Synthesis of Transannular- and Spiro-Substituted Cyclotriphosphazenes: X-ray Crystal Structures of 1,1-[$N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)$], 1,3-[$N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)$], 1,1-[$N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)$], and 1,3-[$N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)$]

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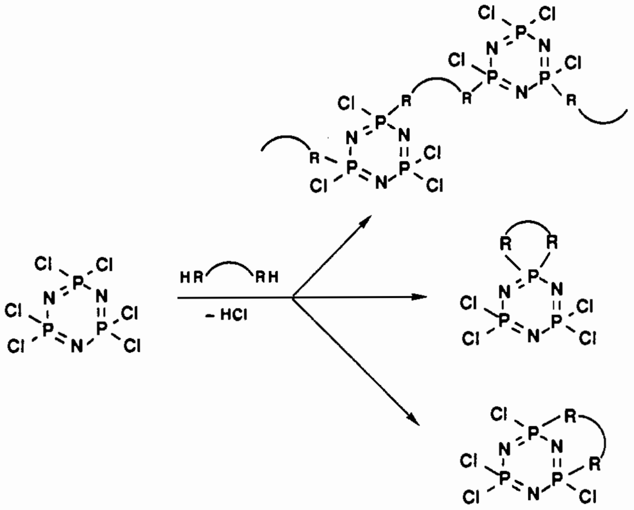
A cyclic triphosphazene with four trifluoroethoxy side groups and two nongeminal chlorine atoms, 1,3-[$N_3P_3(OCH_2CF_3)_4Cl_2$], reacts with difunctional alcohols or amines to give transannular derivatives. Examples of the difunctional reagents used include catechol, 2,2′-biphenol, 1,8-dihydroxynaphthalene, 1,8-diaminonaphthalene, 1,3-propanediol, 1,3-diaminopropane, and 2,2′-dilithiobiphenyl. These are the first examples of transannular-bridged structures derived from aromatic diols or diamines. The analogous spirocyclic derivatives were prepared directly from hexachlorocyclotriphosphazene via a simple two-step reaction pathway using the same difunctional reagents. The solid-state structures of 1,1- and 1,3-[$N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)$] and 1,1- and 1,3-[$N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)$] were determined by X-ray diffraction, and the effects of transannular versus spiro substitution on the planarity of the phosphazene ring and (by implication) on the phosphazene ring strain were studied. These compounds are starting materials for phosphazene ring-expansion or ring-opening polymerization reactions.

Introduction

The reactions of difunctional nucleophiles with cyclic halogenophosphazenes can, in principle, yield three types of products (Scheme I). First, halogen replacement could lead to a linkage of phosphazene rings to form cyclolinear or cyclomatrix polymers. Second, the dinucleophile may replace two chlorine atoms at the same phosphorus atom to form spirocyclic structures. And third, the possibility exists that chlorine units on different phosphorus atoms are replaced to give a transannular-bridged structure.

In earlier reports[1-7] we described the first examples of spirocyclic phosphazenes, formed by the reactions of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, with aromatic diols or a diamine. Several of these products showed interesting solid-state inclusion phenomena, and this behavior has been investigated in some detail.[8-16] Since that time a number of research groups have studied the reactions of $(NPCl_2)_3$ or its derivatives with aliphatic dinucleophiles.[17-20] In general, spirocyclic products have been isolated, although a few examples of transannular bridged structures have also been reported.[21-24]

Scheme I



However, recent work from our laboratory has shown that dilithioferrocene, dilithioruthenocene, or the dilithio reagent from bis(benzene)chromium react with chloro- or fluorocyclophosphazenes to yield mainly transannular derivatives.[25-37] These

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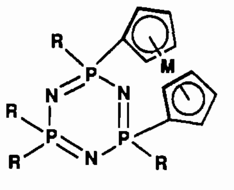
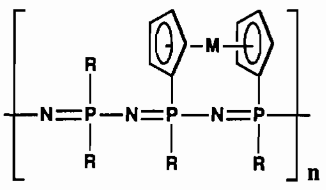
are of special interest because the transannular structures impart considerable strain to the phosphazene ring, and this becomes manifest in severe phosphazene ring puckering and an enhanced tendency for the molecules to undergo phosphazene ring expansion or polymerization. Indeed, the polymerization tendency is so marked that cyclotriphosphazenes of this type (**1**) uniquely undergo polymerization (for example, to **2**) even when all the side groups are organic or organometallic units.[25-37] This is an important result since it had earlier been assumed that the presence of *P*-halogen side group units was a prerequisite for ring-opening polymerization.[38] Moreover, the direct conversion of a fully organo-substituted phosphazene cyclic trimer to a fully organo-substituted high polymer bypasses the need for subsequent macromolecular halogen replacement reactions that are normally needed to ensure that the polymers are hydrolytically stable. Thus, the importance of transannular structures in these compounds extends beyond questions of small-molecule structures and mechanisms.



1

M = Fe or Ru
R = OCH_2CF_3 or OPh



2

M = Fe
R = OCH_2CF_3

The possibility of extending this approach to phosphazenes with *organic* transannular bridges was an appealing prospect. Thus, we have investigated routes to the synthesis of such species via the reactions of difunctional nucleophiles such as catechol, 2,2′-biphenol, 1,8-dihydroxynaphthalene, 1,8-diaminonaphthalene, 1,3-diaminopropane, 1,3-propanediol, and 2,2′-dilithiobiphenyl with organocyclotriphosphazenes that bear two nongeminal chlorine atoms. The preparation of the analogous spirocyclic phosphazenes allowed a comparison to be made of the influence of transannular versus spirocyclic structures on the phosphazene ring and on its ring-expansion or polymerization tendencies.

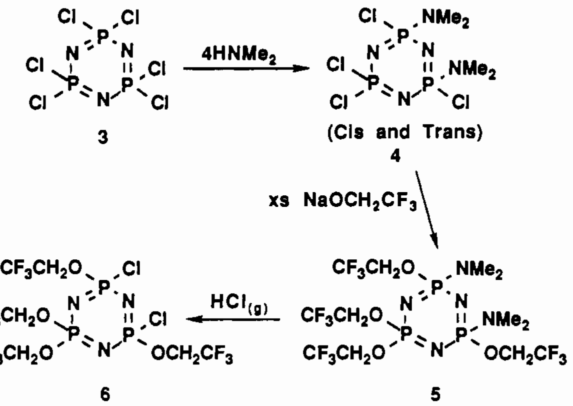
Thus, the objectives of this work were 3-fold: (1) to develop pathways for the synthesis of cyclotriphosphazenes that bear both transannular organic bridges and trifluoroethoxy cosubstituents, (2) to prepare analogous spiro-substituted cyclic phosphazenes, and (3) to compare and contrast their solid-state and solution-state structures.

The ring-expansion and polymerization behavior of these species will be reported in a later publication.[39]

Results and Discussion

Preparation of Transannular-Bridged Cyclotriphosphazenes. The reactions of hexachlorocyclotriphosphazene, $(NPCl_2)_3$ (**3**), with difunctional alcohols and amines are dominated by ring closure at one phosphorus atom to give spirocyclic derivatives, with little or no transannular bridge formation.[1-16] Thus, a general synthetic route to transannular-substituted cyclotriphosphazenes had to be developed starting with a phosphazene cyclic trimer that contained four unreactive side groups plus two chlorine atoms in a cis–nongeminal arrangement. This methodology allowed the preparation of cyclotriphosphazenes with transannular aryloxy substituents that are inaccessible by the direct reaction of **3** with compounds such as biphenols or dihydroxynaphthalenes. The synthetic strategy is outlined in Scheme II, which also illustrates the preparation of the precursor, 1,3-$[N_3P_3(OCH_2CF_3)_4Cl_2]$ (**6**).[40]

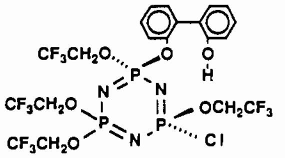
Scheme II



First, $(NPCl_2)_3$ (**3**) was treated with 4 equiv of dimethylamine to produce the diorgano-substituted trimer **4**, in which the two dimethylamino units were arranged nongeminally. (Two of the four equivalents of dimethylamine served as hydrogen chloride acceptors.) The remaining four chlorine atoms were then replaced by reaction with trifluoroethoxide ion to give **5**. Finally, the dimethylamino side groups were removed by treatment with HCl(g) under pressure. This yielded cyclic trimer **6** in 70% yield [based on $(NPCl_2)_3$ (**3**)] with a nongeminal arrangement of the two chlorine atoms.[40] The ratio of cis:trans isomers in **6** was found by integration of the ^{31}P NMR spectrum to be approximately 1:1.

Compound **6** was found to react with a number of dihydroxy and diamino nucleophiles, in the presence of a hydrogen chloride acceptor, such as triethylamine, sodium carbonate, or pyridine, to produce the transannular-substituted cyclic triphosphazenes **7–12**, as shown in Scheme III. Compounds **8–11** were isolated as crystalline solids, whereas **7** and **12** are colorless liquids. Their molecular structures were studied by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis, the results of which are collected in Tables I and II. The solid-state structure of cyclic trimers **8** and **9** were determined by X-ray diffraction and are described later.

The reactions of **6** with biphenol or 1,8-dihydroxynaphthalene yielded a second product in addition to the transannular species. These white crystalline solids were isolated in ca. 40% yield after purification by column chromatography and were found to be the monochloro derivatives, $N_3P_3(OCH_2CF_3)_4(OC_{12}H_8OH)Cl$ (**13**) and $N_3P_3(OCH_2CF_3)_4(OC_{10}H_6OH)Cl$ (**14**) (see Tables I and II). The biphenylenehydroxy side group of **13** did not undergo cyclization to produce trimer **8** even after prolonged heating at 110 °C in the presence of excess sodium carbonate. Therefore, it was concluded that cyclic trimers **13** and **14** are generated from the trans isomer of starting material **6**, whereas the transannular-



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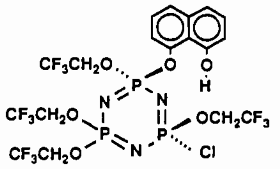

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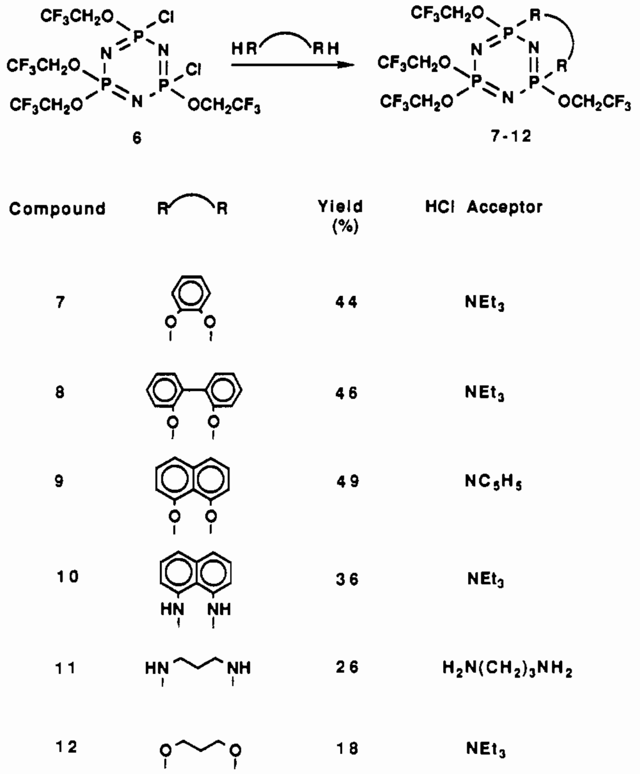
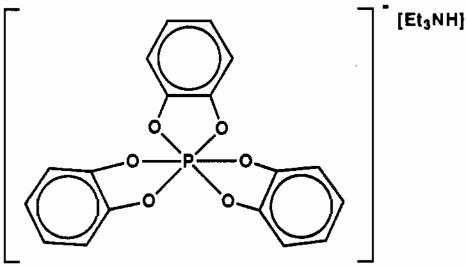
Scheme III



substituted trimers **8** and **9** are formed from the cis isomer. Similar products were detected in the VPC-MS and ^{31}P NMR spectra of the mixtures produced by reaction of **6** with 1,3-propanediol, 1,8-diaminonaphthalene, and 1,3-diaminopropane. However, in those cases it was not possible to isolate the noncyclized products from these reactions by column chromatography techniques.

