $N_3P_3Cl_6$

Compound	δPCl_2[b]	δPspiro[b]	$\delta P(OR)Cl$[b]	$^2J[(\underline{P}spiro-\underline{P}Cl_2)^2]$[c]	$^2J[\underline{P}(OR)Cl-\underline{P}Cl_2]$[c]
(1)	19.9	-	-	-	-
(2)	26.5	24.5	-	68.0	-
(5)	31.3	30.95	-	76.8	-
(8)	-	37.4	-	-	-
(3)	24.1	3.4	-	69.2	-
(6)	26.5	9.1	-	70.8	-
(9)	-	14.1	-	-	-
(4)	24.1	10.3	-	70.5	-
(7)	27.8	16.0	-	76.9	-
(10)	-	21.7	-	-	-
(11)	29.5	-	30.05	-	56.9
(12)	-	10.1	31.2	-	73.0
(15)	23.5	-	16.1	-	61.7
(13)	23.4	-	16.0	-	63.0
(16)	23.5	-	15.9	-	62.1
(14)	23.5	-	15.9	-	61.9
$N_3P_3[O(CH_2)_2NH]Cl_4$	24.9	24.4	-	56.2	-
$N_3P_3[NH(CH_2)_2NH]Cl_4$	23.5	22.9	-	47.1	-

Footnote: [a] At 161.98 MHz in $CDCl_3$ referenced to external 85% H_3PO_4.
[b] in ppm [c] in Hz. [d] $^2J[\underline{P}(OR)Cl-\underline{P}spiro] = 73.0$ Hz.

The ^{31}P nmr spectra at 24.15 MHz of the three monospirodioxy derivatives, $N_3P_3[O(CH_2)_nO]Cl_4$ (n = 2, 3 and 4), are given in Figure 1, those at 162.0 MHz of $N_3P_3[O(CH_2)_2O]Cl_4$, $N_3P_3[O(CH_2)_2NH]Cl_4$ and $N_3P_3[NH(CH_2)_2NH]Cl_4$, in Figure 2. At low or medium field strengths these give rise A_2B spin systems tending to A_3.

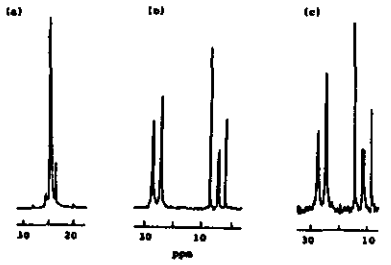


Figure 1 ^{31}P nmr spectra of (a) $N_3P_3Cl_4[O(CH_2)_2O]$, (b) $N_3P_3Cl_4[O(CH_2)_3O]$, and (c) $N_3P_3Cl_4[O(CH_2)_4O]$ at 24.15 MHz, solvent $CDCl_3$, referenced to external 85% H_3PO_4.

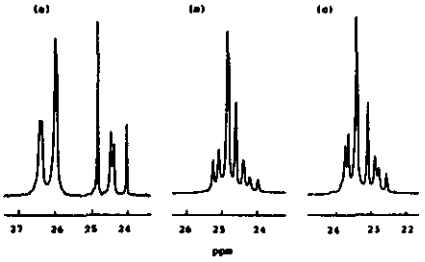


Figure 2 ^{31}P nmr spectra of (a) $N_3P_3Cl_4[O(CH_2)_2O]$ (b) $N_3P_3Cl_4[O(CH_2)_2NH]$ and (c) $N_3P_3Cl_4[NH(CH_2)_2NH]$ at 162.0 MHz solvent $CDCl_3$, referenced to external 85% H_3PO_4.

The following points are noteworthy: (i) The ≡Pspiro nuclei are deshielded in the order 6-membered > 7-membered >> 5-membered spiro rings. (ii) The effect of the spiro substituents on the ≡PCl_2 nuclei shows the same order, giving rise to some of the most deshielded ≡PCl_2 nuclei recorded. (iv) Whilst the chemical shifts of the ≡Pspiro nuclei cover a large range (34 ppm), the shifts of the ≡P(OR)Cl nuclei vary little from δ= 16, if the OR group is acyclic, but changes drastically for the 2 ansa compounds to δ30-31. This may be related to the ring compression, which has been observed,[22d] and is due to the trans-annular link. (v) All two bond coupling constants, $^2J(PP)$, are large and in the range of 57-77 Hz.

