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Synthesis, reactivity and structures of spirocyclic products derived from octachlorocyclotetraphosphazene: comparison with spirocyclic cyclotriphosphazenes and linear phosphazenes

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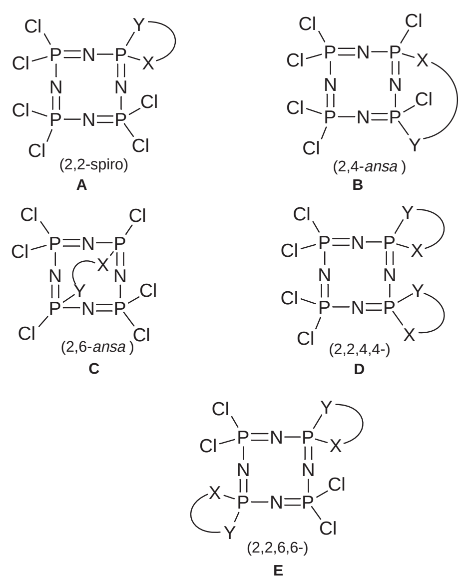
The reaction of $N_4P_4Cl_8$ **1** with the difunctional reagents 2,2′-methylenebis(4,6-di-*tert*-butylphenol) (as its disodium salt) and *N,N*′-diisopropylpropane-1,3-diamine gave the spirocyclic products 2,2-$N_4P_4\{[O\text{-}4,6\text{-}(t\text{-}Bu)_2C_6H_2]_2CH_2\}Cl_6$ **4** and 2,2-$N_4P_4[N(i\text{-}Pr)CH_2CH_2CH_2N(i\text{-}Pr)]Cl_6$ **5**. Further reaction of **1** with 2 mol equivalents of *N,N*′-diisopropylpropane-1,3-diamine afforded the novel dispiro derivative 2,2,6,6-$N_4P_4[N(i\text{-}Pr)CH_2CH_2CH_2N(i\text{-}Pr)]_2Cl_4$ **6**. Whereas the analogous reaction of $N_3P_3Cl_6$ **2** with the above diamine gave the monospiro derivative 2,2-$N_3P_3[N(i\text{-}Pr)CH_2CH_2CH_2N(i\text{-}Pr)]Cl_4$ **7** readily, the reaction of **2** with the diols $CH_2[4,6\text{-}(t\text{-}Bu)_2C_6H_2OH]_2$ or $CH_2(4\text{-}Me\text{-}6\text{-}t\text{-}BuC_6H_2OH)_2$ is sluggish. In the case of the latter diol, a product formulated as $N_3P_3[O\text{-}4\text{-}Me\text{-}6\text{-}t\text{-}BuC_6H_2\text{-}4\text{-}Me\text{-}6\text{-}t\text{-}BuC_6H_2OH]Cl_5$ **9** was identified (^{31}P NMR). The linear phosphazene $Cl_2P(O)N{=}PCl_3$ **3**, by contrast, reacted with $CH_2(4\text{-}Me\text{-}6\text{-}t\text{-}Bu\text{-}C_6H_2OH)_2$ and Et_3N to give the cyclic product $Cl_2P(O)N{=}P[(O\text{-}4\text{-}Me\text{-}6\text{-}t\text{-}BuC_6H_2)_2CH_2]Cl$ **8**. Reaction of the spirocycle **5** with an excess of $MeNH_2/Et_3N$ afforded the new bicyclic phosphazene containing a spirocyclic ring $N_4P_4[N(i\text{-}Pr)CH_2CH_2CH_2N(i\text{-}Pr)](NHMe)_4(NMe)$ as a crystalline solid. The crystal structures of **4**·$0.5C_4H_8Cl_2$ and **5**–**8** have been determined.

Introduction

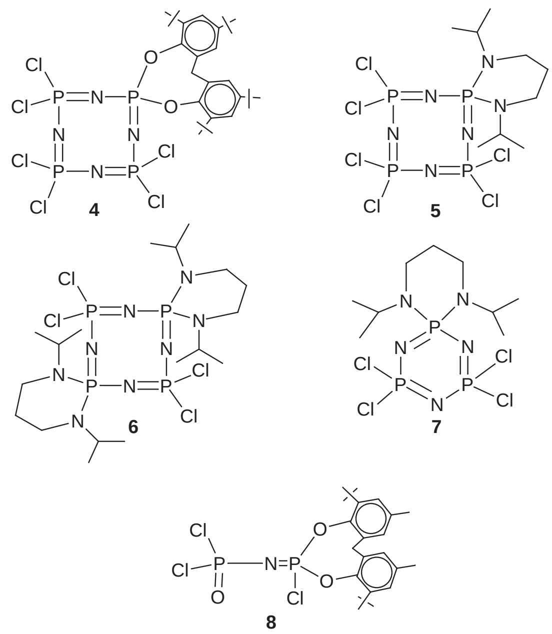
In contrast to the reactions of cyclophosphazenes $(NPX_2)_3$ (X = Cl or F) with monofunctional reagents, reactions with difunctional reagents generally proceed pairwise and can lead to 'spiro', 'ansa' or 'intermolecular' condensation products in which the phosphazene ring is retained.[1] Since the relatively larger ring flexibility coupled with the larger number of replaceable chlorines makes the reaction of octachlorocyclotetraphosphazene, $N_4P_4Cl_8$ **1** (tetramer), more complex than that of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ **2** (trimer), it can be expected that treatment of the former with diamines/diols could lead to a more diverse range of products.[1e,g] As an example illustrating the difference, it can be noted that the reaction of *tert*-butylamine with **2** gives essentially the geminal 2,2-$N_3P_3(NH\text{-}t\text{-}Bu)_2Cl_4$ at the bis stage of substitution,[2] while the analogous reaction with **1** gives the non-geminal 2,4- and 2,6-$N_4P_4(NH\text{-}t\text{-}Bu)_2Cl_6$[3] and hence it may be expected that formation of an 'ansa' product would be more favoured in the reactions of diamines/diols with **1** rather than with **2**. Thus in the reaction of **1** with a difunctional reagent HX–YH at least three intramolecular condensation products **A**–**C** can be envisaged. In addition, at the next stage of substitution for the spiro compounds **A** the incoming reagent could attack at the (4,4) or (6,6) positions leading to two distinct isomeric spirocyclic phosphazenes **D** and **E**; to appreciate the complexity, it can be noted that other 'spiro-ansa' and cross-linked products are also possible at this stage of substitution.



These complexities have resulted in only a meagre number of studies on the reaction of compound **1** with difunctional reagents[1a,c,e] and, to our knowledge, there is no report so far of any derivative in this series that has been structurally characterised by X-ray crystallography.† We also felt that a comparison of these compounds with those obtained from **2** or from the linear phosphazene $Cl_2P(O)N{=}PCl_3$ **3** may be useful in analysing the reactivity pattern and bonding in phosphazenes. In this paper we report the synthesis and structures of (i) spirocyclic

† In ref. 1(*e*) synthesis and ^{31}P NMR characterisation of several derivatives which include $N_4P_4Cl_{8-2n}(OCH_2CH_2CH_2O)_n$ (*n* = 1, 2, 3; all spiro) and $N_4P_4Cl_{8-2n}[O(CH_2)_4O]_n$ (*n* = 1–4) are discussed, but to our knowledge no solid state structural studies were conducted.

cyclotetraphosphazene derivatives **4**–**6** that represent the first examples of this kind to be studied in the solid state, (ii) the spirocyclic cyclotriphosphazene **7** and (iii) the cyclic linear phosphazene derivative **8**. Comparison of the fluorination reactions of **5** and **7**[1f] as well as the possibility of the use of **5** and **6** for the synthesis of transannular bridged phosphazenes (bicyclic phosphazenes)[4] are also discussed.