In the reaction of **6** with catechol another compound was isolated directly from the reaction mixture. This insoluble white powder was found to be $[P(O_2C_6H_4)_3][Et_3NHCl]$ (**15**), which has been



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reported previously as a product formed during the breakdown of $[NP(O_2C_6H_4)]_3$ in the presence of excess catechol and triethylamine.[1-7,41] The formation of **15** is very slow under the reaction conditions employed in this work. It is formed from the trans isomer of **6** in the presence of excess catechol and triethylamine. The phosphazene breakdown pathway presumably involves the presence of an intermediate similar to **13** or **14**.

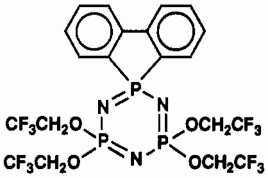
The reaction of **6** with the disodium salt of 1,3-propanediol gave a more complex mixture of products than was obtained in the presence of triethylamine. Two fractions were isolated by column chromatography and were identified as an inseparable mixture of 1,3- and 1,1-$[N_3P_3(OCH_2CF_3)_4\{O(CH_2)_3O\}]$ (**12** and **20**) and a disubstituted product, 1,1-$[N_3P_3(OCH_2CF_3)_2\{O(CH_2)_3O\}_2]$ (**21**). The isolation of the two spirocyclic phosphazene trimers was unexpected and must result from a displacement of trifluoroethoxy groups from **6** under the reaction conditions employed. Similar displacements are well-known for the replacement of amino groups during reactions with alkoxides[42] and have also been reported during the interaction of poly[bis(trifluoroethoxy)phosphazene] with alkoxides.[43,44]

No transannular-substituted cyclic trimers could be isolated from the reaction of **6** with ethylene glycol, either in the presence of triethylamine or in the form of its disodium salt. A similar reaction of **6** with 2,2′-dilithiobiphenyl resulted in the formation of a complex mixture of products which could not be separated by column chromatography, and these were apparently products of a phosphazene ring degradation process.

Preparation of Spirocyclic Phosphazene Trimers. The spirocyclic analogues of cyclic trimers **8–12** were prepared directly from $(NPCl_2)_3$ (**3**) in a two-step, one-reaction vessel reaction, as shown in Scheme IV. To minimize the formation of products with more than one spirocyclic unit per phosphazene ring, the difunctional reagent was added very slowly and was followed by treatment with an excess of sodium trifluoroethoxide to replace the remaining four chlorine atoms. The resulting spirocyclic phosphazenes **16–20** were isolated as crystalline solids (**16–18**) or colorless liquids (**19** and **20**). The characterization data are shown in Tables III and IV.

An aryloxy analogue of **16**, in which phenoxy groups are present as cosubstituents instead of trifluoroethoxy units, has recently been reported.[45] That synthesis involved a two-step route and gave an overall yield of 20% from $(NPCl_2)_3$ (**3**). A similar synthetic pathway has been described recently for the preparation of 1,1-$[N_3P_3(NC_2H_4)_4\{NH(CH_2)_3NH\}]$.[46]

Preparation of the biphenyl-substituted cyclic trimer 1,1-$[N_3P_3(OCH_2CF_3)_4(C_{12}H_8)]$ (**22**) was accomplished by a modification of the reaction described in Scheme III. Dilithiobiphenyl, prepared by the direct lithiation of biphenyl with Bu^nLi,[47] was added to $(NPF_2)_3$ at room temperature, followed by the addition of an excess of sodium trifluoroethoxide. Column chromatography of the reaction mixture gave two products. The minor product was found to be $[N_3P_3(OCH_2CF_3)_5(C_{12}H_9)]$ (**23**) and



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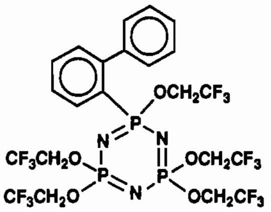

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was generated from a small amount of monolithiated biphenyl in the mixture. The major product was the spirocyclic derivative **22**, which was isolated in 11% yield as colorless crystals from a solution in dichloromethane–hexane. The hexafluorocyclotriphosphazene employed in this reaction is known to undergo cleaner reactions with organolithium reagents than the analogous chlorosubstituted phosphazene.[48]

Variation of the ^{31}P Chemical Shift with Ring Size. Previous studies have shown that the ^{31}P chemical shift of spirocyclic phosphazenes and phosphoranes is dependent on the size of the

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Table I. Mass Spectral, Analytical, and ^{31}P NMR Data for Cyclotriphosphazenes **7–14**

		elemental anal. (%)[a]			^{31}P NMR spectral data[b]	
compd	mass spectral data[a] (*m*/*e*)	C	H	N	δ (ppm)	J_{PNP} (Hz)
7	639 (639)	25.83 (26.31)	1.84 (1.89)	6.74 (6.58)	22.03, 20.56	88
8	715 (715)	33.39 (33.57)	2.23 (2.24)	5.83 (5.87)	26.96, 25.61, 22.0	79, 88, 91
9	689 (689)	31.21 (31.37)	2.07 (2.05)	5.94 (6.10)	22.77, 21.22	87
10	687 (687)	31.69 (31.45)	2.35 (2.35)	10.13 (10.19)	26.14, 21.14	70
11	603 (603)	21.98 (21.90)	2.73 (2.67)	11.31 (11.61)	26.96, 20.66	73
12	605 (605)	21.62 (21.95)	2.02 (2.24)	6.90 (7.15)	22.44, 20.43	87
13	751 (751)	32.05 (31.95)	1.94 (2.28)	5.78 (5.59)[c]	27.17, 14.65, 11.54	84, 89
14	725 (725)	29.96 (29.79)	1.96 (2.08)	5.93 (5.79)[d]	28.02, 15.58, 2.18	89, 93

[a] Calculated values in parentheses. [b] Recorded in $CDCl_3$ at 146 MHz on a Bruker WM 360 NMR spectrometer. [c] Chlorine content found to be 4.91 (4.72). [d] Chlorine content found to be 4.75 (4.89).

Table II. ^{1}H and ^{13}C NMR Data Recorded for Cyclotriphosphazenes **7–14**

compd	^{1}H NMR spectral data[a] (δ)	^{13}C NMR spectral data[a,b] (ppm)
7	7.27–6.99 (m, Ph, 4 H), 4.52 (m, $\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$, 4 H), 4.32 (p, $J = 7$, $\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$, 2 H), 4.13 (p, $J = 7$, $\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$, 2 H)	142.8 (s), 126.6 (s), 122.8 (s), 122.0 (m, CF_3), 63.8 (q, $J = 39$, $\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$), 63.2 (q, $J = 39$, $\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$), 62.5 (dq, $J = 3, 39$, $\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$)
8	7.61–7.16 (m, Ph, 8 H), 4.72 (m, $\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$, 4 H), 4.54 (m, $\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$, 2 H), 3.81 (m, $\mathrm{OCH}\mathit{H}\mathrm{CF}_3$, 1 H), 3.25 (m, $\mathrm{OCH}\mathit{H}\mathrm{CF}_3$, 1 H)	150.58 (d, $J = 7$), 148.55 (d, $J = 6$), 133.50 (d, $J = 2$), 132.92 (d, $J = 1$), 132.76 (d, $J = 4$), 132.05 (d, $J = 4$), 131.05 (d, $J = 3$), 130.86 (d, $J = 2$), 127.02 (d, $J = 2$), 126.49 (d, $J = 2$), 126.28 (d, $J = 4$), 121.96 (d, $J = 2$), 123.90 (m, CF_3), 64.09 (dq, $J = 4, 37$, $\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$), 64.44 (dq, $J = 4, 37$, $\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$), 63.64 (dq, $J = 3, 37$, $\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$), 62.53 (dq, $J = 3, 38$, $\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$)
9	7.80 (m, Ph, 2 H), 7.49 (m, Ph, 2 H), 7.33 (m, Ph, 2 H), 4.44 (m, $\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$, 8 H)	144.67 (m), 137.50 (s), 127.42 (s), 126.12 (s), 122.40 (m, $J_{CF} = 277$, CF_3), 123.14 (s), 120.97 (d, $J = 3$), 64.08 (q, $J = 38$, $\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$), 63.32 (dq, $J = 4, 38$, $\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$), 62.58 (dq, $J = 3, 38$, $\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$)
10	7.78 (m, Ph, 2 H), 7.40 (m, Ph, 2 H), 7.27 (m, Ph, 2 H), 5.26 (s, NH, 2 H), 4.40 (m, $\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$, 4 H), 4.37 (m, $\mathrm{OCH}\mathit{H}\mathrm{CF}_3$, 1 H), 4.32 (m, $\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$, 2 H), 4.23 (m, $\mathrm{OCH}\mathit{H}\mathrm{CF}_3$, 1 H)	137.35 (s), 133.04 (d, $J = 2$), 128.80 (s), 128.40 (s), 127.61 (s), 125.59 (s), 122.7 (m, CF_3, $J_{CF} = 282$), 62.95 (m, $\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$)
11	4.27 (m, $\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$, 8 H), 3.31 (m, NCH_2, 2 H), 3.19 (m, NCH_2, 2 H), 2.88 (m, NH, 2 H), 1.65 (m, $\mathrm{NCH_2CH}\mathit{H}$, 1 H), 1.51 (m, $\mathrm{NCH_2CH}\mathit{H}$, 1 H)	122.84 (m, CF_3), 62.47 (m, $\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$), 40.50 (s, $\mathrm{N}\mathit{C}\mathrm{H_2}$), 34.37 (s, $\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$)
12	4.37 (m, OCH_2, 4 H), 4.33 (m, $\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$, 4 H), 4.26 (m, $\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$, 2 H), 4.15 (m, $\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$, 2 H), 1.75 (m, $\mathrm{OCH_2C}\mathit{H}_2$, 2 H)	122.43 (m, $\mathit{C}\mathrm{F_3}$, $J_{CF} = 284$), 66.54 (m, $\mathrm{O}\mathit{C}\mathrm{H_2}$), 62.93 (q, $J = 39$, $\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$), 62.44 (q, $J = 39$, $\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$), 62.53 (q, $J = 38$, $\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$), 31.83 (s, $\mathrm{OCH_2}\mathit{C}\mathrm{H_2}$)
13	7.47–6.99 (m, Ph, 8 H), 5.13 (s, OH, 1 H), 4.36 (m, $\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$, 2 H), 4.20 (m, $\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$, 2 H), 3.96 (m, $\mathrm{OCH}\mathit{H}\mathrm{CF}_3$, 1 H), 3.87 (m, $\mathrm{OCH}\mathit{H}\mathrm{CF}_3$, 1 H), 3.63 (m, $\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$, 2 H)	152.97 (s), 147.58 (s), 132.49 (s), 131.44 (s), 130.20 (d, $J = 5.4$), 130.02 (s), 129.89 (s), 126.77 (s), 123.68 (s), 121.09 (s), 120.59 (s), 116.40 (s), 62.73 (m, $\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$)
14	7.63 (m, Ph, 2 H), 7.48 (m, Ph, 2 H), 7.10 (m, Ph, 2 H), 6.6 (br, s, OH, 1 H), 4.38 (m, $\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$, 8 H)	146.38 (d, $J = 3$), 146.17 (d, $J = 3$), 135.07 (s), 127.66 (s), 123.40 (s), 123.37 (s), 122.26 (m, $J_{CF} = 275$, CF_3), 113.53 (d, $J = 12$), 112.63 (s), 112.55 (s), 112.46 (s), 64.08 (q, $J = 38$, $\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$), 63.19 (m, $\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$)

[a] Recorded in $CDCL_3$ on a Bruker WM 360 NMR spectrometer, coupling constants (*J*) in Hertz. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, Ph = aryl resonances. [b] Spectrometer operating at 90 MHz.

spirocyclic ring.[49,50] This earlier work indicated that the spirocyclic phosphorus nuclei are deshielded in the order 6-membered > 7-membered > 5-membered rings. The ^{31}P NMR spectra recorded for **16** and **17** show an upfield shift from 25.17 to 5.17 ppm (see Table III). The difference in their chemical shifts of 20 ppm is identical to that reported previously for the corresponding spirocyclic phosphoranes.[50] Similarly, the ^{31}P chemical shifts recorded for the alkylenedioxy- and diamino-substituted trimers **18–20** compare favorably with those described previously for spirocyclic phosphazenes.[51]

By contrast, no studies of the ring size dependence of the ^{31}P chemical shift for transannular-substituted cyclic phosphazenes have been reported. Our results show that phosphorus nuclei which bear both aryloxy and trifluoroethoxy substituents are progressively deshielded in moving from cyclic trimer **8** to **9** to **7** (see Table I). However, this effect is very small compared to that recorded for the spirocyclic analogues. Furthermore, the data for **10–12** suggest that the ^{31}P chemical shift is essentially independent of the size and nature of the transannular bridge and depends solely on the cosubstituents at each phosphorus atom. Indeed, in this system the presence of an AB_2 spin system, with both chemical shifts in the region of 20 ppm, was indicative of a transannular structure formed by the difunctional reagent.