^1H NMR SPECTRA

We have shown earlier that alkoxyphosphazenes can show virtual coupling effects.[38,39] The methoxy (as the dimethylamino) derivatives exhibit hump-like absorptions between the outer doublets,[39] whilst the ethoxyderivatives, gem- $N_3P_3Ph_4(OEt)_2$, gem-$N_3P_3Ph_2(OEt)_4$ and $N_3P_3(OEt)_6$, show the expected fine line splitting.[38] The OCH_2 protons of the alkanedioxy groups appeared to be very suitable to demonstrate virtual coupling. A priori, one would have expected the bis and tris derivatives to show multiplicities arising from virtual coupling to two, respectively three, phosphorus nuclei. This is observed for the 1,3-propylenedioxy and the 1,4-butylenedioxy derivatives, where there are considerable chemical shift differences between the ≡PCl_2 and the ≡Pspiro absorptions. The situation is more complex for the ethylenedioxy compounds, because of the proximity of the absorption signals of the two chemically different types of ^{31}P nuclei. Similar observations have been made previously.[40,41]

The mono-1,3-propylenedioxy, (3) and the mono-1,4-butylenedioxy compounds (4) have relatively simple proton spectra, with some four bond coupling, $^4J(PH)$, observable. That of the monoethylenedioxy derivative, (2), is complicated by the above mentioned effect.

The spectra of the tris spiro compounds are again relatively simple, additional fine structure being observed due to long range virtual coupling, as the three ≡Pspiro nuclei are equivalent and are strongly coupled. That of the ethylenedioxy derivative, (8), gives a beautiful example of this phenomenon, without the need for homonuclear proton-proton decoupling[38] (Figure 3).

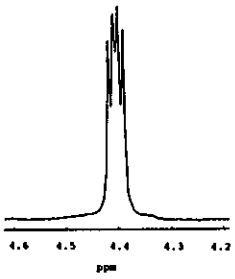


Figure 3 ^1H nmr spectrum of $N_3P_3[O(CH_2)_2O]_3$ at 400 MHz in $CDCl_3$. TMS as internal reference.

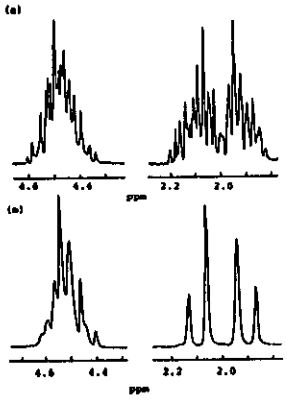


Figure 4 ^1H nmr spectra of $N_3P_3Cl_2[O(CH_2)_3O]_2$, (a) normal spectrum, and (b) homonuclear decoupled spectra at 200 MHz in $CDCl_3$. TMS as internal reference.

The expected quartet structure of the OCH_2 protons becomes also clear in the tris-1,3-propylenedioxy (8) and the tris-1,4-butylenedioxy-derivatives (9), on homonuclear decoupling of the CCH_2 protons.

The ^1H nmr spectra of the bis-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 non-equivalent due to their being part of a cyclic moiety and therefore the two protons of each methylene group see a different environment. This is most pronounced for the 6-membered and least for the 5-membered ring. Thus, over and above the coupling effects observed for the mono and tris derivatives, each methylene group gives rise to an AB quartet structure. This is demonstrated for the bis-1,3-propylenedioxy-derivative, (6), (Figure 4a). Homonuclear decoupling considerably simplifies the spectrum (Figure 4b) and allows the virtual coupling effect to two phosphorus nuclei to be observed.

The $^{3}J(PH)$ coupling constants differ with ring size (Table 2). Those of the ethylenedioxy derivatives are the smallest (10.8-11.6 Hz), those of the 1,3-propylenedioxy compounds are only marginally larger (10.6-12.9 Hz), whilst those of the 1,4-butylenedioxy derivatives are markedly increased to 17.7-18.5 Hz. The acyclics are smaller (9.0 - 9.2 Hz) than any of the above.

Table 2: ^{1}H nmr data for the diol derivatives[a]

Compound	$\delta POCH_2$[b]	δCCH_2[b]	δOH[b]	$\lvert^{3}(JPH)\rvert$[c]	$\lvert^{4}J\rvert(PH)$[c]
(2)	4.48	-	-	11.2	-
(5)	4.44	-	-	10.8	-
(8)	4.40	-	-	11.6	-
(3)	4.53	2.07	-	12.9	1.6
(6)	4.51	2.09	-	10.7	<0.3
	4.94	1.92	-	10.7	<0.3
(9)	4.45	1.96	-	12.7	<0.3
(4)	4.24	1.96	-	18.5	<0.3
(7)	4.19	1.91	-	18.4	<0.3
(10)	4.14	1.87	-	17.7	<0.3
(11)	4.54	2.28	-	20.1	<0.3
	4.31	2.10	-	21.2	<0.3
(12) spiro	4.49	2.01	-	12.8	1.5
	4.48			12.8	
ansa	4.50	2.21	-	20.0	<0.3
	4.24	2.02	-	21.0	<0.3
(15)	4.38	2.22	4.30	9.1	1.5
(13)	4.35	2.20	-	9.1	1.5
(16)	4.25	1.94	4.30	9.2	<0.3
(14)	4.26	1.94	-	9.0	<0.3

Footnote: [a]At 250.13 MHz. in $CDCl_3$ solvent, referenced to TMS. [b] in ppm. [c] in Hz.