4 **5** **6** **7** **8**

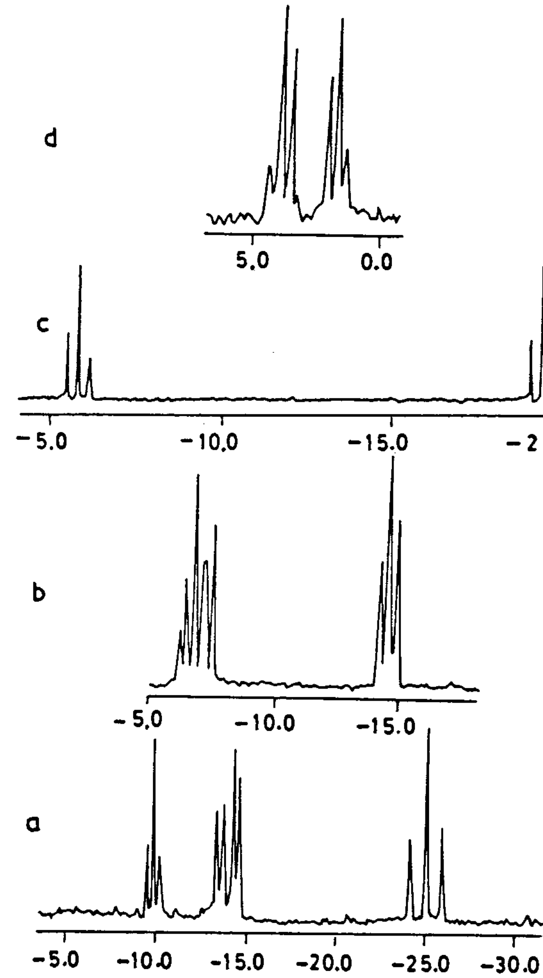


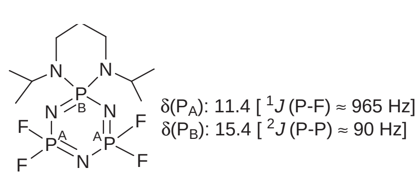
Fig. 1 The ^{31}P NMR spectra of compounds (a) **4**, (b) **5**, (c) **6** and (d) $N_4P_4[N(i\text{-Pr})CH_2CH_2CH_2N(i\text{-Pr})](NHMe)_4$ **13**.

Results and discussion

Synthesis, reactivity and spectra

Whereas compound **4** is obtained by treating $N_4P_4Cl_8$ **1** with the sodium salt of the diol, the linear phosphazene derivative **8** is prepared by treating $Cl_2P(O)N{=}PCl_3$ **3** with the diol using triethylamine as the base. Compounds **5** and **7** are readily obtained by treating **1** or **2** with 2 mol equivalents of the diamine; treating **5** similarly with the diamine leads to the dispirocycle **6**. The yields in all these reactions are moderate (60–90%) except in the case of **4** (≈ 23%); the lower yield of the latter may be due to incomplete formation of the disodium salt of the diol.‡ We did not succeed in isolating a compound analogous to **4** in a pure state using **2**. However when the closely related diol 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) after reacting with sodium was used, the major product (≈30%) showed a doublet at δ 21.8 [2P, ^2J(P–P) = 61.0 Hz] and a triplet at 8.17 (1P) in the ^{31}P NMR; the monosubstituted structure $N_3P_3[O\text{-}4\text{-}Me\text{-}6\text{-}t\text{-}BuC_6H_2\text{-}4\text{-}Me\text{-}6\text{-}t\text{-}BuC_6H_2OH]Cl_5$ **9** is assigned for this compound on the basis of its mass spectrum, analytical data and available data on the trends in ^{31}P NMR.[6]

Compounds **4**–**8** are stable under dry nitrogen in the solid state at room temperature; however the monospiro derivatives **4** and **5** are very unstable to moisture. The difference in stability between the **5** and **7** is also reflected, to some degree, in the fluorination reactions. While **7** can readily be fluorinated by KF–CH_3CN[1b] to give the new fluorospirocycle $N_3P_3[N(i\text{-Pr})CH_2CH_2CH_2N(i\text{-Pr})]F_4$ **10** the hygroscopic product obtained by fluorinating the tetrameric compound **5** had only one discernible PF_2 triplet [δ −13.6, ^1J(P–F) ≈ 850 Hz] in the ^{31}P NMR instead of the expected two; this suggests a partial hydrolysis in the latter case. There are also peaks in the region δ −2.1 to 2.0 and −10.0 to −12.8 which are attributable to the PF(O)NH group but the spectrum was too complicated to analyse further. The ^{1}H NMR also showed a complex spectrum. Mass spectral evidence suggests that it is probably due to $N_4P_4F_5(OH)[N(i\text{-Pr})CH_2CH_2CH_2N(i\text{-Pr})]$;[1b–c] earlier hydrolysed products were obtained in the attempted dimethylaminolysis of the product from the reaction of **1** with 1,2-diaminoethane.[1c]



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Isolation of the spirocyclic products **4**–**6** clearly shows that this pathway is favoured in the reaction of **1** with difunctional reagents under the conditions employed. Formation of 2,2,6,6-$N_4P_4[N(i\text{-Pr})CH_2CH_2CH_2N(i\text{-Pr})]_2Cl_4$ **6** at the second stage in high yields in preference to the 2,2,4,4 (*cf.* structure **D** above) or a 2,2,4,6 product is also a point to be noted; one factor responsible for this observation is the hindrance of the bulky first spirocycle to an incoming reagent at the 4 position.

In the reaction of the linear phosphazene $Cl_2P(O)N{=}PCl_3$ **3** with diol–Et_3N only compound **8** is formed as expected from Allcock's observations.[7]

In contrast to other 2,2-disubstituted derivatives that usually show an AB_2C or AB_2X pattern[1c,6,8] in the ^{31}P NMR, compound **4** exhibits an AM_2X spectrum [Fig. 1(a)] from which the coupling constants can readily be obtained. This is probably a result of the extreme upfield shift caused by the presence of the

‡ This statement is also corroborated by the isolation of the monosodium salt $Na[O\text{-}4,6\text{-}(t\text{-}Bu)_2C_6H_4CH_2(4,6\text{-}t\text{-}Bu)_2C_6H_2OH]$ as a dihydrate (X-ray evidence) even when an excess of sodium is used.[5]

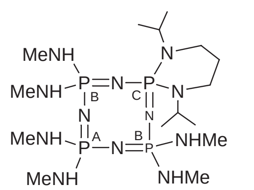
eight-membered phosphocine ring containing aryloxy substituents. Even in **8**, which contains a similar ring, the =P(ORO)Cl ($\delta \approx -14$ ppm) is upfield by *ca.* 10 ppm compared to $=PCl_3$ in **3** [δ(P) −4.1].[9] Other points of interest are as follows.

(i) The δ[P(spiro)] value of compounds **4**–**6** (Fig. 1) is much upfield to $\delta(PCl_2)$, in contrast to those of the five membered ring containing spirocycle $N_4P_4[N(Me)CH_2CH_2N(Me)]Cl_6$ {δ[P(spiro)] 6.1; $\delta(PCl_2)$ −8.3, −6.2}, where P(spiro) appears downfield to PCl_2. This is on expected lines[1c] and is similar to the trends observed in five- and six-co-ordinated phosphoranes.[10]

(ii) The signal for P(spiro) moves upfield upon introduction of a second spiro ring into compound **5** (from δ −14.6 for **5** to −19.4 for **6**; Fig. 1) which is the reverse of that observed for the set $N_3P_3[(Me)N(CH_2)_3NH]Cl_4$ {δ[P(spiro)] 9.8} and $N_3P_3[(Me)N(CH_2)_3NH]_2Cl_2$ {δ[P(spiro)] 21.6}.[1j] However, upon methylamination (see below) the chemical shift range narrows down significantly [Fig. 1(d)].

(iii) The ^2J(P–N–P) values for compounds **5** and **6** are lower than that for **7**. It appears that this is a general trend for (amino)cyclophosphazenes.[1c,6]

The ease of isolation, stability and ready identification of P(spiro) groups by NMR make compounds **5** and **6** excellent probes for studying further reactions on cyclotetraphosphazenes. For example, treatment of **5** with methylamine in chloroform leads to both the normal (**11**) and *trans*-annular fused (bicyclic)[5] (**12**) products; compound **12** is obtained in a pure state. The chemical shift range is clearly in the bicyclic region[6] and as expected an AB_2C spectrum is obtained. The ^1H NMR is also consistent with the assigned structure; the two sets of methyls on the 1,3,2-diazaphosphorinane ring show two separate doublets centred at δ 1.08 and 1.15 since one is facing the bridgehead nitrogen and the other is opposite to it. In the reaction of the dispirocycle **6** with methylamine the fully substituted product $N_4P_4[N(i\text{-Pr})CH_2CH_2CH_2N(i\text{-Pr})]_2(NHMe)_4$ **13** is obtained as a crystalline solid; the residue showed a singlet at δ 18.7 (probably the bicyclic product) and a broad multiplet centred at δ 3.4 (unassigned) in the ^{31}P NMR.



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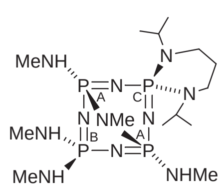
^{31}P NMR: 8.0 [t, P(A), ^2J (P-P) = 34 Hz]
6.2 [br t, P(B), $^2J \approx 27$ Hz]
−1.9 [br t, P(C), $^2J \approx 27$ Hz]



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19.8 [t, or dd, P(A)]
17.1 [t, P(B)]
14.7 [t, P(C)]
^2J (P-P) ≈ 40 Hz

Structures

The molecular structures of compounds $\mathbf{4}\cdot0.5C_4H_8Cl_2$ and **5**–**8** are shown in Figs. 2–6. Selected bond parameters are given in Tables 1–5.

