Retention of Configuration in the Nucleophilic Substitution Reactions of Some Nine-Membered Ansa Derivatives of Cyclotriphosphazatriene

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Abstract: X-ray crystallographic evidence shows that nucleophilic substitution reactions of two different types of cyclophosphazene derivatives with relatively rigid nine-membered ansa rings leads to the first demonstration of retention of configuration in these molecular systems.

Keywords: ansa rings · configuration determination · nucleophilic substitution · phosphazenes · retention of configuration

Introduction

The stereogenic effects of nucleophilic substitution at aliphatic carbon compounds lead predominantly to racemization (S_N1) or inversion (S_N2) at the reaction centre, whereas retention of configuration (e.g. S_Ni) is only rarely observed.[1] Similar observations pertain to phosphorus(v) compounds where the $S_N2(P)$ mechanism leads to inversion,[2] whilst a rarer mechanism, pseudorotation, may give rise to retention of configuration;[2] the latter has generally been associated with five-membered rings. Although there have been many synthetic and mechanistic studies on cyclophosphazenes,[3] which amongst other things demonstrated associative and dissociative pathways,[3,4] the question of inversion or retention of configuration does not seem to have been considered. A major reason may be that the chiral properties of cyclophosphazenes, despite being realised a number of years ago,[5] were not explored experimentally until recently,[6] other than for two types of examples; one in which an optically active acyclic precursor was cyclised[7] and the other in which the substituent group is stereogenic.[8] However, using X-ray crystallographic structural evidence we demonstrated recently that inversion of configuration occurred in nucleophilic substitution reactions on the two phosphorus atoms adjacent to the ansa groups of macrocyclic-cyclophosphazene derivatives in which the ansa ring has sixteen atoms.[6] Starting with a *cis*-ansa macrocyclic-cyclophosphazene, which is *meso*, the first substitution geminal to the ansa bridge gave a racemic product with the ansa ring in a *trans*-configuration, and the second substitution gave a product which is also *meso* with the ansa ring in the *cis*-configuration.[6] We now provide X-ray crystallographic evidence to demonstrate that nucleophilic substitution of cyclophosphazene derivatives with nine-membered *cis*-ansa rings leads to retention of configuration. The effect is observed in two different molecular systems; nucleophilic substitution (Scheme 1) of the tetrafluorobutanedioxy derivative, $N_3P_3Cl_4(OCH_2CF_2CF_2CH_2O)$ (**1**),[9] which has a *cis*-ansa ring with nine atoms including those in the cyclophosphazene ring, and nucleophilic substitution (Scheme 2) of the tricyclic compound (**5**),[10] in which the two atoms linking the nine-membered *cis*-ansa ring in the ansa bridge to the cyclophosphazene group are nitrogen rather than the oxygen atoms as in (**1**) (and the macrocyclic-cyclophosphazene derivatives[6]).

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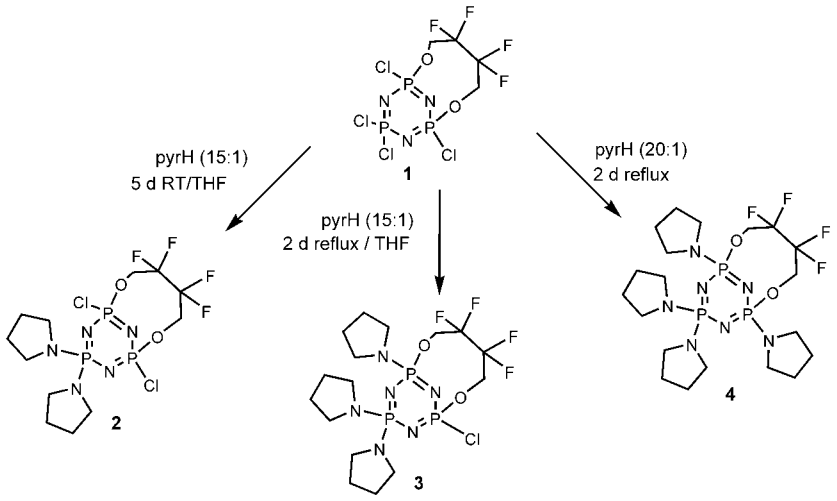
Results