X-ray Crystal Structures of Transannular- and Spiro-Substituted Phosphazenes. The solid state structures of **8**, **9**, **16**, and **17** have been determined by X-ray crystallography and are shown in Figures 1–4. Crystal data and intensity collection parameters are shown in Table V. Significant bond lengths and angles are listed in Tables VI–IX, and the fractional atomic coordinates are collected in Tables X–XIII.

In the solid state, the phosphazene ring of the transannular biphenylenedioxy derivative **8** adopts a boat conformation in which a nitrogen [N(1)] and a phosphorus atom [P(3)] are below the plane of the other four atoms of the ring. The PNP angle at this nitrogen [P(1)–N(1)–P(2) = 117.4 (3)°] is significantly narrower than those at the other two nitrogen atoms [P(2)–N(2)–P(3) = 119.2 (2)° and P(1)–N(3)–P(3) = 120.4 (2)°]. Evidently, the

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Scheme IV

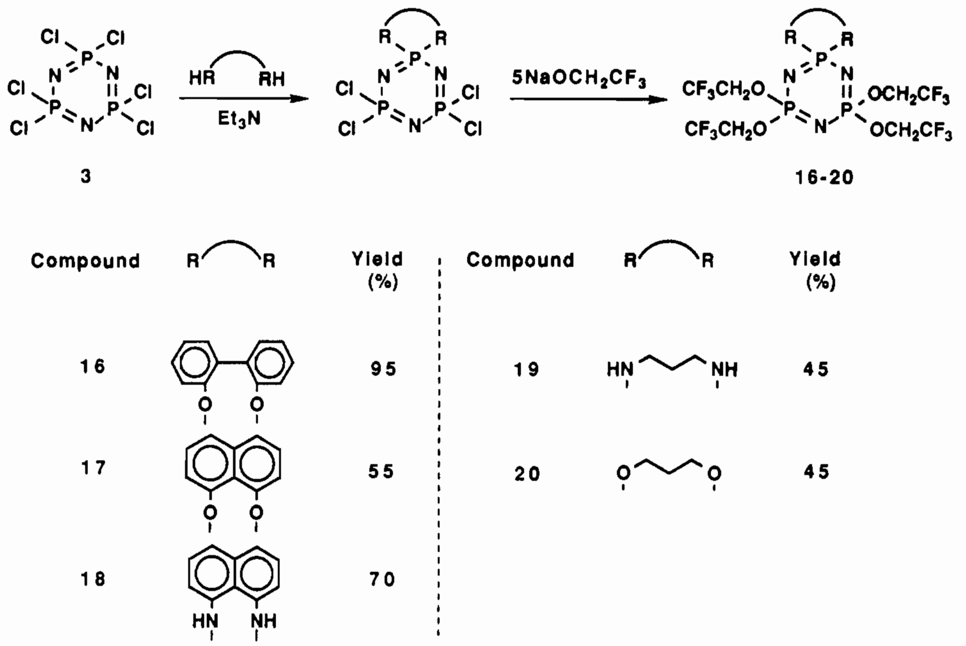

Table III. Mass Spectral, Analytical, and ^{31}P NMR Data for Spiro-Substituted Cyclotriphosphazenes **16–22**

		elemental anal. (%)[a]			^{31}P NMR spectral data[b]	
compd	mass spectral data[a] (*m/e*)	C	H	N	δ (ppm)	J_{PNP} (Hz)
16	715 (715)	33.46 (33.58)	2.03 (2.25)	5.97 (5.88)	25.17, 18.19	92
17	689 (689)	31.07 (31.37)	2.07 (2.05)	5.94 (6.10)	18.24, 5.17	94
18	687 (687)	31.41 (31.45)	2.06 (2.35)	9.98 (10.19)	18.49, -0.22	79
19	603 (603)	22.00 (21.90)	2.55 (2.67)	11.54 (11.61)	18.50, 18.11	65
20	605 (605)	21.95 (21.83)	2.24 (2.33)	7.15 (6.95)	17.98, 14.30	88
21	481 (481)	24.72 (24.96)	3.39 (3.35)	8.76 (8.73)	18.11, 14.36	86
22	683 (683)	34.90 (35.15)	2.45 (2.36)	5.92 (6.15)	31.45, 18.01	31

[a] Calculated values in parentheses. [b] Recorded in $CDCl_3$ at 146 MHz on a Bruker WM 360 NMR spectrometer.

Table IV. H and ^{13}C NMR Data Recorded for Spiro-Substituted Cyclotriphosphazenes **16–22**

compd	^1H NMR spectral data[a] (δ)	^{13}C NMR spectral data[a,b] (ppm)
16	7.57 (m, Ph, 2 H), 7.48 (m, Ph, 2 H), 7.39 (m, Ph, 2 H), 7.23 (m, Ph, 2 H), 4.35 (m, $OC\mathit{H}_2CF_3$, 8 H)	147.67 (d, *J* = 9), 130.0 (s), 129.84 (s), 128.49 (s), 126.5 (s), 122.48 (q, J_{CF} = 278, CF_3), 121.4 (d, *J* = 4), 63.02 (q, *J* = 38, $O\mathit{C}H_2CF_3$)
17	7.63 (m, Ph, 2 H), 7.48 (m, Ph, 2 H), 7.10 (m, Ph, 2 H), 4.33 (m, $OC\mathit{H}_2CF_3$, 8 H)	146.47 (d, *J* = 6), 135.09 (s), 127.65 (s), 123.29 (s), 122.41 (m, 4J_{CF} = 278, CF_3), 123.14 (s), 113.7 (d, *J* = 13), 112.42 (d, *J* = 9), 63.06 (q, *J* = 38, $O\mathit{C}H_2CF_3$)
18	7.29 (m, Ph, 4 H), 6.58 (m, Ph, 2 H), 5.13 (d, *J* = 5, NH, 2 H), 4.33 (ddq, *J* = 5, 8, 17, $OC\mathit{H}_2CF_3$, 2 H)	136.61 (s), 135.28 (s), 127.15 (s), 122.62 (m, J_{CF} = 278, CF_3), 120.57 (s), 109.6 (s), 109.48 (s), 62.90 (q, *J* = 38, $O\mathit{C}H_2CF_3$)
19	4.24 (m, $OC\mathit{H}_2CF_3$, 8 H), 3.29 (dt, *J* = 6, 15, NCH_2, 4 H), 2.49 (br, s, NH, 2 H), 1.71 (p, *J* = 6, $NCH_2C\mathit{H}_2$, 2 H)	122.67 (m, J_{CF} = 278, CF_3), 62.51 (q, *J* = 38, $O\mathit{C}H_2CF_3$), 41.03 (s, $N\mathit{C}H_2$), 26.21 (s, $NCH_2\mathit{C}H_2$)
20	4.45 (dt, *J* = 6, 12, OCH_2, 4 H), 4.24 (ddq, *J* = 4, 8, 12, $OC\mathit{H}_2CF_3$, 8 H), 2.0 (m, $OCH_2C\mathit{H}_2$, 2 H)	122.50 (qt, J_{CF} = 278, 6, CF_3), 67.31 (d, *J* = 6, $O\mathit{C}H_2CH_2$) 62.67 (q, *J* = 38, $O\mathit{C}H_2CF_3$), 25.81 (d, *J* = 7, $OCH_2\mathit{C}H_2$)
21	4.45 (p, *J* = 6, OCH_2, 8 H), 4.24 (p *J* = 8, 4 H), 2.02 (dp, *J* = 6, 14, $OCH_2C\mathit{H}H$, 2 H), 1.95 (dp, *J* = 6, 14, $OCH_2C\mathit{H}H$, 2 H)	122.76 (m, J_{CF} = 278, CF_3), 67.05 (m, $O\mathit{C}H_2$), 62.48 (dq, *J* = 4, 38, $O\mathit{C}H_2CF_3$), 25.97 (t, *J* = 3, $OCH_2\mathit{C}H_2$)
22	7.76 (m, Ph, 2 H), 7.58 (m, Ph, 4 H), 7.46 (m, Ph, 2 H), 4.35 (ddq, *J* = 4, 8, 12, $OC\mathit{H}_2CF_3$, 8 H)	140.56 (d, *J* = 27), 133.63 (d, *J* = 2), 132.03 (m, J_{CF} = 141, CF_3), 129.77 (d, *J* = 12), 127.36 (d, *J* = 10), 124.18 (t, *J* = 7), 121.22 (d, *J* = 6), 62.93 (q, *J* = 37, $O\mathit{C}H_2CF_3$)

[a] Recorded in $CDCl_3$ on a Bruker WM 360 NMR spectrometer, coupling constants (*J*) in Hertz. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, Ph = aryl resonances. [b] Spectrometer operating at 90 MHz.

introduction of the transannular biphenylenedioxy moiety leads to a distortion of the phosphazene ring in a manner similar to that found for the transannular ferrocenyl group in **1**. However, the effect is more pronounced for the transannular ferrocenyl derivative, where a PNP angle of 112° was found for the trifluoroethoxy derivative **1** (M = Fe, R = OCH_2CF_3).[36] This large deviation from the favored angle at nitrogen (120°) has been used to explain why fully organo-substituted cyclic trimers, such as **1**, can be induced to undergo facile ring-opening polymerization in the presence of an initiator.[25,26] The phenyl rings of the bridging biphenylenedioxy group in **8** are arranged at ca. 90° [C(11)–C(16)–C(36)–C(31) torsion angle = 87.1(6)°], presumably to avoid 6,6′, hydrogen–hydrogen interactions. This indicates that the "bite angle" of the 2,2′-biphenol is large enough to bridge the PN ring easily in a transannular fashion.

The X-ray diffraction study of the spirocyclic 1,1-$[N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)]$ (**16**) (see Figure 3) revealed a planar phosphorus–nitrogen ring (to within ±0.008 Å), without the distortion apparent for the transannular analogue (**8**). The angles at the ring nitrogen atoms are all equal [e.g. P(1)–N(1)–P(2) = 122.1

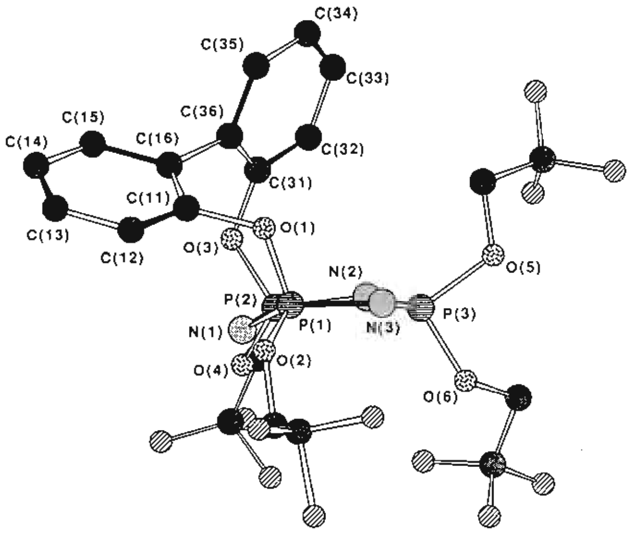

Figure 1. X-ray crystal structure of 1,3-[$N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)$] (**8**).