Compound $\mathbf{4}\cdot0.5C_4H_8Cl_2$ (Fig. 2) crystallises in the space group $P\bar{1}$ with the solvent molecule positioned around the centre of symmetry of the unit cell so that only half of it belongs to the asymmetric unit. There is disorder in the solvent molecule as well as in one of the *tert*-butyl groups in the structure. The P–N distances are in the normal range [1.53(1)–1.569(8) Å] with a mean value of 1.55 Å. Bond angles at phosphorus and nitrogen for the phosphazene ring average to 121(1) and 137(2)° respectively; the angles at the ring nitrogen are thus larger than those generally observed for the trimeric compounds[1h] as well as the aminophosphazenes $N_4P_4(NMe_2)_8$ [130.0(6)°][11] and $N_4P_4(NC_4H_8)_8$ [131.7(4)°][12] but are close to those observed in $N_4P_4(OC_6H_4Me\text{-}2)_8$ (mean 138.5°).[13] The P–O bonds in the 1,3,2-dioxaphosphocine ring [mean 1.567(11) Å] are significantly shorter than those observed in the five-co-ordinated phosphorus compound $(C_6H_{11}NH)P\{[O\text{-}4,6\text{-}(t\text{-}Bu)_2\text{-}C_6H_2]_2CH_2\}(1,2\text{-}O_2C_6H_4)\cdot0.5Et_2O$ [mean 1.632(3) Å] or in the three-co-ordinated derivative $(C_6H_{11}NH)P\{[O\text{-}4,6\text{-}(t\text{-}Bu)_2\text{-}C_6H_2]_2CH_2\}$ [mean 1.666(3) Å].[10c]

Table 1 Selected bond lengths (Å) and angles (°) for compound $\mathbf{4}\cdot0.5C_4H_8Cl_2$ with estimated standard deviations (e.s.d.s) in parentheses

P(2)–Cl(21)	1.970(4)	P(6)–N(7)	1.569(8)
P(2)–Cl(22)	1.962(6)	P(8)–O(1)	1.579(7)
P(2)–N(1)	1.53(1)	P(8)–O(2)	1.555(7)
P(2)–N(3)	1.565(8)	P(8)–N(1)	1.55(1)
P(4)–Cl(41)	1.952(6)	P(8)–N(7)	1.550(7)
P(4)–Cl(42)	1.982(5)	O(1)–C(1)	1.43(1)
P(4)–N(3)	1.552(8)	O(2)–C(8)	1.43(1)
P(4)–N(5)	1.56(1)	C(1)–C(2)	1.35(2)
P(6)–Cl(61)	1.982(4)	C(6)–C(7)	1.49(1)
P(6)–Cl(62)	1.970(5)	C(7)–C(13)	1.50(1)
P(6)–N(5)	1.55(1)	C(8)–C(13)	1.38(2)
Cl(21)–P(2)–Cl(22)	102.8(2)	O(1)–P(8)–O(2)	105.3(4)
Cl(22)–P(2)–N(1)	109.1(3)	O(1)–P(8)–N(1)	104.7(5)
Cl(21)–P(2)–N(3)	105.2(4)	O(1)–P(8)–N(7)	112.9(4)
Cl(22)–P(2)–N(1)	108.4(4)	O(2)–P(8)–N(1)	108.8(4)
Cl(22)–P(2)–N(3)	109.3(4)	O(2)–P(8)–N(7)	105.5(5)
N(1)–P(2)–N(3)	120.5(5)	N(1)–P(8)–N(7)	118.9(5)
Cl(41)–P(4)–Cl(42)	102.2(3)	P(2)–N(1)–P(8)	141.9(5)
Cl(41)–P(4)–N(3)	111.8(5)	P(2)–N(3)–P(4)	134.4(6)
Cl(41)–P(4)–N(5)	105.7(4)	P(4)–N(5)–P(6)	131.4(6)
Cl(42)–P(4)–N(3)	104.1(4)	P(6)–N(7)–P(8)	140.0(7)
Cl(42)–P(4)–N(5)	110.2(4)	O(1)–C(1)–C(6)	116.8(9)
N(3)–P(4)–N(5)	121.2(5)	P(8)–O(1)–C(1)	127.7(6)
Cl(61)–P(6)–Cl(62)	101.0(2)	P(8)–O(2)–C(8)	127.5(6)
Cl(61)–P(6)–N(5)	104.8(4)	C(1)–C(6)–C(7)	123.8(9)
Cl(61)–P(6)–N(7)	110.3(4)	C(6)–C(7)–C(13)	116.4(8)
Cl(62)–P(6)–N(5)	110.1(4)	O(2)–C(8)–C(13)	116.6(8)
Cl(62)–P(6)–N(7)	105.3(4)	C(7)–C(13)–C(8)	124(1)
N(5)–P(6)–N(7)	123.2(5)		

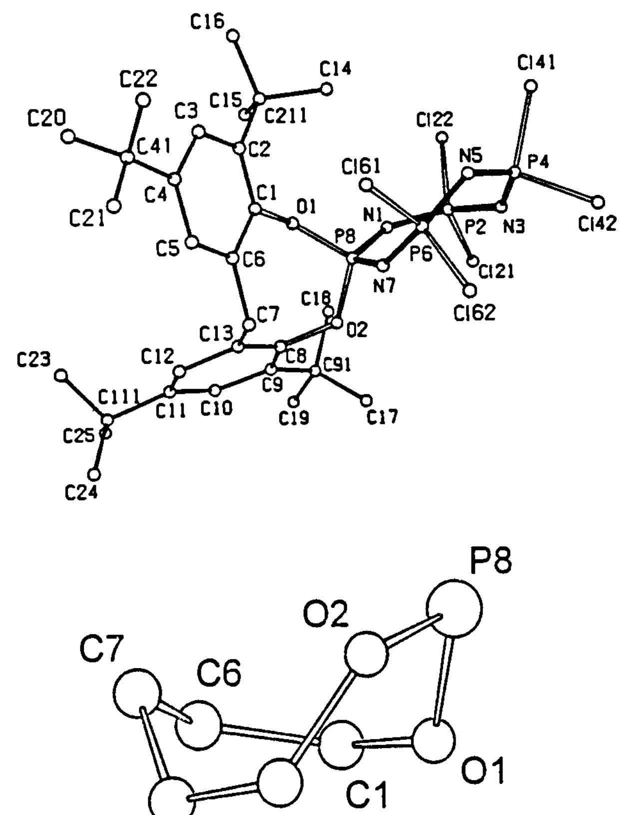

Fig. 2 Molecular structure of compound $\mathbf{4}\cdot0.5C_4H_8Cl_2$. The solvent as well as the hydrogen atoms are omitted for clarity. Also shown at the bottom is the conformation of the eight membered 1,3,2-dioxaphosphocine ring.

Table 2 Selected bond lengths (Å) and angles (°) for compound **5** with e.s.d.s in parentheses

P(2)–Cl(21)	1.987(2)	P(6)–N(5)	1.562(4)
P(2)–Cl(22)	2.012(2)	P(6)–N(7)	1.506(4)
P(2)–N(1)	1.527(4)	P(8)–N(1)	1.577(3)
P(2)–N(3)	1.567(4)	P(8)–N(7)	1.571(4)
P(4)–Cl(41)	1.991(2)	P(8)–N(11)	1.630(4)
P(4)–Cl(42)	1.988(2)	P(8)–N(31)	1.621(4)
P(4)–N(3)	1.552(4)	N(11)–C(61)	1.414(8)
P(4)–N(5)	1.542(3)	N(31)–C(41)	1.43(1)
P(6)–Cl(61)	1.994(2)	C(41)–C(51)	1.42(1)
P(6)–Cl(62)	1.994(2)	C(51)–C(61)	1.408(9)
Cl(21)–P(2)–Cl(22)	101.25(7)	N(5)–P(6)–N(7)	121.9(2)
Cl(21)–P(2)–N(1)	108.5(2)	N(1)–P(8)–N(7)	111.3(2)
Cl(21)–P(2)–N(3)	104.1(1)	N(1)–P(8)–N(11)	110.5(2)
Cl(22)–P(2)–N(1)	109.8(1)	N(1)–P(8)–N(31)	110.8(2)
Cl(22)–P(2)–N(3)	109.1(2)	N(7)–P(8)–N(11)	109.7(2)
N(1)–P(2)–N(3)	121.9(2)	N(7)–P(8)–N(31)	108.9(2)
Cl(41)–P(4)–Cl(42)	101.41(9)	N(11)–P(8)–N(31)	105.6(2)
Cl(41)–P(4)–N(3)	109.8(2)	P(2)–N(1)–P(8)	140.1(3)
Cl(41)–P(4)–N(5)	105.5(2)	P(2)–N(3)–P(4)	135.5(2)
Cl(42)–P(4)–N(3)	105.0(1)	P(4)–N(5)–P(6)	130.8(3)
Cl(42)–P(4)–N(5)	110.6(2)	P(6)–N(7)–P(8)	160.9(3)
N(3)–P(4)–N(5)	122.6(2)	P(8)–N(11)–C(61)	124.2(3)
Cl(61)–P(6)–Cl(62)	101.06(7)	P(8)–N(31)–C(41)	123.2(4)
Cl(61)–P(6)–N(5)	108.1(2)	N(31)–C(41)–C(51)	117.6(7)
Cl(61)–P(6)–N(7)	109.0(2)	C(41)–C(51)–C(61)	121.0(7)
Cl(62)–P(6)–N(5)	104.8(1)	N(11)–C(61)–C(51)	119.5(6)
Cl(62)–P(6)–N(7)	110.0(1)		