Synthesis and characterisation of compounds 2–4 and 6–8: Nucleophilic substitution of **1**[9] with pyrrolidine (pyrH) replaces the remaining four P–Cl bonds with two, three, and then four pyrrolidino groups as shown in Scheme 1. The first two P–Cl bonds to react are those of the PCl_2 group to form $N_3P_3Cl_2(OCH_2CF_2CF_2CH_2O)(pyr)_2$ (**2**) and then there is reaction of the third and fourth P–Cl bonds geminal to the ansa moiety to give compounds, $N_3P_3Cl(OCH_2CF_2CF_2$-

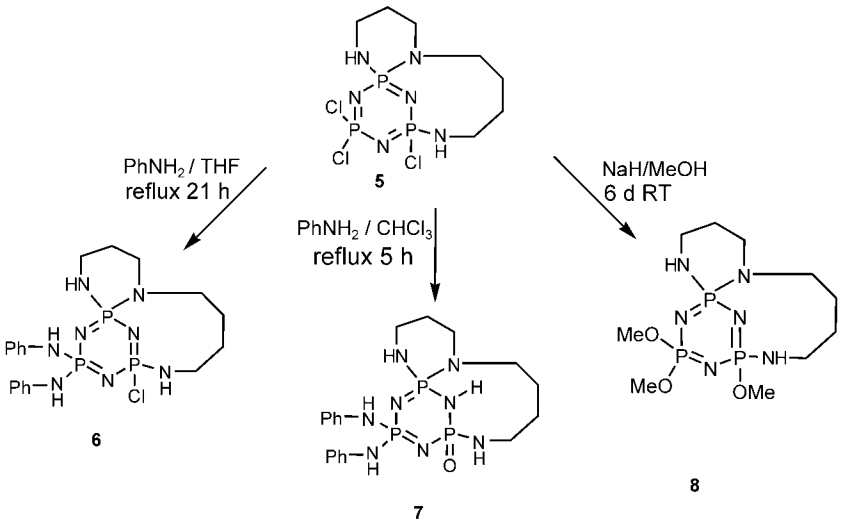
 DOI: 10.1002/chem.200400311



Scheme 1. Successive nucleophilic substitution reactions with pyrrolidine of **1**, which has a nine-membered *cis*-ansa ring with P–O linkages to the cyclophosphazene ring.

$CH_2O)(pyr)_3$ (**3**) and $N_3P_3(OCH_2CF_2CF_2CH_2O)(pyr)_4$ (**4**), respectively.

Cyclophosphazene derivative **5**[10] also has a nine-membered *cis*-ansa ring in which the two atoms linking the ansa bridge to the group are nitrogen rather than the oxygen atoms as in **1** and the macrocyclic cyclophosphazene derivatives.[6] Reactions of **5** with a variety of nucleophiles [for example, NH_2tBu, pyrH, $H_2N(CH_2)_3OH$] initially replace both chlorine atoms at the PCl_2 group to form compounds analogous to **6**, but the reaction seems to be reluctant to proceed further with *neutral* nucleophiles even after prolonged heating of the reaction mixtures under reflux. However, with the weak nucleophile, $PhNH_2$, inadvertent hydrolysis by the even weaker, but smaller, nucleophile, H_2O, also occurred and took place at the remaining P–Cl group to give the tautomerised structure **7** (Scheme 2). Compound **5** also reacted with the sterically small, but strong, *anionic* nucleophile NaOMe, which replaces all three chlorine atoms to give **8** (Scheme 2).



Scheme 2. Nucleophilic substitution reactions of tricyclic compound **5**, which has a nine-membered *cis*-ansa ring with P–N linkages to the cyclophosphazene ring.

Details of the synthesis and characterisation (EA, MS, ^1H NMR) of compounds **2–4** and **6–8** are provided in the Experimental Section and their characterisation by ^{31}P NMR is summarised in Table 1.

X-ray crystal structures of compounds 2–4 and 6–8: The crystal structures of compounds **2**, **3** and **4**, which are fused bicyclic systems, are summarised in Figure 1a–c, respectively. The tetrafluorobutanedioxy ring of the starting compound **1** has a *cis*-ansa configuration[9] and it is also found that the tetrafluorobutanedioxy ring in each of the three compounds **2–4** has retained its *cis*-ansa configuration; in particular, the tripyrrolidino derivative **3** can only be formed with retention of configuration at the >P(OR)Cl site that is substituted by the pyrrolidino group.