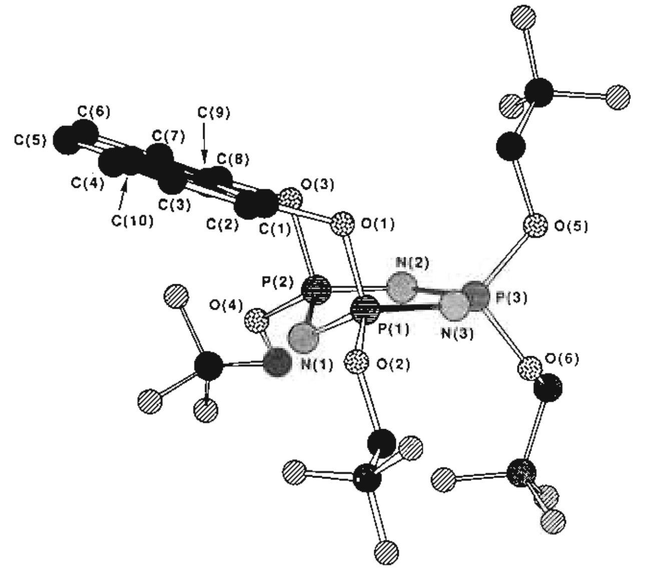

Figure 2. X-ray crystal structure of 1,3-[$N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)$] (**9**).

(2)°, P(2)–N(2)–P(3) = 122.8 (3)°, and P(1)–N(3)–P(3) = 122.3 (2)°] and are significantly wider than those in the transannular derivative **8**. This reinforces the view that the transannular biphenylenedioxy group of **8** produces the compression of the PNP angle at N(1) that results in distortion of the phosphazene ring. The biphenylenedioxy group of **16** adopts a twisted conformation, with a C(11)–C(16)–C(26)–C(21) torsion angle of 44.0 (1)°. This compares favorably with values reported for (biphenylene-2,2′-dioxy)tris(2,6-dimethylphenoxy)phosphorane of 35.6° [50] and for tris(biphenylene-2,2′-dioxy)cyclotriphosphazene of 41°.[51]

The solid-state structure of the transannular naphthylenedioxy compound 1,3-[$N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)$] (**9**) (see Figure 2) shows a greater distortion of the phosphazene ring than found for **8**, with a nitrogen atom [N(1)] located 0.635 Å below the plane of the other five atoms of the phosphazene ring (which are coplanar to within ±0.020 Å). The angle at this nitrogen [P(1)–N(1)–P(2) = 109.5 (3)°] is the narrowest PNP angle yet found for a cyclotriphosphazene and is significantly narrower than that reported for the biphenylenedioxy derivative **8** [P(1)–N(1)–P(2) = 117.4 (3)°]. The conformation of the phosphazene ring is identical to that reported for the ferrocenyl–trifluoroethoxy derivative **1** (M = Fe, R = OCH_2CF_3).[36] The bridging naphthylenedioxy group is bent away from the syn-transannular trifluoroethoxy group [i.e. coordinated via O(5)]. This results in a dihedral angle of 38.6° between the planes formed by the five coplanar atoms of the naphthalenedioxy group [O(1)–C(1)–C(9)–C(8)–O(3)] and P(1)–O(1)–O(3)–P(2). This angle is similar to those reported for the spirocyclic naphthylenedioxy groups of [(naphthylene-1,8-dioxy)tris(2,6-dimethylphenoxy)-phosphorane][50] and [tris(naphthylene-1,8-dioxy)cyclotriphosphazene] (**24**)[52] of 31.5 and 36°, respectively (also see later for **17**). Furthermore, the P(1)–O(1)–C(1) and P(2)–O(3)–C(8)

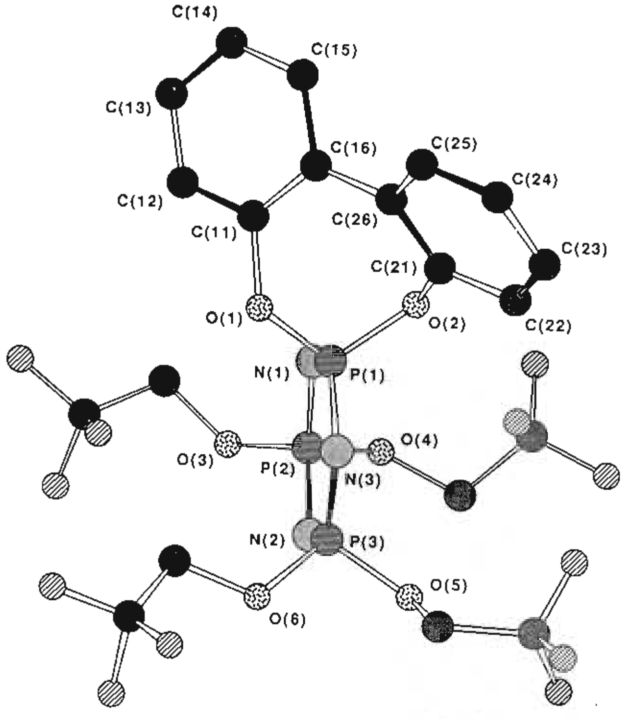

Figure 3. X-ray crystal structure of 1,1-[$N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)$] (**16**).

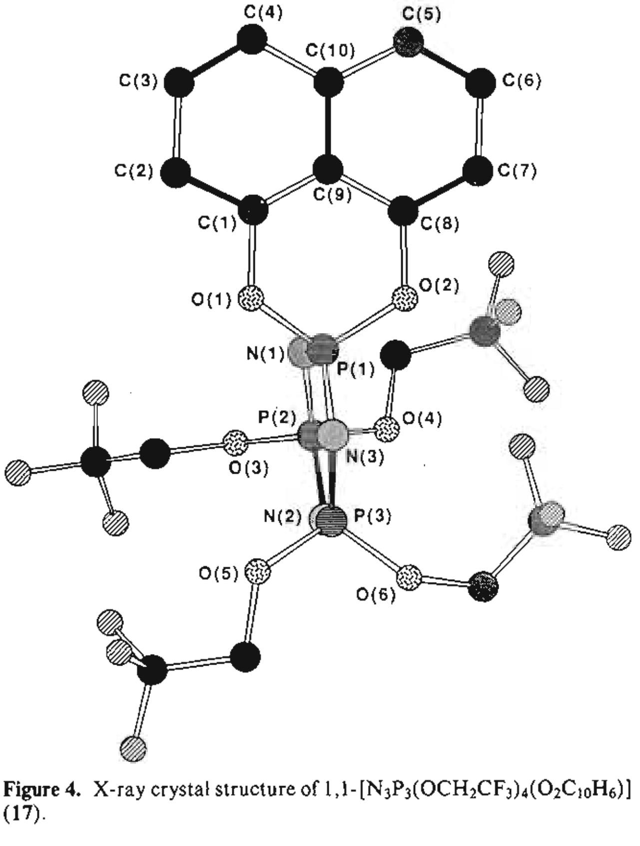

Figure 4. X-ray crystal structure of 1,1-[$N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)$] (**17**).

Table V. Summary of Crystal Data and Intensity Collection Parameters

	8	**9**	**16**	**17**
formula	$P_3N_3O_6C_{20}F_{12}H_{16}$	$P_3N_3O_6C_{18}F_{12}H_{14}$	$P_3N_3O_6C_{20}F_{12}H_{16}$	$P_3N_3O_6C_{18}F_{12}H_{14}$
fw	715	688	715	688
cryst size	0.6 × 0.75 × 0.5	0.6 × 0.85 × 0.6	0.6 × 0.45 × 0.5	0.7 × 0.95 × 0.8
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/a$	$P2_1$
cryst system	triclinic	triclinic	monoclinic	monoclinic
a (Å)	11.369 (2)	10.589 (4)	10.394 (2)	11.23 (1)
b (Å)	11.433 (4)	14.57 (1)	33.002 (8)	9.29 (3)
c (Å)	12.832 (3)	9.11 (1)	8.354 (2)	13.07 (1)
α (deg)	68.88 (2)	97.3 (1)		
β (deg)	72.02 (1)	108.60 (5)	79.13 (2)	103.57 (9)
γ (deg)	78.91 (2)	96.72 (7)		
V, (Å^3)	1421.91	1303.0	2814.7	1326.0
Z	2	2	4	2
d(calcd) (g/cm^3)	1.671	1.699	1.688	1.725
θ limits (deg)	2–25	2–25	2–25	2–25
μ (cm^{-1})	3.201	2.87	3.234	2.88
radiation (λ (Å))	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
T (K)	293	293	293	293
scan method	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
ω-scan width	(1.00 + 0.35 tan θ)	(1.00 + 0.35 tan θ)	(1.00 + 0.35 tan θ)	(1.00 + 0.35 tan θ)
cryst decay (%)	1.9	none	3.8	0.5
empirical abs cor				
min cor factor	0.9744	0.9076	0.9816	0.3185
max cor factor	0.9996	0.9985	0.9994	0.9984
no. of unique data used	5001	5859	5056	4079
no. of data used [$I > 3\sigma(I)$]	5001	3427	3537	3637
data:param ratio	11	9	8	10
R, $R_w = (\sum\Delta^2/\sum wF_o^2)^{1/2}$	0.072, 0.075	0.079, 0.079	0.064, 0.105	0.053, 0.053
$(\Delta/\sigma)_{max}$ in last cycle	0.03	0.06	0.14	0.008
$\Delta\rho$ in final ΔF map (e Å^{-3})	0.898	0.797	0.909	0.423
p (weighting factor)	0.05	0.05	0.08	0.05
error in weights	1.32	1.70	2.272	1.127

Table VI. Selected Internuclear Distances (Å) and Angles (deg) for 1,3-[$N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)$] (**8**)

P(1)–O(1)	1.601 (4)	C(11)–C(12)	1.391 (6)
P(1)–O(2)	1.574 (3)	C(11)–C(16)	1.380 (6)
P(1)–N(1)	1.577 (3)	C(12)–C(13)	1.389 (9)
P(1)–N(3)	1.592 (3)	C(13)–C(14)	1.361 (8)
P(2)–O(3)	1.585 (4)	C(14)–C(15)	1.385 (7)
P(2)–O(4)	1.578 (3)	C(15)–C(16)	1.405 (8)
P(2)–N(1)	1.582 (3)	C(16)–C(36)	1.496 (6)
P(2)–N(2)	1.589 (3)	C(31)–C(32)	1.379 (7)
P(3)–O(5)	1.582 (4)	C(31)–C(36)	1.388 (7)
P(3)–O(6)	1.587 (3)	C(32)–C(33)	1.392 (7)
P(3)–N(2)	1.576 (3)	C(33)–C(34)	1.37 (1)
P(3)–N(3)	1.579 (4)	C(34)–C(35)	1.393 (8)
O(1)–C(11)	1.415 (6)	C(35)–C(36)	1.399 (7)
O(3)–C(31)	1.404 (5)		
O(1)–P(1)–O(2)	99.9 (2)	C(11)–C(12)–C(13)	119.8 (5)
O(1)–P(1)–N(1)	111.2 (2)	C(12)–C(13)–C(14)	118.6 (5)
O(1)–P(1)–N(3)	109.9 (3)	C(13)–C(14)–C(15)	121.9 (6)
N(1)–P(1)–N(3)	116.8 (2)	C(14)–C(15)–C(16)	120.6 (5)
O(3)–P(2)–O(4)	101.0 (2)	C(11)–C(16)–C(15)	116.8 (4)
O(3)–P(2)–N(1)	110.6 (3)	C(11)–C(16)–C(36)	123.4 (4)
O(3)–P(2)–N(2)	107.1 (3)	C(15)–C(16)–C(36)	117.7 (4)
N(1)–P(2)–N(2)	117.2 (2)	O(3)–C(31)–C(32)	118.4 (5)
N(2)–P(3)–N(3)	117.8 (2)	O(3)–C(31)–C(36)	118.5 (3)
P(1)–O(1)–C(11)	121.3 (3)	C(32)–C(31)–C(36)	123.2 (5)
P(1)–O(3)–C(31)	119.0 (3)	C(31)–C(32)–C(33)	118.5 (6)
P(1)–N(1)–P(2)	117.4 (3)	C(32)–C(33)–C(34)	120.4 (5)
P(2)–N(2)–P(3)	119.2 (2)	C(33)–C(34)–C(35)	120.0 (5)
P(1)–N(3)–P(3)	120.4 (2)	C(34)–C(35)–C(36)	121.1 (6)
O(1)–C(11)–C(12)	116.1 (4)	C(16)–C(36)–C(31)	124.0 (4)
O(1)–C(11)–C(16)	121.6 (4)	C(16)–C(36)–C(35)	119.0 (5)
C(12)–C(11)–C(16)	122.3 (6)	C(31)–C(36)–C(35)	116.9 (4)

angles of 121.8 (4) and 122.0 (4)° are identical to those previously reported for **24**[52] and other aryloxy-containing phosphazenes.[53,54]