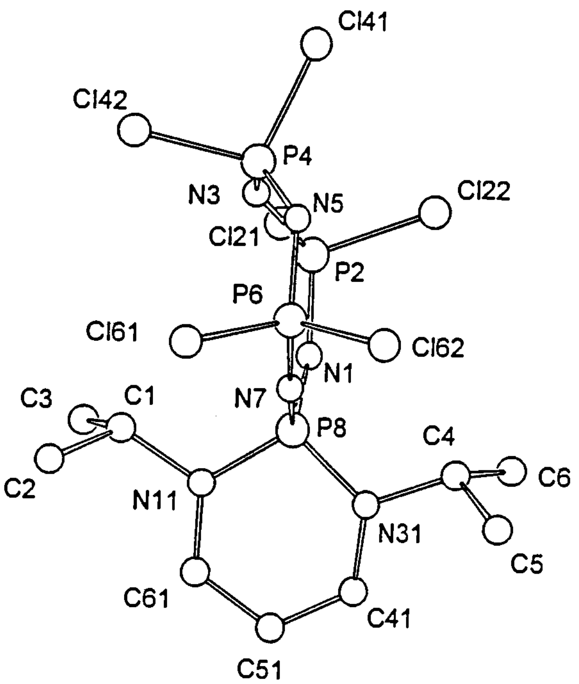

Fig. 3 Molecular structure of compound **5**; only non-hydrogen atoms are shown for clarity.

The phosphazene ring is non-planar as expected and has a 'twisted' conformation. Interestingly, the eight membered 1,3,2-dioxaphosphocine ring in compound **4** has a 'tub' conformation (Fig. 2) with atoms O(1), C(1), C(8) and C(13) co-planar to within ±0.026 Å while atoms P(8), O(2), C(6) and C(7) deviate at the same side from this plane by 1.18, 1.00, 0.46 and 0.93 Å respectively. So far, such a conformation for this ring has been found only for five-co-ordinated phosphoranes in which the ring spans apical-equatorial sites[10c] but not in four-[14] or three-co-ordinated[10c,15] phosphorus derivatives.

In compound **5** (Fig. 3) the phosphazenic P–N bonds at P(8), which bear the 1,3,2-diazaphosphorinane ring, are longer than the rest; the next two [N(1)–P(2), N(7)–P(6)] are shorter, followed by longer [P(2)–N(3), P(6)–N(5)] and again by shorter

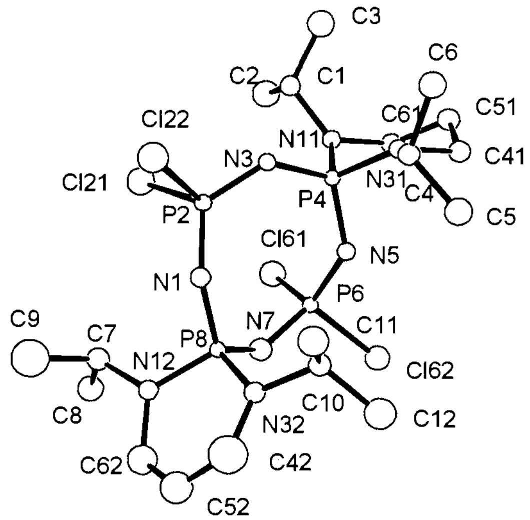

Fig. 4 Molecular structure of compound **6**; only non-hydrogen atoms are shown for clarity.

[N(3)–P(4), N(5)–P(4)] bonds. It would be interesting to see whether other 2,2-diaminocyclotetraphosphazenes also exhibit such an alternating long–short–long–short array of bonds to know more about bonding in cyclotetraphosphazenes; to our knowledge, a crystal structure is not available for any other compound.

Another interesting point in the structure of compound **5** is the unusual widening of the angle at N(7) [160.9(3)°] towards linearity; even in the acyclic derivative **8** (see below) the angle at nitrogen is much lower [140.5(2)°]. Since at N(1), which is electronically equivalent to N(7), there is no significant widening, we attribute this observation to conformational effects. The phosphazene ring is non-planar; if one considers the mean plane of the N_4P_4 ring, P(2), N(1) and N(5) are above this mean plane by 0.54, 0.30 and 0.12 Å whilst P(4), P(6), P(8), N(3) and N(7) are below this plane by 0.30, 0.18, 0.15, 0.28 and 0.22 Å respectively. The conformation of the 1,3,2-diazaphosphorinane ring is that of a flattened chair. Atoms P(8) and C(31) are above and below the mean plane containing N(11), N(31), C(41) and C(61) (coplanar to within 0.038 Å) by 0.18 and 0.31 Å respectively.

The exocyclic (to phosphazene ring) P–N bonds in compound **5** [mean: 1.626(12) Å] are shorter than those observed in $N_4P_4(NMe_2)_8$ [1.69(1) Å][11] or $N_4P_4(NC_4H_8)_8$ [1.677(7) Å],[12] suggesting a greater π character for such P–N bonds in **5**. The sums of the angles at N(11) and N(31) are 358.4 and 359.0° respectively, suggesting that the lone pair on nitrogen is involved in further bonding interactions with phosphorus.

In the dispirocyclic compound **6** (Fig. 4) the P–N bonds in the phosphazene ring are longer for the phosphorus atoms bearing the 1,3,2-diazaphosphorinane ring than those at P(2) which has a PCl_2 group. Such a significant variation is absent in the aryloxy compound 2,2,6,6-N_4P_4(O-2,6-$Cl_2C_6H_3)_4Cl_4$.[7] The average P–N bond length of 1.559 Å in **6** is close to that in the monospiro compound **5** (mean 1.551 Å). The N–P–N angles in the phosphazene ring at P(spiro) atoms P(4) and P(8) are narrower [116.7(2) and 113.0(3)°] than at the PCl_2 ends [125.9(3) and 122.6(3)°]; this feature is similar to that in **5**. Angles at nitrogen vary more [131.5(3)–151.3(4)°], possibly as a result of conformational constraints on the phosphazene ring. The P–N bonds in the six-membered rings are longer than those in the phosphazene ring, as expected.[1f]

The phosphazene ring in compound **6** has an irregular boat structure with the atoms P(8), N(1) and N(5) on the same side. The two six-membered rings show different conformations. The one at P(4) has a 'chair' conformation with P(4) and C(51) at −0.74 and 0.63 Å from the mean plane of the other four which are coplanar to within 0.01 Å. The corresponding ring at P(8)

Table 3 Selected bond lengths (Å) and angles (°) for compound **6** with e.s.d.s in parentheses