It is observed that the ansa loop in each of the three compounds **2–4** has a similar overall conformation of the P-O-CH_2-CF_2-CF_2-CH_2-O-P moiety, in which the CF_2-CF_2 groups and one of the pairs of the CH_2-CF_2 groups adopt staggered conformations, whilst one other of the pairs of CH_2-CF_2 groups is eclipsed. The N_3P_3 ring in cyclophosphazenes is essentially planar, unless the substitution pattern causes strain, which is then relieved by non-planarity of the ring.[3] The N_3P_3 ring in compound **2** shows a slight saddle shape through P(3)···N(1) and the ring atom N(1) between the two ansa bearing phosphorus atoms is slightly forced out of the plane. A similar saddle shape is adopted by compound **4** through P(2)···N(2). Compared with a compound containing the eight-membered ansa ring of the P-O-CH_2-CH_2-CH_2-O-P moiety, where the nitrogen atom deviates by 0.523 Å from the mean N_3P_3 plane,[11] the deviation from the mean plane of the N_3P_3 ring is significantly smaller for compounds **2–4** which have nine-membered ansa rings containing the P-O-CH_2-CF_2-CF_2-CH_2-O moiety, namely 0.184 Å for N(1) of **2**, 0.158 Å for P(1) of compound **4** and only 0.133 Å for N(1) of the asymmetrically substituted compound **3**. Notably compound **3** has two different centres of chirality, >P(OR)Cl and >P(OR)(pyr), and the X-

Table 1. ^{31}P and ^{19}F NMR parameters of some nine-membered ansa derivatives of cyclotriphosphazatriene.

i) 2,2,3,3-Tetrafluoro-1,4-butanedioxy bicyclic ansa derivatives

	$\delta(^{31}P)$ [ppm][a]				$^2J(PP)$ [Hz]	$\delta(^{19}F)$ [ppm][b]		$^2J(FF)$ [Hz]
	P(OR)X	X	PY_2	Y_2		$(CF_2)_2$		CF_2
1	23.6	Cl	25.2	Cl	65.0	−115.5	−116.6	283.5
2	26.9	Cl	15.6	pyr	49.9	−116	−117.5	283.6
3[c]	30.9	Cl	17.8	pyr	46.8, 52.6	−120	−124	283.9
	19.5	pyr			48.4	−108	−117	270.7
4	26.1	pyr	20.2	pyr	45.2	−117	−119	270.8

ii) Tricyclic derivatives

	δ (^{31}P) [ppm][a]					$^2J(PP)$ [Hz]		
	$P(N_{spiro})$	P(NH)X	X	PY_2 or PYZ	Y and/or Z			
	1	2		3		1,2	1,3	2,3
5[d]	9.2	26.7	Cl	25.9	Cl	42.1	41.7	57.1
6	12.1	31.3	Cl	6.9	NHPh	37.9	48.4	50.1
7	10.2	3.2	O	4.9	NHPh	[e]	55	44
8	19.0	24.6	OMe	23.6	OMe	51.4	63.1	67.1

[a] ^{31}P NMR measurements (at 202 MHz) in $CDCl_3$ solutions at 298 K with chemical shifts given with respect to 85% H_3PO_4 as an external reference. [b] ^{19}F NMR measurements (470 MHz) in $CDCl_3$ solutions at 298 K with chemical shifts given with respect to $CFCl_3$ as an internal reference. [c] Calculated as ABX spin system with A, >Ppyr$_2$; B, >P(OR)pyr; X, >P(OR)Cl: $J(AB)=48.4$, $J(AX)=52.6$, $J(BX)=46.8$ Hz. [d] Calculated as an ABX spin system. [e] Coupling constant leads to line broadening, but is too small to determine at the signal-to-noise of the spectrum of compound **7**, which is only slightly soluble in $CDCl_3$ solution.

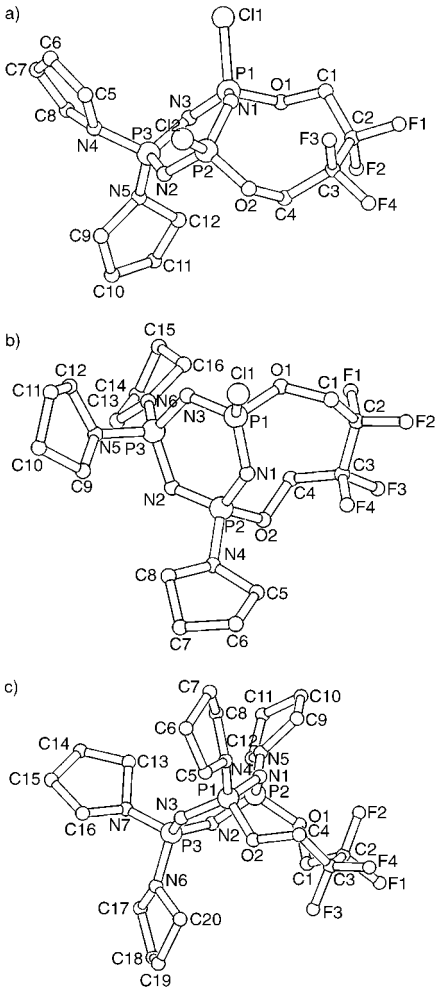


Figure 1. The molecular structures of the compound series a) **2**, b) **3** and c) **4**.