Table VII. Selected Internuclear Distances (Å) and Angles (deg) for 1,3-[$N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)$] (**9**)

P(1)–O(1)	1.597 (6)	O(3)–C(8)	1.408 (7)
P(1)–O(2)	1.560 (5)	C(1)–C(2)	1.385 (9)
P(1)–N(1)	1.566 (6)	C(1)–C(9)	1.402 (10)
P(1)–N(3)	1.567 (6)	C(2)–C(3)	1.404 (11)
P(2)–O(3)	1.577 (4)	C(3)–C(4)	1.352 (12)
P(2)–O(4)	1.573 (5)	C(4)–C(10)	1.446 (10)
P(2)–N(1)	1.593 (5)	C(5)–C(6)	1.382 (12)
P(2)–N(2)	1.571 (6)	C(5)–C(10)	1.411 (11)
P(3)–O(5)	1.573 (5)	C(6)–C(7)	1.415 (11)
P(3)–O(6)	1.579 (5)	C(7)–C(8)	1.360 (9)
P(3)–N(2)	1.562 (6)	C(8)–C(9)	1.437 (9)
P(3)–N(3)	1.602 (5)	C(9)–C(10)	1.438 (9)
O(1)–C(1)	1.398 (8)		
O(1)–P(1)–O(2)	103.9 (3)	C(2)–C(1)–C(9)	123.9 (7)
O(1)–P(1)–N(1)	108.9 (3)	C(1)–C(2)–C(3)	118.9 (8)
O(1)–P(1)–N(3)	106.8 (3)	C(2)–C(3)–C(4)	120.8 (7)
N(1)–P(1)–N(3)	117.3 (3)	C(3)–C(4)–C(10)	121.0 (7)
O(3)–P(2)–O(4)	103.0 (3)	C(10)–C(5)–C(6)	120.8 (8)
O(3)–P(2)–N(1)	109.6 (3)	C(5)–C(6)–C(7)	119.9 (8)
O(3)–P(2)–N(2)	106.5 (3)	C(6)–C(7)–C(8)	119.2 (8)
N(1)–P(2)–N(2)	116.3 (3)	C(7)–C(8)–C(9)	124.4 (6)
N(2)–P(3)–N(3)	117.7 (3)	O(3)–C(8)–C(7)	114.9 (6)
P(1)–O(1)–C(1)	121.8 (4)	O(3)–C(8)–C(9)	120.6 (6)
P(1)–O(3)–C(8)	122.0 (4)	C(1)–C(9)–C(8)	129.2 (6)
P(1)–N(1)–P(2)	109.5 (3)	C(1)–C(9)–C(10)	116.2 (6)
P(2)–N(2)–P(3)	119.8 (3)	C(4)–C(9)–C(10)	114.6 (6)
P(1)–N(3)–P(3)	117.6 (4)	C(4)–C(10)–C(5)	119.6 (7)
O(1)–C(1)–C(2)	113.9 (7)	C(4)–C(10)–C(9)	119.2 (7)
O(1)–C(1)–C(9)	122.1 (6)	C(5)–C(10)–C(9)	121.2 (7)

An X-ray diffraction study of the spirocyclic analogue 1,1-[$N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)$] (**17**) (see Figure 4) shows only a slight distortion of the phosphazene ring, with N(1) and P(3) slightly above the plane of the other four atoms of the ring [0.013 and 0.073 Å, respectively]. This distortion is similar to that reported for **24** in which the phosphazene ring also adopts a boat conformation.[52] However, the distortion is very small when compared to that found for **9**. Furthermore, the PNP angles at

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Table VIII. Selected Internuclear Distances (Å) and Angles (deg) for 1,1-[$N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)$] (**16**)

P(1)–O(1)	1.589 (3)	C(11)–C(12)	1.375 (8)
P(1)–O(2)	1.584 (3)	C(11)–C(16)	1.394 (8)
P(1)–N(1)	1.582 (4)	C(12)–C(13)	1.420 (9)
P(1)–N(3)	1.569 (4)	C(13)–C(14)	1.370 (9)
P(2)–O(3)	1.569 (4)	C(14)–C(15)	1.386 (8)
P(2)–O(4)	1.579 (3)	C(15)–C(16)	1.432 (7)
P(2)–N(1)	1.573 (4)	C(16)–C(26)	1.461 (7)
P(2)–N(2)	1.581 (4)	C(21)–C(22)	1.386 (8)
P(3)–O(5)	1.570 (4)	C(21)–C(26)	1.385 (7)
P(3)–O(6)	1.585 (3)	C(22)–C(23)	1.389 (8)
P(3)–N(2)	1.567 (4)	C(23)–C(24)	1.410 (9)
P(3)–N(3)	1.592 (4)	C(24)–C(25)	1.358 (9)
O(1)–C(11)	1.397 (5)	C(25)–C(26)	1.394 (8)
O(2)–C(21)	1.419 (5)		
O(1)–P(1)–O(2)	103.1 (2)	C(12)–C(13)–C(14)	119.4 (6)
O(1)–P(1)–N(1)	111.9 (2)	C(13)–C(14)–C(15)	121.6 (5)
O(1)–P(1)–N(3)	105.2 (2)	C(14)–C(15)–C(16)	120.6 (5)
O(2)–P(1)–N(1)	105.3 (2)	C(11)–C(16)–C(15)	116.1 (5)
O(2)–P(1)–N(3)	112.7 (2)	C(11)–C(16)–C(26)	123.4 (4)
N(1)–P(1)–N(3)	117.9 (3)	C(15)–C(16)–C(26)	120.4 (5)
N(1)–P(2)–N(2)	117.2 (2)	O(2)–C(21)–C(22)	116.7 (4)
N(2)–P(3)–N(3)	117.1 (3)	O(2)–C(21)–C(26)	119.1 (5)
P(1)–O(1)–C(11)	120.6 (2)	C(22)–C(21)–C(26)	124.1 (4)
P(1)–O(2)–C(21)	122.4 (2)	C(21)–C(22)–C(23)	118.2 (5)
P(1)–N(1)–P(2)	122.1 (2)	C(22)–C(23)–C(24)	119.5 (6)
P(2)–N(2)–P(3)	122.8 (3)	C(23)–C(24)–C(25)	119.6 (5)
P(1)–N(3)–P(3)	122.3 (2)	C(24)–C(25)–C(26)	123.3 (5)
O(1)–C(11)–C(12)	117.5 (4)	C(16)–C(26)–C(21)	121.6 (4)
O(1)–C(11)–C(16)	118.7 (4)	C(16)–C(26)–C(25)	123.1 (5)
C(12)–C(11)–C(16)	123.8 (5)	C(21)–C(26)–C(25)	115.4 (5)
C(11)–C(12)–C(13)	118.6 (5)		

Table IX. Selected Internuclear Distances (Å) and Angles (deg) for 1,1-[$N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)$ (**17**)

P(1)–O(1)	1.580 (4)	O(2)–C(8)	1.418 (7)
P(1)–O(2)	1.606 (4)	C(1)–C(2)	1.386 (9)
P(1)–N(1)	1.573 (5)	C(1)–C(9)	1.407 (8)
P(1)–N(3)	1.585 (5)	C(2)–C(3)	1.410 (10)
P(2)–O(3)	1.596 (4)	C(3)–C(4)	1.359 (12)
P(2)–O(4)	1.577 (4)	C(4)–C(10)	1.456 (11)
P(2)–N(1)	1.581 (5)	C(5)–C(10)	1.434 (10)
P(2)–N(2)	1.592 (5)	C(5)–C(6)	1.376 (12)
P(3)–O(5)	1.589 (5)	C(6)–C(7)	1.450 (10)
P(3)–O(6)	1.578 (4)	C(7)–C(8)	1.397 (9)
P(3)–N(2)	1.567 (5)	C(8)–C(9)	1.386 (9)
P(3)–N(3)	1.568 (5)	C(9)–C(10)	1.403 (7)
O(1)–C(1)	1.402 (7)		
O(1)–P(1)–O(2)	103.7 (2)	C(1)–C(2)–C(3)	119.4 (7)
O(1)–P(1)–N(1)	106.5 (3)	C(2)–C(3)–C(4)	117.6 (7)
O(1)–P(1)–N(3)	110.6 (2)	C(3)–C(4)–C(10)	124.5 (6)
O(2)–P(1)–N(1)	106.6 (3)	C(10)–C(5)–C(6)	120.8 (6)
O(2)–P(1)–N(3)	109.7 (3)	C(5)–C(6)–C(7)	122.7 (7)
N(1)–P(1)–N(3)	118.6 (3)	C(6)–C(7)–C(8)	113.1 (7)
N(1)–P(2)–N(2)	118.2 (2)	C(7)–C(8)–C(9)	126.6 (6)
N(2)–P(3)–N(3)	118.3 (3)	O(2)–C(8)–C(7)	113.4 (6)
P(1)–O(1)–C(11)	120.2 (4)	O(2)–C(8)–C(9)	120.0 (5)
P(1)–O(2)–C(21)	119.4 (4)	C(1)–C(9)–C(8)	123.2 (5)
P(1)–N(1)–P(2)	120.9 (3)	C(1)–C(9)–C(10)	118.1 (6)
P(2)–N(2)–P(3)	121.7 (3)	C(8)–C(9)–C(10)	118.7 (6)
P(1)–N(3)–P(3)	121.2 (3)	C(4)–C(10)–C(5)	125.2 (6)
O(1)–C(1)–C(2)	117.6 (6)	C(4)–C(10)–C(9)	116.7 (6)
O(1)–C(1)–C(9)	118.7 (5)	C(5)–C(10)–C(9)	118.1 (6)
C(2)–C(1)–C(9)	123.6 (6)		