P(2)–Cl(21)	2.033(3)	P(8)–N(1)	1.578(5)
P(2)–Cl(22)	2.000(2)	P(8)–N(7)	1.569(5)
P(2)–N(1)	1.517(5)	P(8)–N(12)	1.624(5)
P(2)–N(3)	1.530(4)	P(8)–N(32)	1.631(5)
P(4)–N(3)	1.590(4)	N(11)–C(61)	1.469(8)
P(4)–N(5)	1.603(5)	N(31)–C(41)	1.466(7)
P(4)–N(11)	1.642(5)	C(41)–C(51)	1.517(10)
P(4)–N(31)	1.642(4)	C(51)–C(61)	1.513(9)
P(6)–Cl(61)	2.012(2)	N(12)–C(62)	1.440(9)
P(6)–Cl(62)	2.000(2)	N(32)–C(42)	1.393(9)
P(6)–N(5)	1.547(5)	C(42)–C(52)	1.342(14)
P(6)–N(7)	1.534(5)	C(52)–C(62)	1.413(12)
Cl(21)–P(2)–Cl(22)	100.23(14)	N(1)–P(8)–N(12)	110.1(2)
Cl(21)–P(2)–N(1)	109.2(2)	N(1)–P(8)–N(32)	108.9(3)
Cl(21)–P(2)–N(3)	107.1(2)	N(7)–P(8)–N(12)	109.7(3)
Cl(22)–P(2)–N(1)	106.5(2)	N(7)–P(8)–N(32)	111.5(3)
Cl(22)–P(2)–N(3)	104.95(19)	N(12)–P(8)–N(32)	103.2(3)
N(1)–P(2)–N(3)	125.9(3)	P(2)–N(1)–P(8)	151.3(4)
N(3)–P(4)–N(5)	116.7(2)	P(2)–N(3)–P(4)	131.5(3)
N(3)–P(4)–N(11)	111.1(3)	P(4)–N(5)–P(6)	137.0(3)
N(3)–P(4)–N(31)	107.4(2)	P(6)–N(7)–P(8)	134.5(4)
N(5)–P(4)–N(11)	108.7(2)	P(4)–N(11)–C(61)	112.5(4)
N(5)–P(4)–N(31)	107.6(3)	P(4)–N(31)–C(41)	114.1(4)
N(11)–P(4)–N(31)	104.6(2)	P(8)–N(12)–C(62)	124.2(3)
N(5)–P(6)–N(7)	122.6(3)	P(8)–N(32)–C(42)	123.1(6)
Cl(61)–P(6)–Cl(62)	98.61(13)	N(31)–C(41)–C(51)	111.6(6)
Cl(61)–P(6)–N(5)	111.9(2)	C(41)–C(51)–C(61)	113.7(5)
Cl(61)–P(6)–N(7)	107.9(3)	N(11)–C(61)–C(51)	112.0(5)
Cl(62)–P(6)–N(5)	106.5(2)	N(32)–C(42)–C(52)	123.2(9)
Cl(62)–P(6)–N(7)	106.5(3)	C(42)–C(52)–C(62)	123.0(7)
N(1)–P(8)–N(7)	113.0(3)	N(12)–C(62)–C(52)	115.5(7)

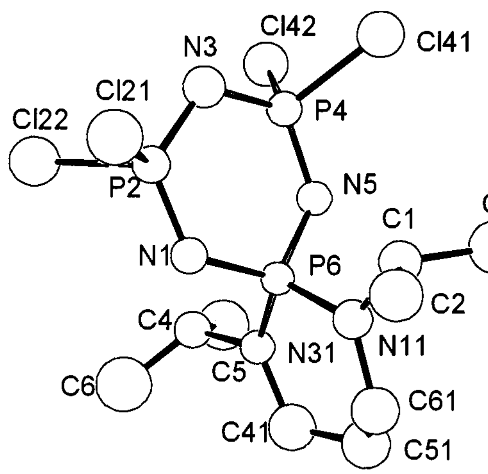

Fig. 5 Molecular structure of compound **7**; only non-hydrogen atoms are shown for clarity.

has a flattened 'boat' conformation with N(12) and C(42) at 0.37 and 0.09 Å above the mean of the remaining four (coplanar to within 0.03 Å). This latter feature is similar to that found in the five-co-ordinated phosphorane $(C_{14}H_8O_2)$(2,6-$Me_2C_6H_3O$)P[(Me)$NCH_2CH_2CH_2N$(Me)].[16]

As is observed in other monospirocyclic diaminocyclotriphosphazenes,[1h] the P–N bond lengths in compound **7** (Fig. 5) vary as *P*(spiro)-*N*-PCl_2 > Cl_2*P*-*N*-PCl_2 > P(spiro)-*N*-*P*Cl_2. However, the interesting point in the structure of **7** is that the P–N bonds to the 1,3,2-diazaphosphorinane ring [mean: 1.623(4) Å] are nearly of the same length as the phosphazenic P(spiro)–N bonds [mean: 1.623(6) Å]. The phosphazene N–P(spiro)–N angle is close to that observed for the analogous derivative **5**. The phosphazene ring is planar to within ±0.09 Å and the diazaphosphorinane ring has a chair conformation.

The sums of the bond angles at N(11) and N(31) are, respectively, 359.8 and 359.3° and are thus close to planarity; these deviate from the plane of the three atoms to which they are

Table 4 Selected bond lengths (Å) and angles (°) for compound **7** with e.s.d.s in parentheses

P(2)–Cl(21)	1.994(2)	P(6)–N(5)	1.617(4)
P(2)–Cl(22)	2.016(2)	P(6)–N(11)	1.622(4)
P(2)–N(1)	1.545(4)	P(6)–N(7)	1.623(4)
P(2)–N(3)	1.574(4)	N(11)–C(1)	1.472(6)
P(4)–Cl(41)	2.0027(19)	N(31)–C(4)	1.470(6)
P(4)–Cl(42)	2.002(2)	N(31)–C(41)	1.443(6)
P(4)–N(3)	1.585(4)	C(41)–C(51)	1.426(8)
P(4)–N(5)	1.550(4)	C(51)–C(61)	1.419(9)
P(6)–N(1)	1.629(4)		
Cl(21)–P(2)–Cl(22)	99.54(10)	N(5)–P(6)–N(11)	109.2(2)
Cl(21)–P(2)–N(1)	108.84(17)	N(5)–P(6)–N(31)	110.7(2)
Cl(21)–P(2)–N(3)	107.7(2)	N(11)–P(6)–N(31)	105.6(2)
Cl(22)–P(2)–N(1)	110.13(17)	P(2)–N(1)–P(8)	124.9(2)
Cl(22)–P(2)–N(3)	107.67(19)	P(2)–N(3)–P(4)	117.1(2)
N(1)–P(2)–N(3)	120.9(2)	P(4)–N(5)–P(6)	125.1(2)
Cl(41)–P(4)–Cl(42)	99.58(10)	P(6)–N(11)–C(61)	124.2(3)
Cl(41)–P(4)–N(3)	106.58(19)	P(6)–N(11)–C(1)	118.1(3)
Cl(41)–P(4)–N(5)	110.66(16)	C(1)–N(11)–C(61)	118.2(4)
Cl(42)–P(4)–N(3)	108.7(2)	P(6)–N(31)–C(41)	123.2(4)
Cl(42)–P(4)–N(5)	108.97(18)	P(6)–N(31)–C(4)	117.5(3)
N(3)–P(4)–N(5)	120.4(2)	C(4)–N(31)–C(41)	117.4(4)
N(1)–P(6)–N(5)	110.35(18)	N(31)–C(41)–C(51)	117.6(7)
N(1)–P(6)–N(11)	111.6(2)	C(41)–C(51)–C(61)	121.0(7)
N(1)–P(6)–N(31)	109.3(2)	N(11)–C(61)–C(51)	119.5(6)

Table 5 Selected bond lengths (Å) and angles (°) for compound **8** with e.s.d.s in parentheses

P(1)–O(1)	1.437(3)	P(2)–Cl(3)	1.9764(13)
P(1)–N(1)	1.560(3)	O(2)–C(1)	1.432(4)
P(1)–Cl(1)	2.020(2)	O(3)–C(11)	1.432(4)
P(1)–Cl(2)	2.003(2)	C(1)–C(6)	1.388(5)
P(2)–N(1)	1.526(3)	C(6)–C(21)	1.512(5)
P(2)–O(3)	1.558(2)	C(11)–C(16)	1.390(5)
P(2)–O(2)	1.560(2)	C(16)–C(21)	1.512(5)
O(1)–P(1)–N(1)	119.2(2)	O(3)–P(2)–Cl(3)	106.60(10)
O(1)–P(1)–Cl(2)	110.3(2)	O(2)–P(2)–Cl(3)	106.21(10)
N(1)–P(1)–Cl(2)	105.62(14)	P(2)–O(2)–C(1)	126.8(2)
O(1)–P(1)–Cl(1)	110.8(2)	P(2)–O(3)–C(11)	129.4(2)
N(1)–P(1)–Cl(1)	108.07(14)	P(1)–N(1)–P(2)	140.5(2)
Cl(1)–P(1)–Cl(2)	101.34(8)	O(2)–C(1)–C(6)	116.5(3)
N(1)–P(2)–O(3)	109.8(2)	C(1)–C(6)–C(21)	122.0(3)
N(1)–P(2)–O(2)	111.5(2)	O(3)–C(11)–C(16)	117.1(3)
O(3)–P(2)–O(2)	110.55(13)	C(11)–C(16)–C(21)	121.6(3)
N(1)–P(2)–Cl(3)	112.04(14)	C(6)–C(21)–C(16)	117.2(3)

bonded by 0.03 and 0.08 Å respectively. In the compound 2,2-N_3P_3[(Me)$NCH_2CH_2CH_2N$(Me)]Cl_4 reported by Shaw and co-workers,[1d] the corresponding sum of the angles is 351° suggesting an appreciable amount of sp^3 character; this was the reason attributed to the lower coupling constants in the ^{13}C NMR of this compound. However, for **5** also ^2J(P–C) and ^3J(P–C) values are very low (<3 Hz; only singlets observed) and hence we believe that other factors may also be operative which lead to this observation.