ray crystal structure shows that it exists as a racemic mixture of *RR*/*SS* forms.

It was also observed by Allcock and co-workers[12] that the N_3P_3 ring is considerably puckered in the ansa structures $N_3P_3(OCH_2CF_3)_4(ORO)$ (R = biphenylenedioxy, 1,8-dioxynaphthalene or ferrocenyl) and that the bond angle at the nitrogen atom separating the two phosphorus atoms carrying the ansa moiety is considerably decreased in the order: biphenylenedioxy < ferrocenyl < 1,8-dioxynaphthalene. A closer look shows that these nitrogen atoms are forced a great deal out of the plane of the other ring atoms. The resultant strain, observed earlier,[11] facilitated easier ring opening-polymerisations. However, the subject of inversion versus retention of configuration was not addressed, the ansa grouping being usually the last to be introduced.

There are bond length changes in compounds **2**–**4** as a result of progressive replacement of the electron-withdrawing substituent Cl by the strongly electron-donating pyrrolidino group. Thus, there is an increase in the average exocyclic P–N bond length for the geminal $P(pyr)_2$ group from 1.625 (**2**) to 1.639 (**3**) to 1.648 Å (**4**) with a concomitant decrease in the exocyclic $_{pyr}$N-P-N$_{pyr}$ bond angle, 104.0 (**2**), 103.0 (**3**) and 101.4° (**4**), due to a smaller mesomeric back-donation. The average P–O bond lengths for the symmetrical ansa group increases in compound **1** from 1.573 to 1.620 Å in compound **4**, with the two bond lengths in the asymmetric compound **3** with intermediate values of 1.596 and 1.616 Å, as expected. The P–Cl(OR) bond lengths also increase similarly from 1.986 Å in compound **1** to 2.016 Å in compound **3**. The first of these differs little from those of the geminal PCl_2 group of 1.995 Å; this demonstrates that there is only a very small electron release of the fluorinated butoxy group relative to chlorine. On the other hand, if this bond length is compared with that of a stereochemically analogous structure, namely, *cis*-$N_3P_3Cl_4(NMe_2)_2$,[13] which has two strongly electron-releasing substituents, NMe_2, the

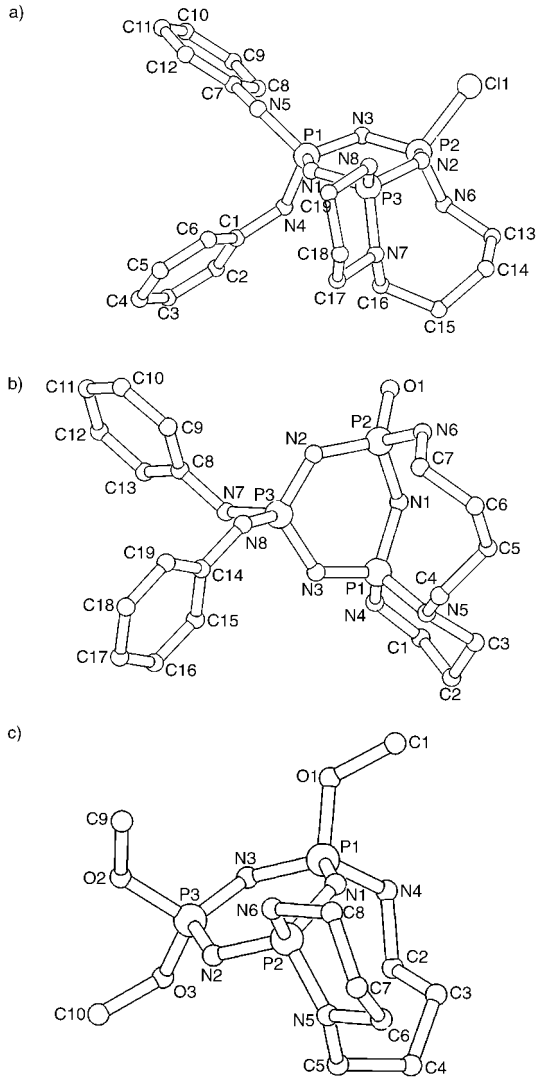


Figure 2. The molecular structures of the compound series a) **6**, b) **7** and c) **8**.