In three of the propylenedioxy derivatives (6, 11 and 12) the OCH_2 protons and to a somewhat lesser extent the CCH_2 protons show non-equivalence.

EXPERIMENTAL

Chemicals were obtained as follows:
benzene, light petroleum (bp 40–60°C), anhydrous diethyl ether (May & Baker Ltd.), tetrahydrofuran (Fluka-Garantie 99.5%), acetonitrile, deuteriated solvents for nmr spectroscopy, propane-1,3-diol, butane-1,4-diol (Aldrich Chem. Co. Ltd.), pyridine, ethanediol (B.D.H. Chemical Co. Ltd.), hexachlorocyclotriphosphazatriene (Shin Nisso Kako Co. Ltd.). Solvents were dried by conventional methods.

All reactions were monitored by using Kieselgel 60 F 254 (silica gel) precoated tlc plates and sprayed with ninhydrin (0.5w/v%) in butanol solution and developed at approximately 130°C. Separation of products were carried out by flash column chromatography[42] using Kieselgel 60. Melting points were carried out on a Reichert-Kofler micro heating stage and a Mettler FB 82 hot stage connected to a FP 800 central processor both fitted with a polarising microscope. ^{1}H 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 - Kings College, London) and a Varian XL 400 spectrometer (operating at 399.95 MHz - University College, London). Samples were dissolved in $CDCl_3$ and placed in 5 mm nmr tubes. Measurements were carried out using a $CDCl_3$ lock, TMS as internal reference and sample concentrations of 15–20 mg/cm^3.

^{31}P Nmr spectra were recorded using a *JEOL JNM FX-60 spectrometer (operating at 24.15 MHz)*, a Varian XL-200 spectrometer (operating at 80.98 MHz - University College, London), a Bruker WH 400 spectrometer (operating at 162.0 MHz - Queen Mary College) and a Varian VXR 400 (operating at 162.0 MHz - University College, London), 85% H_3PO_4 was used as an external reference.

The mass spectra were recorded using a VG 7070H Mass Spectrometer with Finningan INCOS Data System at University College, London and a VG ZAB IF mass spectrometer at the School of Pharmacy.

Reactions with ethanediol: – (a) 1 equivalent. To $N_3P_3Cl_6$ (10g, 28.8 mM) in CH_2Cl_2 (100 ml) was added ethanediol (1.78g, 28.8 mM) and pyridine (5g, 63.3 mM) in CH_2Cl_2 (50 ml). The reaction was monitored by tlc and ^{31}P nmr spectroscopy. After 48 h, the bulk of pyridine hydrochloride was filtered off, the remainder being removed by column chromatography using a mixture of CH_2Cl_2/Et_2O (2:1). To separate individual phosphazenes, the product was *rechromatographed using* Et_2O *as eluent*. Three main fractions were obtained (i) $N_3P_3Cl_6$, (ii) the monospiro derivative, $N_3P_3[O(CH_2)_2O]Cl_4$ and (iii) the bis spiroderivative, $N_3P_3[O(CH_2)_2O)_2Cl_2$. Fractions (i) and (ii) contained two trace components, which were identified by ^{31}P nmr spectroscopy and mass spectrometry as the bridge derivative

$N_3P_3Cl_5[O(CH_2)_2O]N_3P_3Cl_5$($M^+$, 680) and the dangler $N_3P_3[O(CH_2)_2OH]Cl_5$(M^+, 371). Fraction (ii) further purified by sublimation 110-120°C/20 mm followed by recrystallisation from CH_2Cl_2 to give (2), mp 169-170°C (lit.[14] 166°C) Yield 25%.

(b) 2 equivalents. Procedure as for (a). Three fractions were obtained from column chromatography using CH_2Cl_2/Et_2O (2:1) as eluent:
(i) $N_3P_3Cl_6$, (ii) (2) and (iii) (5). (iii) Was recrystallised from CH_2Cl_2, followed by sublimation at 170°C/20 mm and again recrystallised from CH_2Cl_2, mp 227-228°C (decomp), yield 15%.

(c) 3 equivalents. Reaction procedure as in (a). The reaction mixture was freed from floating amine hydrochloride and then filtered through a glass crucible. The precipitate was washed with CH_2Cl_2 and traces of (5) were removed to give (8), yield 20%.