In the monocyclic derivative **8** (Fig. 6) the P=N distance is short but close to that in the parent compound $Cl_2P(O)$-N=PCl_3 **3** (mean 1.521 Å)[17] and $Cl_2P(O)N$=P(O-2,6-$C_6H_3Cl_2)_3$ **14** [1.515(4) Å].[7] What is probably more significant is the $Cl_2P(O)$–N bond length of 1.560(3) Å; this is shorter than that in the parent compound **3** (mean 1.587 Å) but is close to that in **14** [1.567(4) Å]. Noting that in this linear phosphazene there are no resonance forms available as in cyclotri- or cyclotetra-phosphazenes, this P–N bond should be essentially a single bond for book-keeping purposes, but still is considerably shorter than the P–N single bond distance of 1.769(19) Å in the phosphoramidate salt NaH_3NPO_3[18a] or of 1.800(4) Å in KH_3NPO_3.[18b]

In contrast to the 'boat' conformation found in compound **4** for the 1,3,2-dioxaphosphocine ring, a 'boat-chair' conform-

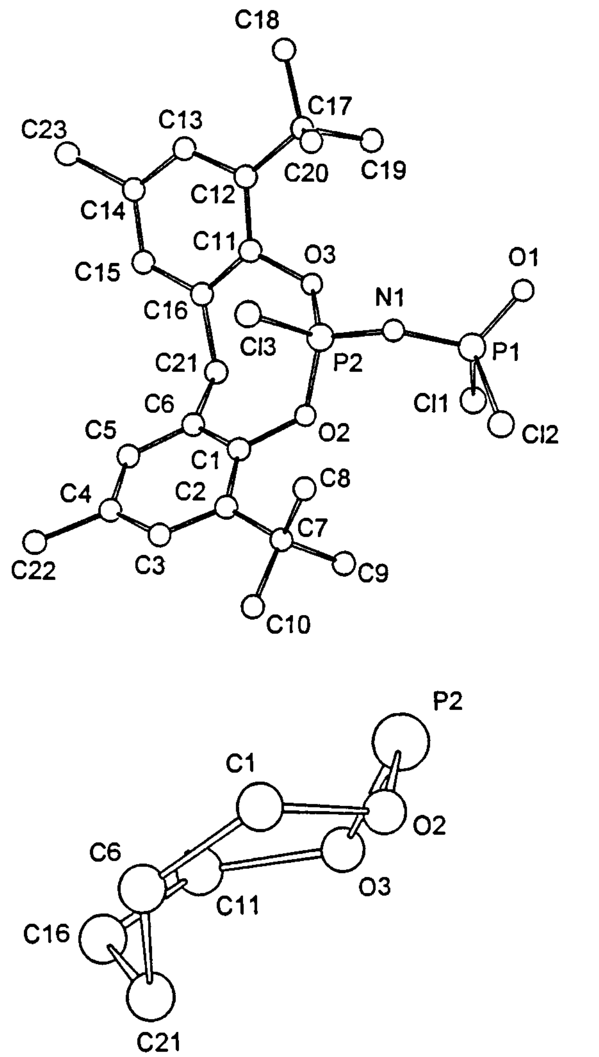

Fig. 6 Molecular structure of compound **8**; only non-hydrogen atoms are shown for clarity.

ation[10b] is found for the same ring in **8** (*cf.* Fig. 6); the atoms C(1), C(6), C(11) and C(16) are coplanar to within ±0.02 Å while P(2), O(2), O(3) and C(2) are above this plane by 0.16, 0.67, 0.61 and 0.76 Å respectively.

Conclusion

This study shows that the formation of spirocyclic derivatives in the reaction of $N_4P_4Cl_8$ **1** with diamines/diols is a favoured pathway. The relatively greater stability of these compounds may be associated with steric factors that make sites close to P(spiro) hindered. The spirocyclic tetraphosphazenes **4**–**6** represent the first members in this series to be studied by X-ray crystallography; these studies are likely to be useful in understanding the nature of the P–N bond in cyclic tri- *vs.* tetra-phosphazenes. While considering the bonding in cyclophosphazenes, often an sp^2 mixing of orbitals[19] for nitrogen is assumed; in view of the wide angles at nitrogen (≈ 160°) observed in the tetraphosphazene series (*e.g.* **5**) it may be worth reconsidering this model.

Experimental

Chemicals and solvents were from Aldrich/Fluka or from local manufacturers. Further purification was done according to standard procedures.[20] All operations, unless stated otherwise, were carried out under a dry nitrogen atmosphere using standard Schlenk techniques.[21] The ^1H, ^{13}C and ^{31}P (operating at 80.961 MHz) NMR spectra were recorded on a Bruker 200 MHz spectrometer in $CDCl_3$ solutions with shifts referenced to $SiMe_4$ (^1H, ^{13}C; δ 0) and external 85% H_3PO_4 (δ 0) respectively. The IR spectra were recorded on either a Perkin-Elmer 1310 or a JASCO FT-IR 5300 spectrophotometer. Elemental analyses were carried out on a Perkin-Elmer 240C CHN analyser. Melting points are uncorrected.

Syntheses

(a) 2,2-N_4P_4\{[O-4,6-(*t*-Bu)$_2C_6H_2]_2CH_2$\}Cl_6·0.5$C_4H_8Cl_2$ 4·0.5$C_4H_8Cl_2$. Methylenebis(4,6-di-*tert*-butylphenol)[22] (0.55 g, 1.3 mmol) was refluxed with an excess of sodium leaves in dry THF (20 cm^3) for 3 d. Unchanged sodium was then removed by forceps. To the remaining suspension, $N_4P_4Cl_8$ **1** (0.6 g, 1.3 mmol) in THF (10 cm^3) was added dropwise (10 min) and the mixture refluxed for 1 d. Then THF was removed *in vacuo* and hexane added to the residue. The insoluble material was filtered off and the solvent removed from the filtrate. The gummy residue was crystallised from cyclohexane at 25 °C to afford **4**·0.5$C_4H_8Cl_2$ [*cf.* crystal structure; the source of 1,4-dichlorobutane ($C_4H_8Cl_2$) is likely to be THF. It is known that HBr reacts with THF to give 1,4-$C_4H_8Br_2$.[23] In our case the reaction of THF with HCl is possibly mediated by $N_4P_4Cl_8$; formation of 1,4-dichlorobutane from THF has been found to occur in the presence of P(O)Cl_3 also.[24] We had earlier experienced facile chlorination of α-hydroxy phosphonates by $N_4P_4Cl_8$.[25]]. Yield 0.26 g (23%); mp 178–179 °C [Found (after drying at 0.5 mmHg, 4 h): C, 42.42; H, 5.28; N, 6.90. $C_{29}H_{42}Cl_6N_4O_2P_4$ requires C, 42.72; H, 5.19; N, 6.87%. $C_{31}H_{46}Cl_7N_4O_2P_4$ requires C, 42.37; H, 5.28; N, 6.38%]. ^1H NMR (after evacuating at 0.5 mmHg, 4 h): δ 1.30, 1.42, 1.44, 1.47 (s each, 36 H, *t*-Bu), 4.10 (br, 2H, CH_2), 7.20, 7.40 (s each, 4H, aryl H); two triplets of low intensity at 3.45 and 3.50, assignable to 1,2-dichlorobutane, were also observed. ^{31}P NMR: δ −25.2 [t, P(spiro), ^2J(P–P) = 72.0], −14.1 [dd, 2PCl_2, ^2J(P–P) = 72.0, 26.4] and −9.9 [t, PCl_2, ^2J(P–P) = 26.4 Hz].

An analogous reaction using 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) did not give any isolable product.

(b) 2,2-N_4P_4[(*i*-Pr)$NCH_2CH_2CH_2N$(*i*-Pr)]Cl_6 5. To a stirred solution of compound **1** (0.59 g, 1.27 mmol) in CH_2Cl_2 (10 cm^3) at 5 °C was added dropwise a solution of *N*,*N*′-diisopropylpropane-1,3-diamine (0.40 g, 2.54 mmol) in CH_2Cl_2 (10 cm^3). The mixture was stirred at 25 °C for 4 h and the solvent removed *in vacuo*. Toluene was added and the insoluble amine hydrochloride filtered off. The filtrate was concentrated to a small volume (0.2 cm^3) and kept at −20 °C to give crystals of **5**; on evaporation of the mother-liquor more compound was obtained. Total yield 0.46 g (66%); mp 90–92 °C (Found: C, 19.82; H, 3.80; N, 15.48. $C_9H_{20}Cl_6N_6P_4$ requires C, 19.69, H, 3.67; N, 15.31%). ^1H NMR: δ 1.16 [d, 12H, ^3J(H–H) = 6.4, CH_3], 1.80 [qnt, 2H, ^3J(H–H) = 6.0, CCH_2], 3.05 [dt, 4H, ^3J(P–H) ≈ 16, ^3J(H–H) = 6.0 Hz, NCH_2] and 3.86 (m, 2H, NC*H*Me_2). ^{13}C NMR: δ 20.6, 27.2, 37.8 and 46.5. ^{31}P NMR: δ −14.6 [t, ^2J(P–P) = 26.0 Hz, P(spiro)], −6.2 to −7.5 (m, PCl_2).