P–Cl bond of 2.052 Å for the $PCl(NMe_2)$ group is, as expected, significantly longer.

The crystal structures of compounds **6–8** are summarised in Figure 2a–c, respectively. Compounds **6–8** contain a nine-membered ansa ring that is part of a fused tricyclic system with linking nitrogen atoms, in contrast to compounds **1–4**, which are based on a fused bicyclic system with the linking atoms of the ansa moiety being both oxygen atoms.

Although the structures of compounds **5–8** do not form such a systematic series as do those of compounds **1–4**, the constraints of the fused tricyclic system results in overall similar conformations for analogous rings in each molecule. The six-membered ring containing the P(N-spiro) group is an approximate chair form in all cases and the nine-membered P-N-$(CH_2)_4$-NH-P ansa ring for each structure is best described as a twist-boat-chair, which exhibits similar puckering parameters[14] for each compound **5–8**.

The six-membered N_3P_3 ring of the starting compound **5** exhibits a slight saddle shape along the P1···N2 axis, that for compound **6** appears to have a slight chair conformation, whereas that for compound **8** is almost planar. There is no evidence for compression of the N_3P_3 ring of compounds **5**, **6** and **8** as shown by the non-bonded P···P distances, which vary from 2.734–2.819 Å and are in the normal range found for cyclophosphazenes.[12] On the other hand, compound **7**, which is strictly speaking a cyclotriphosphazadiene, has a badly distorted N_3P_3 ring that might be described as saddle-shaped along the P2···N1 axis; it also has a THF molecule in its crystal structure. Although two of the non-bonded P···P distances of compound **7**, 2.811 and 2.819 Å, are in the normal range, that for the P-NH-P ring segment has a value of 3.059 Å, which is in keeping with its phosphazane character. The same characteristic is reflected in the endocyclic P–N bonds with lengths of 1.665 and 1.704 Å compared with values of 1.57–1.59 Å in the rest of the N_3P_3 ring.

Discussion

The chirality of 4-coordinate aliphatic carbon compounds[1] and of P^V compounds[2] has been extensively investigated in nucleophilic substitution reactions. In similar reactions in cyclophosphazenes (one of the most investigated inorganic ring systems), inversion of configuration appears to have been tacitly assumed. The main reason is that, although the chiral properties of cyclophosphazenes were foreseen 40 years ago,[5] they had not been experimentally explored until quite recently. For example, we have proved by X-ray crystallography that inversion of configuration occurs for nucleophilic substitution of cyclophosphazene derivatives with 16-membered ansa rings.[6] Nucleophilic substitution of **1** with pyrrolidine (pyrH) replaces the remaining four P-Cl bonds with 2, 3 then 4 pyrrolidino groups as shown in Scheme 1. The first two P–Cl bonds to react are those of the PCl_2 group to form $N_3P_3Cl_2(OCH_2CF_2CF_2CH_2O)(pyr)_2$ (**2**). Reactions of the third and fourth P–Cl bonds geminal to the ansa moiety take place with retention of the *cis*-ansa configuration in both products, $N_3P_3Cl(OCH_2CF_2CF_2CH_2O)(pyr)_3$ (**3**) and $N_3P_3(OCH_2CF_2CF_2CH_2O)(pyr)_4$ (**4**). This behaviour is in striking contrast to that observed for the macrocyclic derivatives with a sixteen-membered ring, which is sufficiently long to allow inversion of configuration.[6]

The cyclophosphazene derivative **5**[10] has a nine-membered *cis*-ansa ring in which the two atoms linking the ansa bridge to the group are nitrogen rather than the oxygen atoms in **1** and the macrocyclic cyclophosphazene derivatives.[6] Reactions of **5** with a variety of nucleophiles [for example, NH_2tBu, pyrH, $H_2N(CH_2)_3OH$] initially replace both chlorine atoms at the PCl_2 group to form compounds analogous to **6**, but the reaction seems to be reluctant to proceed further with *neutral* nucleophiles even after prolonged heating under reflux of the reaction mixture. However, with the weak nucleophile, $PhNH_2$, inadvertent hydrolysis by the even weaker, but smaller, nucleophile, H_2O, also occurred and took place at the remaining P–Cl group to give the tautomerised structure **7**, again with retention of the *cis*-ansa configuration (Scheme 2). Final proof of retention of configuration in such nucleophilic substitution reactions is provided by the reaction of **5** with the sterically small, but strong,

anionic nucleophile NaOMe, which replaces all three chlorine atoms to give **8** (Scheme 2).