Reactions with propane-1,3-diol:- (d) 1 equivalent. To (1) (60 g, 173 mM) in anhydrous Et_2O (300 ml) was added with stirring pyridine (27.4 ml, 347 mM) in Et_2O (25 ml). The diol (13.2 g, 173 mM) in Et_2O (25 ml) was then added with stirring (1h). After standing (12 h), the mixture was refluxed until tlc indicated completion of the reaction. On attaining room temperatues, the pyridine hydrochloride was removed by filtration and the filtrate concentrated to 50 ml. One third of the filtrate was column chromatographed using 60 g of silica gel and eluted with light petroleum/benzene (2:1). Four major fractions were obtained: (i) $N_3P_3Cl_6$ (6%), (ii) the dangler (15) an oil (12%), (iii) the bridge compound (13), mp 69°C, yield 18%, and (iv) a mixture of two isomeric compounds. (iv) Was rechromatographed using benzene as eluent. The ansa isomer (11) was isolated first and recrystallised from light petroleum, mp 135°C, yield 4%. The second component was the mono sprio derivative (3), mp 155-156°C (lit.[14] 156 °C), yield 41%.

(e) 2 equivalents. Procedure as for (d). There were isolated the previous compounds (15), (13) and (3), together with the dispiro derivative (6), recrystallised from light petroleum, mp 227°C (decomp), yield 58%.

(f) 3 equivalents. Procedure as for (a). Elution with Et_2O gave three fractions: (i) the spiro-ansa compound (12), the dispiro (6) and the trispiro (9). Compound (12) was recrystallised from diethyl ether, mp 173.5-174.5°C, yield 1%. Compound (9) recrystallised from CH_2Cl_2, mp 250-265°C (decomp), yield 45%.

Reactions with butane-1,4-diol:- (g) 1 equivalent. Procedure as for (d). Three fractions were obtained: (i) the dangler (16), an oil, yield 11%; (ii) the bridge derivative (14),

recrystallised from a mixture of light petroleum/CH_2Cl_2 (2:1), mp 82°C, yield 32% and (iii) the monospiro compound (4), recrystallised from light petroleum/CH_2Cl_2 (2:1), mp 160.0-160.5°C, (lit[14] 156°C), yield 35%.

(b) 2 equivalents. Procedure as for (d). The dispiro compound (7) was recrystallised from light petroleum/CH_2Cl_2 (2:1), mp 215°C(decomp), yield 38%.

(i) 3 equivalents. Procedure as for (a). The trispiro derivative (10) was recrystallised from CH_2Cl_2, mp 245-255°C (decomp), yield 25%.

Characterisation details are given in Table 3.

Table 3: Characterisation details for compounds (2)-(16)

			M	Elemental analysis/percentage Composition					
				Calc.			Found		
Compound	Formula	Calc.[a]	Obs.	C	H	N	C	H	N
(2)	$C_2H_4O_2N_3P_3Cl_4$	335	335	7.1	1.2	12.5	7.6	1.3	12.6
(3)	$C_3H_6O_2N_3P_3Cl_4$	349	349	10.3	1.7	12.0	10.3	1.7	12.0
(4)	$C_4H_8O_2N_3P_3Cl_4$	363	363	13.2	2.2	11.5	13.3	2.1	11.7
(5)	$C_4H_8O_4N_3P_3Cl_2$	325	325	14.2	2.5	12.9	14.7	2.45	12.9
(6)	$C_6H_{12}O_4N_3P_3Cl_2$	353	353	20.3	3.4	11.9	20.6	3.6	12.05
(7)	$C_8H_{16}O_4N_3P_3Cl_2$	381	381	25.1	4.2	11.0	25.2	4.0	11.1
(8)	$C_6H_{12}O_6N_3P_3$	315	315	22.9	3.8	13.3	22.85	3.8	13.3
(9)	$C_9H_{18}O_6N_3P_3$	357	357	30.3	5.1	11.8	30.4	4.9	11.8
(10)	$C_{12}H_{24}O_6N_3P_3$	399	399	36.1	6.1	10.5	36.2	6.0	10.5
(11)	$C_3H_6O_2N_3P_3Cl_4$	349	349	10.3	1.7	12.0	10.4	1.7	12.05
(12)	$C_6H_{12}O_4N_3P_3Cl_2$	353	353	20.3	3.4	11.9	20.4	3.6	11.8
(13)	$C_3H_6O_2N_6P_6Cl_{10}$	694	694	5.15	0.9	12.0	5.35	0.9	12.05
(14)	$C_4H_8O_2N_6P_6Cl_{10}$	708	708	6.7	1.1	11.8	7.0	1.1	11.8
(15)	$C_3H_7O_2N_3P_3Cl_5$	385	385	9.3	1.8	10.85	9.7	1.7	10.4
(16)	$C_4H_9O_2N_3P_3Cl_5$	399	399	12.0	2.2	11.0	12.3	2.1	10.5

[a]Based on the mass of the most abundant isotope.

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