Table X. Atomic Positional Parameters for **8** with Esd's in Parentheses

atom	*x*	*y*	*z*
P(1)	0.2674 (1)	0.3107 (1)	0.67395 (9)
P(2)	0.5106 (1)	0.2416 (1)	0.60988 (9)
P(3)	0.3717 (1)	0.0936 (1)	0.8310 (1)
F(21)	–0.0927 (3)	0.5400 (3)	0.8447 (4)
F(22)	0.0536 (5)	0.6505 (4)	0.7043 (5)
F(23)	0.0856 (5)	0.5351 (4)	0.8656 (4)
F(41)	0.8050 (3)	0.1953 (4)	0.7104 (4)
F(42)	0.8738 (3)	0.3500 (5)	0.5472 (4)
F(43)	0.8152 (3)	0.3803 (4)	0.7094 (3)
F(51)	0.1908 (5)	0.1517 (4)	0.1946 (3)
F(52)	0.3672 (5)	0.2267 (4)	0.0908 (4)
F(53)	0.2209 (6)	0.2843 (4)	0.0088 (4)
F(61)	0.1560 (5)	0.7454 (4)	0.8803 (4)
F(62)	0.1130 (5)	–0.1340 (6)	0.9724 (6)
F(63)	0.2423 (6)	–0.2925 (5)	1.0190 (5)
O(1)	0.1934 (3)	0.3092 (3)	0.5868 (2)
O(2)	0.1953 (3)	0.4302 (3)	0.7014 (3)
O(3)	0.5259 (3)	0.1915 (3)	0.5089 (2)
O(4)	0.6395 (3)	0.3017 (3)	0.5693 (2)
O(5)	0.3934 (3)	0.1075 (3)	0.9409 (3)
O(6)	0.3446 (3)	–0.0564 (3)	0.8929 (3)
N(1)	0.4033 (3)	0.3535 (3)	0.6032 (3)
N(2)	0.4995 (3)	0.1166 (4)	0.7335 (3)
N(3)	0.2533 (3)	0.1775 (3)	0.7909 (3)
C(11)	0.2016 (4)	0.1983 (4)	0.5622 (4)
C(12)	0.1094 (4)	0.1114 (5)	0.6336 (4)
C(13)	0.1066 (5)	0.0038 (5)	0.6110 (5)
C(14)	0.1964 (5)	–0.0147 (5)	0.5200 (5)
C(15)	0.2880 (5)	0.0719 (5)	0.4481 (4)
C(16)	0.2920 (4)	0.1823 (4)	0.4681 (4)
C(21)	0.0668 (5)	0.4261 (5)	0.7591 (5)
C(22)	0.0259 (5)	0.5401 (5)	0.7883 (5)
C(31)	0.5001 (4)	0.2797 (4)	0.3994 (4)
C(32)	0.5901 (5)	0.3617 (5)	0.3140 (4)
C(33)	0.5662 (7)	0.4467 (6)	0.2040 (5)
C(34)	0.4557 (7)	0.4476 (6)	0.1813 (5)
C(35)	0.3662 (5)	0.3638 (5)	0.2690 (4)
C(36)	0.3868 (4)	0.2775 (4)	0.3807 (4)
C(41)	0.6607 (4)	0.3658 (4)	0.6354 (4)
C(42)	0.2123 (5)	0.6794 (6)	0.3488 (5)
C(51)	0.3042 (5)	0.0711 (5)	1.0539 (4)
C(52)	0.2687 (7)	0.1848 (6)	1.0863 (5)
C(61)	0.3025 (6)	–0.1136 (5)	0.8341 (5)
C(62)	0.2039 (8)	0.8000 (7)	0.9278 (7)

the ring nitrogen atoms are all equal [P(1)–N(1)–P(2) = 120.9 (3)°, P(2)–N(2)–P(3) = 121.7 (3)°, and P(1)–N(3)–P(3) = 121.2 (3)°] and are significantly wider than at nitrogen atom N(1) in cyclic trimer **9** [P(1)–N(1)–P(2) = 109.5 (3)°]. The naphthylenedioxy group is bent at the oxygen atoms O(1) and O(2) in a manner similar to the arrangement in cyclic trimers **9** and **24**,[52] with a dihedral angle of 33 (2)° between the planes formed by O(1)–C(1)–C(9)–C(8)–O(2) (coplanar to within ±0.05 (3) Å) and O(1)–P(1)–O(2). Alternatively, the phosphorus atom [P(1)] is displaced from the O(1)–C(1)–C(9)–C(8)–O(2) plane by 0.517 (4) Å.

These X-ray crystallographic results show that decreasing the "bite angle" of the transannular bridge on moving from a biphenylenedioxy to a naphthylenedioxy group increases the strain in the phosphazene ring, as measured both by the size of the PNP angle at N(1) and its displacement below the phosphazene ring. The conformation of the phosphazene ring is also dependent on the nature of the transannular bridge. Bridges with large "bite angles", such as the biphenylenedioxy group, favor a boat conformation of the phosphazene ring, with a phosphorus and a nitrogen displaced from the ring plane. On the other hand, smaller bridges such as a naphthylenedioxy or a ferrocenyl group,[36] favor a conformation in which only the nitrogen atom N(1) between the transannular bridge is displaced below the plane of the other five atoms of the ring.

Conclusions

A general synthetic route to transannular substituted cyclotriphosphazenes is described. This synthetic route has allowed the preparation of hitherto inaccessible cyclotriphosphazenes with transannular aryloxy substituents. These are not accessible via the direct reaction of $(NPCl_2)_3$ (**3**) with reagents such as biphenols or dihydroxynaphthalenes. The analogous spirocyclic derivatives can be prepared directly from $[NPCl_2]_3$ (**3**) in a two-step reaction. The solid-state structures of 1,3-[$N_3P_3(OCH_2CF_3)_4\{O_2C_{12}H_8\}$]

Table XI. Atomic Positional Parameters for **9** with Esd's in Parentheses

atom	*x*	*y*	*z*
P(1)	0.3258 (2)	0.8512 (1)	0.3008 (2)
P(2)	0.2103 (2)	0.7067 (1)	0.3317 (2)
P(3)	0.4405 (2)	0.6573 (1)	0.2565 (2)
F(21)	0.3852 (10)	1.1283 (6)	0.2254 (9)
F(22)	0.3834 (7)	1.1121 (5)	0.0112 (8)
F(23)	0.2166 (7)	1.1338 (5)	0.0764 (8)
F(41)	−0.1505 (6)	0.5892 (6)	−0.0002 (7)
F(42)	−0.1834 (5)	0.6764 (5)	0.1765 (7)
F(43)	−0.0831 (7)	0.5275 (6)	0.1985 (9)
F(51)	0.3577 (6)	0.6077 (4)	−0.1775 (5)
F(52)	0.4964 (9)	0.6921 (6)	−0.2019 (6)
F(53)	0.3460 (7)	0.7598 (4)	−0.1017 (6)
F(61)	0.7815 (7)	0.6232 (5)	0.6895 (6)
F(62)	0.8212 (6)	0.5363 (7)	0.5115 (8)
F(63)	0.7736 (8)	0.6911 (7)	0.4968 (8)
O(1)	0.3733 (4)	0.8718 (3)	0.4671 (5)
O(2)	0.3033 (6)	0.9578 (4)	0.2328 (6)
O(3)	0.2410 (4)	0.7139 (3)	0.4984 (4)
O(4)	0.0761 (5)	0.6687 (4)	0.2890 (5)
O(5)	0.4455 (5)	0.6102 (3)	0.1067 (5)
O(6)	0.5761 (5)	0.5980 (3)	0.3496 (5)
N(1)	0.1901 (5)	0.8170 (4)	0.2674 (5)
N(2)	0.3239 (6)	0.6240 (4)	0.2970 (6)
N(3)	0.4422 (5)	0.7763 (4)	0.2594 (6)
C(1)	0.2891 (7)	0.9302 (5)	0.5411 (7)
C(2)	0.3088 (8)	1.0288 (5)	0.5679 (8)
C(3)	0.2329 (9)	1.0933 (6)	0.6460 (8)
C(4)	0.1404 (8)	1.0605 (6)	0.6924 (8)
C(5)	0.0241 (8)	0.9250 (7)	0.7182 (8)
C(6)	0.0034 (8)	0.8265 (8)	0.6963 (8)
C(7)	0.0759 (7)	0.7580 (6)	0.6173 (8)
C(8)	0.1681 (6)	0.7894 (5)	0.5675 (6)
C(9)	0.1963 (6)	0.8900 (5)	0.5865 (6)
C(10)	0.1198 (7)	0.9574 (6)	0.6665 (7)
C(21)	0.3506 (10)	0.9765 (6)	0.1196 (10)
C(22)	0.3349 (9)	1.0889 (7)	0.1074 (9)
C(41)	0.0274 (8)	0.6439 (8)	0.1410 (9)
C(42)	−0.0963 (8)	0.6118 (7)	0.1304 (9)
C(51)	0.5212 (7)	0.6395 (6)	0.0254 (7)
C(52)	0.4279 (10)	0.6757 (7)	−0.1154 (8)
C(61)	0.6047 (7)	0.6102 (6)	0.5023 (7)
C(62)	0.7448 (10)	0.6183 (7)	0.5486 (9)

(**8**) and 1,3-[$N_3P_3(OCH_2CF_3)_4\{O_2C_{10}H_6\}$] (**9**) were determined by X-ray diffraction and show that a decrease in the "bite angle" of the transannular bridge increases the strain in the phosphazene ring. X-ray diffraction studies of 1,1-[$N_3P_3(OCH_2CF_3)_4\{O_2C_{12}H_8\}$] (**16**) and 1,1-[$N_3P_3(OCH_2CF_3)_4\{O_2C_{10}H_6\}$] (**17**) confirmed that a transannular arrangement of the difunctional reagent is necessary to produce a distortion in the phosphorus–nitrogen ring.

Experimental Section

Materials. Hexachlorocyclotriphosphazene was provided by Ethyl Corp. It was recrystallized from hexane and sublimed (30 °C, 0.05 mmHg) before use. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl under dry argon before use. Hexane was distilled from CaH_2. 2,2,2-Trifluoroethanol (Halocarbon) and 1,3-propanediol (Aldrich) were distilled from anhydrous BaO and were stored over 4-Å molecular sieves. Biphenol, 1,3-diaminopropane, Bu^{n}Li (as a 1.6 M solution in hexane), pyridine, sodium, and sodium carbonate were purchased from Aldrich and were used as received. Catechol, 1,8-diaminonaphthalene, and biphenyl (Aldrich) were sublimed before use. Dimethylamine was purchased from Matheson and was dried over sodium before use. Triethylamine (Aldrich) was distilled from CaH_2 before use. All manipulations were performed under an atmosphere of dry argon using standard Schlenk line techniques. Column chromatography was carried out on silica gel columns of varying lengths using CH_2Cl_2 and hexane as the eluting solvents. 1,3-[$N_3P_3(OCH_2CF_3)_4Cl_2$],[40] $(NPF_2)_3$,[54] and 1,8-dihydroxynaphthalene[55] were prepared by standard literature procedures. Compound **6**, 1,3-[$N_3P_3(OCH_2CF_3)_4Cl_2$], was prepared by a method described earlier.[40]

Table XII. Atomic Positional Parameters for **16** with Esd's in Parentheses

atom	*x*	*y*	*z*
P(1)	0.4184 (1)	0.15155 (4)	0.4954 (1)
P(2)	0.3948 (1)	0.10388 (4)	0.7703 (1)
P(3)	0.4907 (1)	0.07070 (4)	0.4678 (1)
F(31)	0.7176 (4)	0.1070 (2)	0.9768 (8)
F(32)	0.7078 (4)	0.1352 (2)	0.7493 (6)
F(33)	0.2372 (4)	0.3301 (2)	−0.0524 (6)
F(41)	−0.0189 (3)	0.0588 (2)	0.7162 (6)
F(42)	0.0141 (4)	0.1140 (2)	0.8324 (8)
F(43)	0.1328 (4)	0.0984 (2)	0.5947 (5)
F(51)	0.2575 (4)	−0.0188 (2)	0.2791 (5)
F(52)	0.3154 (4)	0.0052 (2)	0.0368 (4)
F(53)	0.2093 (4)	0.0411 (2)	0.2248 (6)
F(61)	−0.1455 (5)	0.0520 (2)	0.1590 (5)
F(62)	−0.1094 (4)	0.0281 (2)	0.3718 (6)
F(63)	−0.0361 (4)	0.0867 (2)	0.3027 (8)
O(1)	0.5247 (3)	0.1862 (1)	0.4390 (4)
O(2)	0.2888 (3)	0.16950 (9)	0.4500 (3)
O(3)	0.4671 (3)	0.1089 (1)	0.9205 (4)
O(4)	0.2573 (3)	0.0897 (1)	0.8720 (4)
O(5)	0.4086 (3)	0.0372 (1)	0.4011 (4)
O(6)	0.6354 (3)	0.0552 (1)	0.3967 (4)
N(1)	0.3858 (4)	0.1462 (1)	0.6865 (4)
N(2)	0.4553 (4)	0.0675 (1)	0.6606 (5)
N(3)	0.4718 (4)	0.1133 (1)	0.3884 (4)
C(11)	0.4925 (4)	0.2274 (1)	0.4770 (6)
C(12)	0.5499 (5)	0.2465 (2)	0.5934 (7)
C(13)	0.5285 (6)	0.2875 (2)	0.6227 (7)
C(14)	0.4487 (6)	0.3072 (2)	0.5401 (8)
C(15)	0.3904 (6)	0.2888 (2)	0.4231 (7)
C(16)	0.4103 (5)	0.2468 (1)	0.3902 (6)
C(21)	0.2882 (4)	0.1890 (1)	0.2996 (5)
C(22)	0.2208 (5)	0.1700 (2)	0.1924 (6)
C(23)	0.2113 (6)	0.1884 (2)	0.0475 (7)
C(24)	0.2706 (7)	0.2261 (2)	0.0114 (7)
C(25)	0.3373 (6)	0.2455 (2)	0.1198 (7)
C(26)	0.3471 (5)	0.2273 (2)	0.2696 (6)
C(31)	0.5278 (5)	0.1437 (2)	0.9611 (6)
C(32)	0.6727 (6)	0.1393 (2)	0.9092 (8)
C(41)	0.1707 (5)	0.0624 (2)	0.8211 (7)
C(42)	0.0690 (6)	0.0846 (2)	0.7472 (9)
C(51)	0.4298 (5)	0.0270 (2)	0.2292 (6)
C(52)	0.3005 (5)	0.0138 (2)	0.1971 (6)
C(61)	0.7435 (5)	0.0806 (2)	0.4062 (8)
C(62)	−0.1400 (6)	0.0642 (2)	0.3059 (9)

Caution! We emphasize that deamination reactions of the type used to prepare **6** should be carried out only by experienced investigators using adequate shielding to guard against a pressure explosion if the HCl pressure within the sealed tube exceeds a safe level.