Reaction mechanisms in phosphazene chemistry have been discussed by Allen[3] and Krishnamurthy.[4] Whilst "apical entry and apical departure"[15,16] is the general rule for displacement reactions at tetrahedral P^V centres, other possibilities have been proposed, including attack in the plane of the ring with or without pseudorotation.[15–17] It is possible that some mechanistic feature of the latter type is responsible for the relatively slow reaction and retention of configuration in the work described here. We think that the rigidity of the molecular framework in these two sets of compounds is an important factor for the present observations and may indicate that mechanisms involving retention of configuration are more common than observed previously.[3] We are investigating various factors, such as the nature of the nucleophile, the substrate, the reaction medium and above all, the size of the ansa ring, which determine when retention of configuration changes to inversion of configuration.

Experimental Section

Materials: Hexachlorocyclotriphosphazatriene was purified by fractional crystallization from hexane. Sodium hydride, 60% dispersion in mineral oil (Merck) the oil being removed by washing with dry heptane followed by decantation. 2,2,3,3-Tetrafluoro-1,4-butanediol (Aldrich), spermidine (Fluka), pyrrolidine (Sigma) and from Merck; THF, hexane, methanol, aniline, dichloromethane, ethyl acetate, sodium sulphate, chloroform and carbon tetrachloride. THF was distilled over a sodium/potassium alloy under an atmosphere of dry argon. For column chromatography silica gel (230–400 mesh Merck) was used. All reactions were performed under a dry argon atmosphere. For column chromatography silica gel (230–400 mesh Merck) was used.

Reaction of 1 with pyrrolidine to give 2,4-(2′,2′,3′,3′-tetrafluoro-1′,4′-butanedioxy)-6,6-dipyrrolidino-2,4-dichlorocyclotriphosphazatriene $[N_3P_3(OCH_2CF_2CF_2CH_2O)(pyr)_2Cl_2]$ (2): 2,4-(2′,2′,3′,3′-tetrafluoro-1′,4′-butanedioxy)-2,4,6,6-tetrachlorocyclotriphosphazatriene (**1**),[9] (0.87 g, 2 mmol; m.p. 95 °C) and pyrrolidine (2.13 g, 30 mmol) were dissolved in dry THF (10 mL) under an argon atmosphere. The reaction mixture was stirred for 5 d at room temperature and the reaction followed on TLC silica gel plates using hexane/dichloromethane 1:3 until there was no starting material and only one product was obtained. The solvent was removed under reduced pressure and the resulting colourless oil subjected to column chromatography by using hexane/dichloromethane 1:3. The product was isolated as a white solid (0.52 g, 51%), which was recrystallised from hexane. M.p. 105 °C; MS (FAB + LCSIMS): *m/z*: calcd for 506.15; found: 506; elemental analysis calcd (%) for $C_{12}H_{20}Cl_2F_4N_5O_2P_3$: C 28.48, H 3.98, N 13.84; found: C 28.58, H 4.07, N 13.80.

Reaction of 1 with pyrrolidine to give 2,4-(2′,2′,3′,3′-tetrafluoro-1′,4′-butanedioxy)-2,6,6-tripyrrolidino-4-chlorocyclotriphosphazatriene $[N_3P_3(OCH_2CF_2CF_2CH_2O)(pyr)_3Cl]$ (3): Compound **1**[9] (0.87 g, 2 mmol) and pyrrolidine (2.13 g, 30 mmol) were dissolved in dry THF (10 mL) under an argon atmosphere. The reaction mixture was refluxed for 2 d and the reaction followed on TLC silica gel plates using hexane/dichloromethane 1:3 to show the absence of starting material and gave only one product. The solvent was removed under reduced pressure and the resulting colourless oil subjected to column chromatography by using hexane/dichloromethane 1:1. The product was obtained as a white solid (0.63 g, 58%), which was recrystallised from hexane/dichloromethane 3:1. M.p. 112 °C; MS (FAB + LCSIMS): *m/z*: calcd for: 540; found: 541; elemental analysis calcd (%) for $C_{16}H_{28}ClF_4N_6O_2P_3$: C 35.54, H 5.22, N 15.54; found: C 35.50, H 5.27, N 15.55.