(c) 2,2,6,6-N_4P_4[(*i*-Pr)$NCH_2CH_2CH_2N$(*i*-Pr)]$_2Cl_4$ 6. To compound **5** (0.68 g, 1.23 mmol) in CH_2Cl_2 (10 cm^3), *N*,*N*′-diisopropylpropane-1,3-diamine (0.39 g, 2.47 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise (15 min) and the mixture stirred overnight at 30 °C. The solvent was completely removed, and hexane (15 cm^3) added to the residue. Filtration followed by concentration of the solution to *ca.* 2 cm^3 afforded crystalline **6**. Yield 0.4 g (51%); mp 200–202 °C (Found: C, 33.98; H, 6.20; N, 17.60. $C_{18}H_{40}Cl_4N_8P_4$ requires C, 34.08; H, 6.35; N, 17.66%). ^1H NMR: δ 1.17 (d, 12 H, CH_3), 1.81 (qnt, 2H, CCH_2), 3.10 [dt, 4H, ^3J(P–H) = 16.0, ^3J(H–H) ≈ 6.0 Hz, NCH_2] and 3.60 (m, 2H, NC*H*Me_2). ^{13}C NMR: δ 19.9, 26.3, 38.2 and 45.7. ^{31}P NMR: δ −19.4 [t, P(spiro), ^2J(P–P) = 25.6] and −5.8 [t, ^2J(P–P) = 25.6 Hz, PCl_2].

(d) 2,2-N_3P_3[(*i*-Pr)$NCH_2CH_2CH_2N$(*i*-Pr)]Cl_4 7. This compound was prepared by a route analogous to that for **5** using $N_3P_3Cl_6$ **2** (0.69 g, 2 mmol) and *N,N′*-diisopropylpropane-1,3-diamine (0.63 g, 4 mmol). It was crystallised from hexane. Yield 0.61 g (70%); mp 150–152 °C (Found: C, 24.85; H, 4.60; N, 16.05. $C_9H_{20}Cl_4N_5P_3$ requires C, 24.96; H, 4.65; N, 16.17%). ^{1}H NMR: δ 1.13 [d, 12H, ^3J(H–H) = 6.4, CH_3], 1.75 (qnt, 2H, CCH_2), 3.00 (dt, J = 16.0, 6.0 Hz, NCH_2) and 3.95 (m, 2H, C*H*Me_2). ^{13}C NMR: δ 19.9, 26.3, 38.2 and 45.7. ^{31}P NMR: δ 6.3 [t, ^2J(P–P) = 36.8] and 20.6 [d, ^2J(P–P) = 36.8 Hz].

(e) $Cl_2P(O)N{=}P$[(O-4-Me-6-*t*-Bu$C_6H_2)_2CH_2$]Cl 8. To Cl_2-P(O)N=PCl_3 **3** (0.78 g, 2.9 mmol) in toluene (25 cm^3) a solution of 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) (0.99 g, 2.9 mmol) and triethylamine (0.58 g, 5.8 mmol) in toluene (10 cm^3) was added dropwise at 25 °C (15 min). The mixture was stirred overnight, filtered and the filtrate concentrated to *ca.* 10 cm^3. An oily material separated, which was extracted with hot benzene. Cooling the benzene solution to 25 °C afforded compound **8**. Yield 0.9 g (52%); mp 188 °C (Found: C, 49.85; H, 5.37; N, 2.40. $C_{23}H_{30}Cl_3NO_3P_2$ requires C, 49.97; H, 5.47; N, 2.53%). ^{1}H NMR: δ 1.40 (s, 18H, *t*-Bu), 2.30 (s, 6H, CH_3), 3.60 [d, ^{1}H, $^2J(H_A–H_B)$ = 18.0, $C_6H_2CH_AH_B$], 4.32 (d, ^2J = 18.0 Hz, $C_6H_2CH_AH_B$), 7.15, 7.20 (s each, 4H, aryl H). ^{31}P NMR: δ −15.4, −13.8 [AB quartet; J(AB) ≈ 60 Hz].

(f) N_3P_3[O-4-Me-6-*t*-Bu$C_6H_2CH_2$-4-Me-6-*t*-BuC_6H_2OH]Cl_5 9. A procedure similar to (**a**) above was followed using the diol (1.08 g, 3.1 mmol) and compound **2** (1.06 g, 3.11 mmol). The reaction mixture was chromatographed (hexane, CH_2Cl_2) to remove the unchanged diol and the residue was heated at 100 °C, 0.5 mmHg to remove most unchanged **2** (*ca.* 0.2 g) to afford 0.3 g of a gummy material. ^{31}P NMR: (a) δ (*ca.* 80%) 21.7 [d, 2P, ^2J(P–P) = 61.0] and 8.2 [t, 1P, ^2J(P–P) = 61 Hz] (assigned to **9**); (b) δ (*ca.* 10%) 19.3 (assigned to **2**); (c) (*ca.* 10%) 21.1 [d, ^2J(P–P) ≈ 72] and −7.63 [t, ^2J(P–P) ≈ 72 Hz]. Pure **9** could be obtained as a semisolid by column chromatography using dichloromethane–hexane as eluent (Found: C, 42.61; H, 4.91; N, 6.55. $C_{23}H_{31}Cl_5N_3O_2P_3$ requires C, 42.39; H, 4.79; N, 6.45%). ^{1}H NMR: δ 1.42, 1.50 (s each, 18H, *t*-Bu), 2.22, 2.32 (s each, 6H, $C_6H_2CH_3$), 4.20 (s, 2H, $C_6H_2CH_2$), 6.65, 6.80, 7.20,7.30 (s each, total 4H, aryl H). ^{31}P NMR: δ 21.7 [d, 2P, ^2J(P–P) = 61.0] and 8.2 [t, 1P, ^2J(P–P) = 61 Hz]. MS: *m*/*z* 649, [M(^{35}Cl)]$^+$; 613, [M(^{35}Cl) − HCl]$^+$.

(g) N_3P_3[(*i*-Pr)$NCH_2CH_2CH_2N$(*i*-Pr)]F_4 10. To a stirred solution of compound **7** (0.52 g, 1.2 mmol) in methyl cyanide (20 cm^3) was added KF (dried at 120 °C for 2 d, 1.04 g, 18 mmol) in one portion at 25 °C. The mixture was heated under reflux for 36 h, cooled and filtered. Removal of solvent gave a solid that was crystallised from toluene to give compound **10**. Yield 0.35 g (80%); mp 64–66 °C (Found: C, 28.95; H, 5.20; N, 18.58. $C_9H_{20}F_4N_5P_3$ requires C, 29.43; H, 5.45; N, 19.07%). ^{1}H NMR: δ 1.16 (d, J = 6.0, 12 H, CH_3), 1.88 (qnt, J = 6.0, 2H, CCH_2), 3.07 (td, 4H, J = 14.1, 6.6 Hz, NCH_2) and 3.56–3.65 (m, 2H, NC*H*Me_2). ^{13}C NMR: δ 20.1, 26.5, 37.9 and 45.7. ^{31}P NMR: δ 15.4 [1P, P(spiro), ^2J(P–P) ≈ 90] and 11.4 [2P, ^1J(P–F) ≈ 965 Hz, PF_2].

(h) Fluorination of compound 5. The procedure was the same as above in (**g**) using compound **5** (0.66 g, 1.2 mmol) and KF (1.04 g, 18 mmol). A very hygroscopic solid (0.35 g), probably $N_4P_4F_5$(OH)[N(*i*-Pr)$CH_2CH_2CH_2N$(*i*-Pr)] (**A**, see mass spectrum below), was isolated (Found: C, 23.75; H, 4.96; N, 18.55. $C_9H_{21}F_5N_6OP_4$ requires C, 24.12; H, 4.72; N, 18.75%). ^{1}H NMR: δ 1.10–1.30 (br m, ≈12H, CH_3), 1.60–1.90 (br, 2H, CCH_2), 2.80–3.20 (br, 4H, NCH_2) and 3.80–4.20 (br, 2H, NC*H*Me_2). ^{31}P NMR: δ −14.6 [tt, ^1J(P–F) ≈ 850, ^2J(P–P) ≈ 81 Hz, PF_2], −2.3 to 2.5 [m, P(spiro)] and −11.0 (m, unassigned). MS: *m*/*z* 434 {80, [**A** − CH_3 + H]$^+$}, 349 (10), 334 (25), 293 {25%, [$N_4P_4HF_5$(OH)]$^+$; this type of ion with the phosphazene skeleton intact is typical for fluorocyclotriphosphazenes N_3P_3(X–Y)F_4;[16] the latter compounds show peaks at *m*/*z* corresponding to [$N_3P_3HF_4$]$^+$}.