Equipment. ^{31}P (36.2 MHz) NMR spectra were recorded using a JEOL FX 90Q NMR spectrometer. High-field ^{31}P (146 MHz), ^{13}C (90 MHz), and ^{1}H (360 MHz) NMR spectra were obtained by use of a Bruker WM 360 NMR spectrometer. Both ^{31}P and ^{13}C NMR spectra were proton decoupled unless otherwise specified. ^{31}P NMR spectra were referenced relative to external 85% H_3PO_4, with positive shifts recorded downfield from the reference. ^{1}H and ^{13}C NMR spectra were referenced relative to external tetramethylsilane. Vapor phase chromatography was carried out by means of a Varian 3700 unit with a flame ionization detector. A Supelco OV-101 column with injector and detector temperatures set at 350 °C was used. An initial temperature of 100 °C and a heating rate of 10 °C/min to a maximum temperature of 350 °C were employed. Typical sample sizes varied between 1 and 3 μL in CH_2Cl_2. Retention times were in the range of 10–20 min. Reactions were routinely followed by ^{31}P NMR spectroscopy, thin layer chromatography, and VPC-MS. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN.

Reaction of 1,3-[$N_3P_3(OCH_2CF_3)_4Cl_2$] (6) with Catechol. Compound **6** (5 g, 8.31 mmol) and triethylamine (20 mL, 7 mmol) were dissolved in 500 mL of dry THF. Catechol (1.5 g, 13.6 mmol) was added, and the reaction mixture was heated at reflux for 40 h, followed by cooling to room temperature. The solvent was removed at reduced pressure, and the resulting oil was dissolved in diethyl ether (200 mL). A white

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[55] Parker, K. A.; Iqbal, T. *J. Org. Chem.* **1980**, *45*, 1149.

Table XIII. Atomic Positional Parameters for **17** with Esd's in Parentheses

atom	*x*	*y*	*z*
P(1)	0.2157 (1)	0.3565 (0)	0.2079 (1)
P(2)	0.0682 (1)	0.2293 (2)	0.0344 (1)
P(3)	0.2292 (1)	0.0645 (2)	0.1796 (1)
F(31)	−0.0757 (4)	0.2291 (8)	0.2259 (4)
F(32)	−0.2557 (5)	0.1405 (6)	0.1871 (4)
F(33)	−0.2155 (5)	0.3434 (6)	0.1234 (5)
F(41)	0.1031 (5)	0.0954 (6)	−0.3154 (4)
F(42)	0.1536 (5)	0.3113 (6)	−0.2633 (4)
F(43)	0.2497 (4)	0.1335 (6)	−0.1796 (4)
F(51)	0.5630 (5)	−0.0353 (7)	0.0090 (5)
F(52)	0.4523 (5)	−0.2102 (6)	0.0470 (5)
F(53)	0.5768 (4)	−0.1043 (6)	0.1690 (5)
F(61)	0.0828 (6)	−0.1472 (9)	0.4129 (5)
F(62)	0.1259 (7)	0.0773 (8)	0.4311 (6)
F(63)	0.2305 (6)	−0.0769 (7)	0.5317 (4)
O(1)	0.1566 (4)	0.4125 (5)	0.2988 (3)
O(2)	0.3162 (4)	0.4769 (5)	0.2011 (3)
O(3)	−0.0777 (3)	0.2180 (5)	0.0068 (3)
O(4)	0.0910 (4)	0.2654 (5)	−0.0773 (3)
O(5)	0.3395 (4)	−0.0267 (5)	0.1562 (4)
O(6)	0.1831 (4)	−0.0423 (5)	0.2558 (3)
N(1)	0.1133 (5)	0.3676 (5)	0.1030 (4)
N(2)	0.1245 (5)	0.0776 (5)	0.0770 (4)
N(3)	0.2811 (4)	0.2063 (6)	0.2386 (4)
C(1)	0.2309 (6)	0.4701 (7)	0.3911 (5)
C(2)	0.1880 (7)	0.4631 (8)	0.4820 (6)
C(3)	0.2570 (8)	0.5259 (8)	0.5753 (6)
C(4)	0.3633 (8)	0.5928 (8)	0.5710 (5)
C(5)	0.5218 (7)	0.6750 (7)	0.4704 (6)
C(6)	0.5604 (7)	0.6761 (8)	0.3780 (7)
C(7)	0.4936 (6)	0.6046 (7)	0.2833 (6)
C(8)	0.3856 (5)	0.5394 (6)	0.2951 (5)
C(9)	0.3420 (5)	0.5361 (6)	0.3858 (4)
C(10)	0.4120 (6)	0.6008 (7)	0.4773 (5)
C(31)	−0.1455 (6)	0.1295 (7)	0.0592 (5)
C(32)	−0.1719 (6)	0.2107 (8)	0.1492 (5)
C(41)	0.0461 (5)	0.1697 (7)	−0.1634 (4)
C(42)	0.1384 (7)	0.1775 (8)	−0.2300 (5)
C(51)	0.4048 (6)	0.0300 (7)	0.0854 (5)
C(52)	0.4997 (6)	−0.0836 (8)	0.0769 (6)
C(61)	0.2561 (6)	−0.0658 (7)	0.3601 (5)
C(62)	0.1732 (8)	−0.0538 (9)	0.4322 (6)

precipitate was isolated by filtration and was washed with 3 × 100 mL of deionized water. This was found to be $[P(O_2C_6H_4)_3][Et_3NHCl]$ (**15**) (1.2 g, 29%) by comparison with an authentic sample. The soluble portion was subjected to column chromatography, and 1,3-$[N_3P_3(OCH_2CF_3)_4\{O_2C_6H_4\}]$ (**7**) (2.35 g, 44%) was eluted with dichloromethane. This compound is a colorless liquid.

Reaction of 1,3-$[N_3P_3(OCH_2CF_3)_4Cl_2]$ (6) with Biphenol. In a 1-L round-bottomed flask was placed **6** (5.0 g, 8.31 mmol), triethylamine (4.6 mL, 32 mmol), and 500 mL of dry THF. A solution of biphenol (3.1 g, 16.7 mmol) in THF (30 mL) was added dropwise to the above solution over a period of 5 min. The resulting reaction mixture was heated at reflux for 17 h, allowed to cool, and then filtered through a glass frit to remove any triethylamine hydrochloride. The solvent was removed at reduced pressure, the resultant white solid was extracted with dichloromethane (5 mL), and the solution was chromatographed. The first band eluted with 1:5 dichloromethane/hexane gave 2.76 g (46%) of 1,3-$[N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)]$ (**8**) as white crystals after recrystallization from dichloromethane/hexane. A second band eluted with 1:1 dichloromethane/hexane gave 2.70 g (43%) of $[N_3P_3(OCH_2CF_3)_4(OC_{12}H_8OH)Cl]$ (**13**) as white crystals.

Reaction of 1,3-$[N_3P_3(OCH_2CF_3)_4Cl_2]$ (6) with 1,8-Dihydroxynaphthalene. In a 500-mL round-bottomed flask was placed **6** (5.0 g, 8.31 mmol), triethylamine (10 mL, 70 mmol), and 300 mL of dry THF. A solution of 1,8-dihydroxynaphthalene (1.5 g, 9.4 mmol) in THF (5 mL) was added dropwise to the above solution over a period of 5 min. The resultant reaction mixture was heated at reflux for 17 h and then filtered through silica gel to remove the triethylamine hydrochloride. The solvent was removed at reduced pressure, and the resultant white solid was extracted with dichloromethane (5 mL) and chromatographed. The first band eluted with 1:9 dichloromethane/hexane gave 1.0 g (17%) of $[N_3P_3(OCH_2CF_3)_4(OC_{10}H_6OH)Cl]$ (**14**) as a colorless oil. A second band, eluted with 1:5 dichloromethane/hexane, gave 2.82 g (49%) of 1,3-$[N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)]$ (**9**) as white crystals when recrystallized from hexane at 0 °C.

Reaction of 1,3-$[N_3P_3(OCH_2CF_3)_4Cl_2]$ (6) with 1,8-Diaminonaphthalene. Compound **6** (1 g, 1.65 mmol) and triethylamine (0.5 mL, 3.5 mmol) were dissolved in 150 mL of dry THF. 1,8-Diaminonaphthalene (0.53 g, 3.4 mmol) was added dropwise from an addition funnel as a solution in THF (50 mL). The reaction was heated at reflux for 1 week and was then cooled to room temperature. After removal of the solvent at reduced pressure, the resultant red oil was subjected to chromatography. 1,3-$[N_3P_3(OCH_2CF_3)_4\{(NH)_2C_{10}H_6\}]$ (**10**) (0.41 g, 36%) was eluted with dichloromethane and was recrystallized from dichloromethane/hexane to give colorless crystals.

Reaction of 1,3-$[N_3P_3(OCH_2CF_3)_4Cl_2]$ (6) with 1,3-Diaminopropane. To a 200-mL Schlenk flask was added **6** (3 g, 4.95 mmol) and 100 mL of dry THF. 1,3-Diaminopropane (1 g, 13 mmol) was added dropwise from a syringe, and an immediate white precipitate was formed. The solution was stirred for 2 h and was then filtered to remove the amine hydrochloride salt. The THF was removed at reduced pressure to leave a colorless oil, which was chromatographed with dichloromethane (10 mL). 1,3-$[N_3P_3(OCH_2CF_3)_4\{NH(CH_2)_3NH\}]$ (**11**) (0.8 g, 26%) was obtained after elution with 1:4 diethyl ether/hexane. It was isolated as a white microcrystalline powder.

Reaction of 1,3-$[N_3P_3(OCH_2CF_3)_4Cl_2]$ (6) with 1,3-Propanediol. To a 500-mL 3-necked round-bottomed flask was added **6** (1 g, 1.65 mmol), pyridine (0.5 g, 6.6 mmol), and 350 mL of dry THF. 1,3-Propanediol (0.26 g, 3.4 mmol) was added dropwise from a syringe, and the reaction was heated at reflux for 3 days. The resulting solution was filtered, and the solvent was removed at reduced pressure. The brown oil obtained was dissolved in dichloromethane (1 mL) and was chromatographed. 1,3-$[N_3P_3(OCH_2CF_3)_4\{O(CH_2)_3O\}]$ (**12**) (0.18 g) eluted with dichloromethane and was isolated in 18% yield as a colorless liquid.