Reaction of 1 with pyrrolidine to give 2,4-(2′,2′,3′,3′-tetrafluoro-1′,4′-butanedioxy)-2,4,6,6-tetrapyrrolidinocyclotriphosphazatriene $[N_3P_3(OCH_2CF_2CF_2CH_2O)(pyr)_4]$ (4): Compound **1**[9] (0.87 g, 2 mmol) was dissolved in pyrrolidine (2.84 g, 40 mmol) under an argon atmosphere and the reaction mixture was refluxed for 2 d. The reaction followed on TLC silica gel plates using hexane/dichloromethane 1:1, which showed the absence of starting material and the presence of two products. The solvent was removed under reduced pressure and the resulting colourless oil subjected to column chromatography by using hexane/dichloromethane 1:1. The first product was compound **3** (0.12 g, 11%) and the second was a white solid, compound **4** (0.3 g, 26%), which was recrystallised from hexane. M.p. 71 °C; MS (FAB + LCSIMS): m/z: calcd for: 575; found: 577; elemental analysis calcd (%) for $C_{20}H_{36}F_4N_7O_2P_3$: C 41.74, H 6.31, N 17.04; found: C 41.93, H 6.30, N 17.00.

Reaction of 5 with aniline in THF to give 12-chloro-14,14-bisanilino-2,6,11,13,15,16-hexaaza-1,12-diphosphatricyclohexadeca-1,12,14-triene (6): 12,14,14,-trichloro-2,6,11,13,15,16-hexaaza-1,12-diphosphatricyclohexadeca-1,12,14-triene (**5**)[18] (0.82 g, 2.14 mmol) and aniline (5.97 g, 64.10 mmol) were dissolved in THF (50 mL) in a 250 mL three-necked round-bottomed flask and the reaction mixture was refluxed for 21 h. The reaction mixture was followed on TLC silica gel plates using THF/hexane 1:3, which showed formation of only one product and the absence of starting material. The reaction mixture was then cooled to room temperature, 100 mL of distilled water added and the mixture extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure at 30 °C. The crude product was precipitated with hexane (200 mL) and the purple solid was subjected to column chromatography by using THF/hexane 1:3. The product was separated (0.35 g, 29%) and recrystallised from THF/methanol 1:1. M.p. 248 °C; elemental analysis calcd (%) for $C_{19}H_{28}ClN_8P_3$: C 45.93, H 5.68, N 22.55, found: C 46.20, H 6.28, N 23.01; MS (FAB): calcd for 496.86; found: 496.83 $[M+H]^+$.

Reaction of 5 with aniline in $CHCl_3$ to give 12-oxo-14,14-bisanilino-2,6,11,13,15,16-hexaaza-1,12-diphosphatricyclohexadeca-12,14-diene (7): Compound **5**[18] (1 g, 2.61 mmol) and aniline (16.95 g, 182 mmol) were dissolved in $CHCl_3$ (50 mL) in a 250 mL three-necked round-bottomed flask and the reaction mixture was refluxed for 5 h. The reaction mixture was followed on TLC silica gel plates using ethyl acetate/dichloromethane 1:3, which showed the absence of starting material and formation of only one product. The reaction mixture was then cooled to room temperature, distilled water (100 mL) was added and the mixture extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure at 30 °C. The crude product was precipitated with hexane (200 mL) and the purple solid was subjected to column chromatography by using dichloromethane/ethyl acetate 3:1. The product was separated (0.1 g, 8%) and recrystallised from THF/methanol 1:1. M.p. > 250 °C; elemental analysis calcd (%) for $C_{19}H_{29}N_8OP_3$: C 47.70, H 6.11, N 23.42; found: C 47.65, H 6.10, N 23.30; MS (FAB): *m/z*: calcd for: 478.42; found: 479.5 $[M+H]^+$.