(i) Reaction of compound 5 with methylamine: formation of 11 and 12. To a stirred solution of an excess of methylamine (*ca.* 1 g, 33 mmol) and triethylamine (2 cm^3) in chloroform (10 cm^3) maintained at −60 °C was added compound **5** (0.4 g, 0.7 mmol) all at once with continuous stirring. After the reaction mixture reached 25 °C it was refluxed (using acetone slush on the top) for 2 h. The solvent was removed and toluene (10 cm^3) added to the residue. Filtration followed by concentration of the solution gave a solid mixture. Yield ≈ 0.26 g. From this, compound **12**, mp 214–216 °C (*ca.* 50 mg) was isolated in a pure state (^{31}P NMR) using CH_2Cl_2 solvent at 66 °C (Found: C, 34.68; H, 8.14; N, 31.82. $C_{14}H_{39}N_{11}P_4$ requires C, 34.63; H, 8.11; N, 31.74%). ^{1}H NMR: δ 1.08 (d, J = 6.7, 6H, CHC*H*$_3$), 1.15 (d, J = 6.6, 6H, CHC*H*$_3$), 1.72 (qnt, J = 6.2 Hz, CCH_2), 2.10 (br, ≈2H, N*H*Me), 2.50–2.75 (complex, 11 lines, 15H, NCH_3), 3.00 (two q, 4H, NCH_2) and 4.20 (m, 2H, NCH). ^{31}P NMR: δ 19.8 (dd or t, 2P, J = 40), 17.1 (t, 1P, J ≈ 40) and 14.7 (t, 1P, J ≈ 40 Hz). MS: 485 (M$^+$), 473, 442, 426, 411, 384, 361, 330 {100%, [M−(*i*-Pr)$NCH_2CH_2CH_2N$(*i*-Pr) + H]$^+$}. Two peaks of low intensity at *m*/*z* 538 and 516 were also observed.

^{1}H NMR (residue; **11** + **12**, *ca.* 1:1 based on ^{31}P NMR): δ 1.10 [d, J ≈ 6.0, CH(C*H*$_3$)$_2$], 1.70 (m, CH_2), 2.45 [d, ^3J(P–H) ≈ 20 Hz, NCH_3], 2.60 (m, NCH_3), 2.80–3.20 (m, NCH_2) and 3.90–4.20 (m, C*H*Me_2). ^{31}P NMR (excluding peaks for **12**): δ 8.0 (t or dd, 1P, ^2J ≈ 34), 6.2 (t, 1P, ^2J ≈ 27) and −1.9 (t, 1P, ^2J ≈ 27 Hz). An attempt to obtain compound **12** in a pure state by treating **5** with an excess of methylamine in diethyl ether was not successful; only **11** could be isolated in a pure state from this reaction also.

(j) 2,2,6,6-N_4P_4[(*i*-Pr)$NCH_2CH_2CH_2N$(*i*-Pr)]$_2$(NHMe)$_4$ 13. To methylamine (*ca.* 1 cm^3; taken in excess) in dichloromethane (10 cm^3) maintained at −78 °C, compound **6** (0.19 g, 0.3 mmol) in dichloromethane (10 cm^3) was added and the mixture stirred at this temperature for 4 h. Then the contents were allowed to attain room temperature while stirring (8 h). Solvent was removed and toluene (10 cm^3) added to the residue. Filtration followed by concentration afforded **13** as a crystalline solid. Yield 0.1 g (53%); mp 163 °C (Found: C, 43.94; H, 9.45; N, 26.49. $C_{11}H_{28}N_6P_2$ requires C, 43.12; H, 9.21; N, 27.4%). ^{1}H NMR: δ 1.06 (d, J = 14.0, 24 H, CHC*H*$_3$), 1.61 (qnt, J = 6.2, 4H, CCH_2), 2.50 (d, J = 20.0 Hz, 12H, NCH_3), 3.05 (two q, 8H, NCH_2) and 4.20 (m, 4H, NCH). ^{13}C NMR: δ 21.2, 27.3, 28.5, 39.2 and 45.7. ^{31}P NMR: δ 1.8 (t, 2P, ^2J = 33) and 4.1 (t, 2P, ^2J = 33 Hz).

X-Ray crystallography

Suitable crystals were mounted inside a capillary (**4**·0.5$C_4H_8Cl_2$, **5**, **6**, **8**) or on a glass fibre (**7**). Data were collected on an Enraf-Nonius CAD4 (**4**·0.5$C_4H_8Cl_2$, **6**, **8**) or MACH3 (**5**, **7**) diffractometer using Mo-Kα (λ = 0.7107 Å) radiation. The details pertaining to data collection and refinement are listed in Table 6. The structures were solved by conventional methods.[26] Refinement was done on F for compound **4**·0.5$C_4H_8Cl_2$ and **5** (XTAL 3)[27] and on F^2 for **6**–**8** [SHELXL 93, SHELXL 97].[26] Only in the case of **8** an absorption correction based on ψ scans was applied. In view of the observation that (i) for **8** T_{max} and T_{min} differed only by 1% at maximum, (ii) compound **4** underwent decomposition under the X-ray beam and (iii) μ values are not high, absorption corrections for **4**–**7** were not applied. All non-hydrogen atoms were refined anisotropically. The H atoms were placed at calculated positions and not refined [U(H) = 0.035 Å^2] for **4**·0.5$C_4H_8Cl_2$, whereas for **5** they were refined isotropically except for H611 and H612. For **6**–**8** H atoms were

Table 6 Crystal data for compounds $\mathbf{4}\cdot0.5C_4H_8Cl_2$ and **5–8**

	$\mathbf{4}\cdot0.5C_4H_8Cl_2$	**5**	**6**	**7**	**8**
Empirical formula	$C_{29}H_{42}Cl_6N_4O_2P_4\cdot0.5C_4H_8Cl_2$	$C_9H_{20}Cl_6N_6P_4$	$C_{18}H_{40}Cl_4N_8P_4$	$C_9H_{20}Cl_4N_5P_3$	$C_{23}H_{30}Cl_3NO_3P_2$
M	880.80	568.91	634.26	433.01	536.77
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$	$P2_1/n$	$Pbca$
a/Å	11.154(14)	11.373(3)	10.058(11)	12.449(3)	11.188(2)
b/Å	11.703(2)	16.955(6)	16.7959(14)	11.725(3)	17.743(2)
c/Å	17.428(5)	12.570(4)	18.0196(18)	13.366(3)	26.405(2)
α/°	106.34(2)				
β/°	104.25(5)	111.28(2)		90.67(2)	
γ/°	89.85(4)				
V/Å^3	2110.9(9.7)	2259(6)	3044(3)	1950.8(7)	5241.6(12)
Z	2	4	4	4	8
D_c/g cm^{-3}	1.383	1.614	1.384	1.474	1.360
T/K	293	173	293	293	293
μ/mm^{-1}	0.59	1.06	0.623	0.852	0.497
F(000)	910	1112	1328	888	2240
Crystal size/mm	0.7 × 0.5 × 0.3	0.8 × 0.4 × 0.3	0.4 × 0.3 × 0.3	0.5 × 0.4 × 0.3	0.42 × 0.42 × 0.4
Reflections collected	7632	4304	3051	3576	4539
Independent reflections	7367	3953	3051	3418	4536
R_{int}	0.043	0.022	0.000	0.0402	0.0065
Data	3850 [$I > 4\sigma(I)$]	3806 [$I > 2\sigma(I)$]	2655 [$I > 2\sigma(I)$]	2228 [$I > 2\sigma(I)$]	3059 [$I > 2\sigma(I)$]
Parameters	433	298	315	194	301
R	0.106	0.048	0.0457	0.0567	0.0562
wR	0.062	0.036	0.1187	0.1426	0.1311
S	2.27	2.60	1.058	1.028	1.082
Maximum, minimum peak in difference map/e Å^{-3}	1.3, −1.6	0.55, −0.59	0.567, −0.434	0.535, −0.354	0.414, −0.615

included at idealised positions using a riding model and not refined. In the structure of $\mathbf{4}\cdot0.5C_4H_8Cl_2$ there is some high residual density in the neighbourhood of two chlorine atoms Cl(01) and Cl(61); this is a consequence of poor quality of the crystals and hence the data. There was 8.5% decay during data collection for $\mathbf{4}\cdot0.5C_4H_8Cl_2$; in the structure there is a highly disordered 1,4-dichlorobutane (half molecule in the asymmetric unit) in addition to a disordered *tert*-butyl group. Hence the R value for this compound is rather high.

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See http://www.rsc.org/suppdata/dt/1999/891/ for crystallographic files in .cif format.

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