Reaction of 1,3-$[N_3P_3(OCH_2CF_3)_4Cl_2]$ (6) with the Disodium Salt of 1,3-Propanediol. 1,3-Propanediol (0.25 mL, 3.5 mmol) was added dropwise to a suspension of sodium hydride (0.2 g, 8.3 mmol) in 50 mL of dry THF. Hydrogen gas was evolved as a white precipitate formed. After the mixture had been stirred for 1 h, **6** (1.0 g, 1.65 mmol) was added as a solution in 10 mL of dry THF. A slight bleaching of the solution was observed. After 2 h, complete consumption of the starting material had occurred. The reaction mixture was filtered through silica gel, and the solvent was removed at reduced pressure. Two fractions were isolated by column chromatography. The first, eluted with 4:1 dichloromethane/hexane, yielded 0.33 g (33%) of a mixture of 1,1- and 1,3-$[N_3P_3(OCH_2CF_3)_4\{O(CH_2)_3O\}]$ (**12** and **20**) as a colorless liquid. The second, eluted with dichloromethane, was found to be 1,1-$[N_3P_3(OCH_2CF_3)_2\{O(CH_2)_3O\}_2]$ (**21**) (0.33 g, 41%). It was recrystallized from dichloromethane/hexane to give colorless crystals.

Similar procedures were used for the preparation of the spirocyclic phosphazenes, 1,1-$[N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)]$ (**16**), 1,1-$[N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)]$ (**17**), 1,1-$[N_3P_3(OCH_2CF_3)_4\{(NH)_2C_{10}H_6\}]$ (**18**), 1,1-$[N_3P_3(OCH_2CF_3)_4\{NH(CH_2)_3NH\}]$ (**19**), and 1,1-$[N_3P_3(OCH_2CF_3)_4\{O(CH_2)_3O\}]$ (**20**), and a representative example is shown below for compound **16**.

Preparation of 1,1-$[N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)]$ (16). In a 1-L round-bottomed flask was placed $(NPCl_2)_3$ (20 g, 57 mmol), triethylamine (20 mL, 0.14 mol), and 500 mL of dry THF. A solution of biphenol (10.7 g, 57 mmol) in THF (150 mL) was added dropwise over a period of 3 h. The immediate formation of a white precipitate occurred. After a further 1 h of reaction at room temperature, the stirring was discontinued and the triethylamine hydrochloride salts were allowed to settle. The colorless solution was transferred to a fritted addition funnel, and the salts were washed with 100 mL of dry THF. This solution was then added dropwise to an excess of sodium trifluoroethoxide, prepared from 10.1 g (0.25 mol) of 60% sodium hydride dispersed in mineral oil and trifluoroethanol (18.4 mL, 0.25 mol). Heating at 40 °C for 17 h produced a white precipitate of sodium chloride. This was removed by filtration through silica gel at room temperature followed by washing with 2 × 50 mL of THF. The solvent was then removed, and the remaining colorless oil was redissolved in diethyl ether (300 mL), washed with 3 × 300 mL of deionized water, and dried with anhydrous magnesium sulfate. 1,1-$[N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)]$ (**16**) was isolated as a microcrystalline solid (39.1 g, 95%) by removal of the solvent and drying under vacuum (10 μmHg) for 24 h. This solid was recrystallized from dichloromethane/hexane to give colorless crystals.

Preparation of 1,1-$[N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)]$ (17). $(NPCl_2)_3$ (3 g, 8.6 mmol), triethylamine (10 mL, 70 mmol), and 1,8-dihydroxynaphthalene (1.4 g, 8.8 mmol) were allowed to react as described in the previous example, and the mixture was added to a solution of sodium trifluoroethoxide (43 mmol) in 300 mL of THF. Recrystallization from dichloromethane/hexane gave 1,1-[$N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)$] (**17**) in 55% yield (3.2 g) as colorless crystals.

Preparation of 1,1-[$N_3P_3(OCH_2CF_3)_4\{(NH)_2C_{10}H_6\}$] (18). $(NPCl_2)_3$ (5 g, 14.3 mmol), triethylamine (10 mL, 70 mmol), and 1,8-diaminonaphthalene (2.3 g, 14.6 mmol) were allowed to interact using the procedure described above, and the mixture was added to a solution of sodium trifluoroethoxide (63 mmol) in 300 mL of THF. 1,1-[$N_3P_3(OCH_2CF_3)_4\{(NH)_2C_{10}H_6\}$] (**18**) was isolated by recrystallization from dichloromethane/hexane to give 7.1 g of colorless crystals (71%).

Preparation of 1,1-[$N_3P_3(OCH_2CF_3)_4\{NH(CH_2)_3NH\}$] (19). $(NPCl_2)_3$ (5 g, 14.3 mmol) and 1,3-diaminopropane (2.1 g, 28 mmol) were allowed to react in THF as described above, and the mixture was added to a solution of sodium trifluoroethoxide (63 mmol) in 350 mL of THF. After removal of the solvent the colorless oil was dissolved in diethyl ether (300 mL), washed with 3 × 300 mL of deionized water, and dried with anhydrous magnesium sulfate. Precipitation from hexane gave 8.1 g (94%) of 1,1-[$N_3P_3(OCH_2CF_3)_4\{NH(CH_2)_3NH\}$] (**19**) as a colorless oil.

Preparation of 1,1-[$N_3P_3(OCH_2CF_3)_4\{O(CH_2)_3O\}$] (20). $(NPCl_2)_3$ (10 g, 29 mmol), triethylamine (9 mL, 63 mmol), and 1,3-propanediol (2.1 mL, 29 mmol) were allowed to react as described above, and the solution was added to a solution of sodium trifluoroethoxide (0.14 mol) in 350 mL of THF. Column chromatography and elution with 1:1 dichloromethane/hexane gave 7.7 g (45%) of 1,1-[$N_3P_3(OCH_2CF_3)_4$-$\{O(CH_2)_3O\}$] (**20**) as a colorless oil.

Preparation of 1,1-[$N_3P_3(OCH_2CF_3)_4(C_{12}H_8)$] (22). 2,2′-Dilithiobiphenyl was prepared by the direct lithiation of biphenyl (1.3 g, 9 mmol) with Bu^nLi (10.5 mL of a 1.6 M solution in hexane) in the presence of tetramethylethylenediamine (3 mL, 36 mmol), as described in the literature.[45] The dilithium reagent was then added to a THF solution of $(NPF_2)_3$ (2.1 g, 8.4 mmol), and the mixture was stirred at room temperature for 30 min. The solvent and any unreacted $(NPF_2)_3$ were removed under vacuum, and the resultant red solid was dissolved in 30 mL of dry THF. To this solution was added sodium trifluoroethoxide, prepared from sodium hydride (0.8 g of a 60% dispersion in mineral oil) and trifluoroethanol (2.5 mL, 34 mmol) in 30 mL of dry THF. After 30 min of reaction the solvent was removed and the reaction mixture was subjected to chromatography. Two fractions were removed with 1:4 dichloromethane/hexane. The first was isolated as a colorless oil and was found to be $N_3P_3(OCH_2CF_3)_5(C_{12}H_9)$ (**23**), and the second gave colorless crystals (0.6 g, 11%) from dichloromethane/hexane and was characterized as 1,1-[$N_3P_3(OCH_2CF_3)_4(C_{12}H_8)$] (**22**).

Crystal Structure Determinations. Data were collected using an Enraf-Nonius CAD4 diffractometer (293 K, Mo Kα X-radiation, graphite monochromator, $\lambda = 0.710\,73$ Å) by a least-squares refinement of the setting angles of 25 reflections with θ in the range 10–15°. Intensity data were collected by the $\omega/2\theta$ scan method in the range of $2 < \theta < 25$, with ω scan width $= 1.00 + 0.35 \tan \theta$. The intensities of three reflections, chosen as standards, were monitored at regular intervals over the course of the data collection; any decay was corrected for by appropriate scaling. Data were corrected for Lorentz and polarization factors and for empirical absorption.

The structures were solved by direct methods.[56] Refinement of the structure was by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic temperature factors for the non-hydrogen atoms, and with hydrogens in calculated positions. Programs and computers used in this study are described in ref 57. Additional refinements for the structures of **9** and **17** were performed using the SHELX 76 refinement package.

Crystals of **8** were grown from dichloromethane/hexane as clear, colorless prisms. Of the 5386 reflections measured, 5001 were unique with $I > 3\sigma(I)$ [merging $R = 0.013$ after absorption correction (max, min transmission factors = 0.9996, 0.9744)].

Crystal Data: $C_{20}H_{16}F_{12}N_3O_6P_3$, $M_r = 715$, triclinic, space group $P\bar{1}$, $a = 11.369$ (2) Å, $b = 11.433$ (4) Å, $c = 12.832$ (3) Å, $\alpha = 68.88$ (2)°, $\beta = 72.02$ (1)°, $\gamma = 78.91$ (2)°, $U = 1421.91$ Å^3, $Z = 2$, $D_c = 1.671$ g cm^{-3}, $F(000) = 716$. Crystal decay was less than 2% of total. Refinement converged with $R = 0.073$ and $R_w = (\sum\Delta^2/\sum wF_o^2)^{1/2} = 0.075$. A difference map calculated at the conclusion of the refinement had no chemically significant features.

Crystals of **9** were grown from toluene/dodecanol as clear, colorless prisms. Of the 6018 reflections measured, 3427 were unique with $I > 3\sigma(I)$ [merging $R = 0.033$ after absorption correction (max, min transmission factors = 0.9076, 0.9985)].

Crystal Data: $C_{18}H_{14}F_{12}N_3O_6P_3$, $M_r = 689$, triclinic, space group $P\bar{1}$, $a = 10.589$ (4) Å, $b = 14.57$ (2) Å, $c = 9.11$ (1) Å, $\alpha = 97.3$ (1)°, $\beta = 108.61$ (5)°, $\gamma = 96.72$ (8)°, $U = 1303$ Å^3, $Z = 2$, $D_c = 1.699$ g cm^{-3}, $F(000) = 688$. Crystal decay was less than 0.1% of total. Refinement converged with $R = 0.080$ and $R_w = (\sum\Delta^2/\sum wF_o^2)^{1/2} = 0.080$. A difference map calculated at the conclusion of the refinement had no chemically significant features.

Crystals of **16** were grown from dichloromethane/hexane as clear, colorless prisms. Of the 5734 data collected, 5056 were unique and 3537 had $I > 3\sigma(I)$ [merging $R = 0.043$ after absorption correction (max, min transmission factors = 0.9994, 0.9816)].

Crystal Data: $C_{20}H_{16}F_{12}N_3O_6P_3$, $M_r = 715$, monoclinic, space group $P2_1/a$, $a = 10.3945$ (2) Å, $b = 33.0018$ (8) Å, $c = 8.3549$ (2) Å, $\beta = 79.13$ (2)°, $U = 2814.7$ Å^3, $Z = 4$, $D_c = 1.689$ g cm^{-3}, $F(000) = 1432$. Crystal decay was less than 4% of total. Refinement converged with $R = 0.065$ and $R_w = (\sum\Delta^2/\sum wF_o^2)^{1/2} = 0.105$. A difference map calculated at the conclusion of the refinement had no chemically significant features.

Crystals of **17** were grown from dichloromethane/hexane as clear, colorless prisms. Of the 4252 reflections measured, 3637 were unique with $I > 3\sigma(I)$ [merging $R = 0.215$ after absorption correction (max, min transmission factors = 0.3185, 0.9984)].

Crystal Data: $C_{18}H_{14}F_{12}N_3O_6P_3$, $M_r = 689$, monoclinic, space group $P2_1$, $a = 11.23$ (1) Å, $b = 9.29$ (3) Å, $c = 13.08$ (2) Å, $\beta = 103.57$ (9)°, $U = 1326$ Å^3, $Z = 2$, $D_c = 1.725$ g cm^{-3}, $F(000) = 688$. Crystal decay was less than 0.5% of total. Refinement converged with $R = 0.053$ and $R_w = (\sum\Delta^2/\sum wF_o^2)^{1/2} = 0.053$. A difference map calculated at the conclusion of the refinement had no chemically significant features.

Acknowledgment. We thank the Dow Chemical Co. for the support of this work.

Supplementary Material Available: Listings of bond distances and angles and general displacement parameters and ORTEP diagrams (17 pages). Ordering information is given on any current masthead page.

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(56) MULTAN 82.

(57) The computer programs used were part of the Enraf-Nonius Structures Determination Package (SDP Plus, Version 1.0), Enraf Nonius, Delft, Holland, 1982, implemented on a PDP 11/34 computer.