Reaction of compound 5 with sodium methoxide to give 12,14,14-trimethoxy-2,6,11,13,15,16-hexaaza-1,12-diphosphatricyclohexadeca-1,12,14-triene (8): Compound **5**[18] (0.8 g, 2.088 mmol) and NaH (60% oil suspension, 0.25 g, 10.6 mmol) were dissolved in excess methanol (35 mL) in a 100 mL three-necked round-bottomed flask under an argon atmosphere. The reaction mixture was stirred for 6 d at room temperature and the reaction followed on TLC silica gel plates using THF/dichloromethane 1:1 to give only one product and no starting material remaining. Sodium chloride was filtered off, the solvent removed under reduced pressure at 30 °C and the crude product was subjected to column chromatography by using THF/dichloromethane 1:5. The product was separated (0.3 g, 39%) and recrystallised from CCl_4. M.p. 136 °C; elemental analysis calcd (%) for $C_{10}H_{25}N_6O_3P_3$: C 32.44, H 6.81, N 22.70; found: C 32.40, H 6.15, N 21.98; MS (FAB): *m/z*: 370; found: 371.0 $[M+H^+]$.

X-ray crystallography: Data were collected at a temperature of 120 K on an Bruker-Nonius KappaCCD area detector diffractometer located at the window of a Bruker-Nonius FR591 rotating anode X-ray generator, equipped with a molybdenum target (λ $Mo_{K\alpha}$ = 0.71073 Å), see Table 2. Structures were solved and refined using the SHELX-97 suite of programs.[19] Data were corrected for absorption effects by means of comparison of equivalent reflections using the program SORTAV.[20] Non-hydrogen atoms were refined anisotropically, whilst hydrogen atoms were gen-

Table 2. X-ray crystallographic data for compounds **2**–**4** and **6**–**8**.

	2	**3**	**4**	**6**	**7**	**8**
Empirical formula	$C_{12}H_{20}Cl_2F_4N_5O_2P_3$	$C_{16}H_{28}ClF_4N_6O_2P_3$	$C_{20}H_{36}F_4N_7O_2P_3$	$C_{19}H_{28}ClN_8P_3$	$C_{23}H_{37}N_8O_2P_3$	$C_{10}H_{25}Cl_0N_6O_3P_3$
F_w	506.14	540.80	575.47	496.85	550.52	370.27
crystal system	monoclinic	triclinic	monoclinic	monoclinic	triclinic	orthorhombic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1$	$P\bar{1}$	*Pbca*
a [Å]	8.5314(3)	9.3371(2)	9.9843(3)	10.39010(10)	8.5083(2)	9.34480(10)
b [Å]	25.0735(8)	10.0319(2)	23.3106(10)	19.0419(2)	11.7741(3)	12.96150(10)
c [Å]	9.8642(4)	14.0836(3)	11.5248(5)	12.5550(2)	13.6493(4)	27.4860(4)
α [°]	90	69.4950(10)	90	90	91.3840(10)	90
β [°]	95.270(2)	83.0270(10)	98.733(4)	110.29(6)	98.0770(10)	90
γ [°]	90	69.3210(10)	90	90	99.484(2)	90
V [Å^3]	2101.15(13)	1156.00(4)	2651.19(18)	2329.79(5)	1333.72(6)	3329.18(7)
Z	4	2	4	4	2	8
ρ_{calcd} [Mg m^{-3}]	1.600	1.554	1.442	1.417	1.371	1.477
crystal size [mm]	0.34×0.12×0.03	0.48×0.18×0.1	0.26×0.18×0.07	0.30×0.06×0.06	0.14×0.1×0.03	0.4×0.03×0.02
indep reflns	4618	5172	5068	10479	5821	3801
R(int)	0.0513	0.0298	0.0592	0.0812	0.0352	0.0938
final R indices $F^2>2\sigma F^2$						
$R1$	0.0483	0.0282	0.0504	0.0396	0.0459	0.0374
$wR2$ (all)	0.1322	0.0825	0.1266	0.0953	0.1220	0.1138
$\Delta\rho$ max/min [e Å^{-3}]	0.273/−0.328	0.374/−0.409	0.817/−0.544	0.311/−0.348	0.917/−0.548	0.518/−0.444

erally fixed in idealised positions with their thermal parameters riding on the values of their parent atoms. The absolute structure of the two molecules in compound **6** was confirmed by refinement of the Flack parameter to a value of 0.0(4). Compound **7** co-crystallises with a molecule of THF.

CCDC-215794 (**2**), -215795 (**3**), -215796 (**4**), -215797 (**6**), -215798 (**7**), -215799 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

Acknowledgement

The authors would like to thank the Shin Nisso Kako Co Ltd for gifts of $N_3P_3Cl_6$, the EPSRC for funding the National Crystallographic Service (Southampton, UK) and Gebze Institute of Technology (GIT) Research Fund for partial support (S.B., H.İ. and A.K.).

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Received: March 30, 2004
Published online: August 20, 2004

