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Reactivity and Polymerization Behavior of a Pentachlorocyclocarbophosphazene, $N_3P_2CCl_5$[1]

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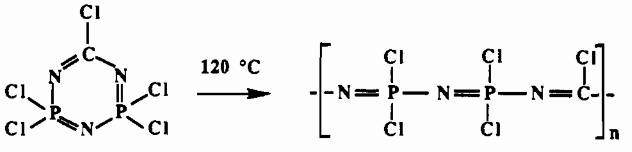
The cyclic carbophosphazene $N_3P_2CCl_5$ reacts with sodium methoxide, sodium trifluoroethoxide, and sodium phenoxide to yield the corresponding pentaalkoxy- and pentakis(aryloxy)cyclocarbophosphazenes. By contrast, $N_3P_2CCl_5$ does not react with the main group and transition metal nucleophiles lithium diphenylphosphide and lithium pentacarbonylmanganate and reacts incompletely with sodium dicarbonyl(η^5-2,4-cyclopentadien-1-yl)ferrate. The title compound undergoes thermal ring-opening polymerization when heated to 120 °C. This polymerization was monitored by ^{31}P NMR spectroscopy. Aspects of the mechanism of polymerization are discussed. Crystal structures of $N_3P_2CCl_5$ and $N_3P_2C(OPh)_5$ were obtained by X-ray diffraction. The crystals of $N_3P_2CCl_5$ are orthorhombic, of space group *Pbca*, with a = 7.7880 Å, b = 29.3560 Å, c = 16.7990 Å, β = 90.00°, V = 3840 Å^3, and Z = 16, whereas crystals of $N_3P_2C(OC_6H_5)_5$ are triclinic, of space group $P\bar{1}$, with a = 10.249(2) Å, b = 12.290(4) Å, c = 14.437(2) Å, α = 84.65(2)°, β = 85.57(1)°, γ = 70.82(2)°, V = 1708.08 Å^3, and Z = 2.

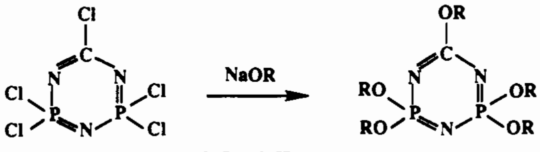
Introduction

The thermal ring-opening polymerization of cyclic phosphazenes is a well-known route to high molecular weight polyphosphazenes.[2] Recently, we reported the thermal (120 °C) ring opening polymerization of $N_3P_2CCl_5$ (**1**), a hydrolytically sensitive crystalline compound, to give novel inorganic polymers that contain phosphorus, nitrogen, and carbon in the macromolecular backbone (see Scheme I).[3] Replacement of the chlorine atoms by aryloxy nucleophiles at the macromolecular level resulted in the formation of hydrolytically stable inorganic/organic polymers. Here, we describe studies of the reactivity of the cyclic compound **1** toward selected and representative alkoxy and aryloxy nucleophiles and main group and transition metal nucleophiles as possible model systems for the corresponding polymers. We also report the X-ray crystal structures of **1** and $N_3P_2C(OC_6H_5)_5$ (**2**). To date, two other structural studies of PNC heterocycles have appeared in the literature ($N_6P_3C_3Cl_9$, a twelve-membered ring, and $[NP(C_6H_5)_2]_2[NC(C_6H_4CH_3\text{-}4)]_2$, an eight-membered ring).[4,5] The thermal polymerization of **1** is discussed using information obtained from ^{31}P NMR studies at 110, 120, and 130 °C.

Scheme I



Scheme II


1

2: R = C_6H_5
3: R = CH_3
4: R = CH_2CF_3

2-4

Results and Discussion

Reactivity of $N_3P_2CCl_5$ (1) toward Aryloxide and Alkoxide Nucleophiles. The synthesis of the cyclocarbophosphazene **1** was reported in 1975 by Fluck, Schmid, and Haubold.[6] To our knowledge, the only prior reactivity study of **1** was that by the same authors in 1977, which involved the synthesis of dialkylamino derivatives (fully substituted and monosubstituted at the carbon position) and alkylated and arylated derivatives (monosubstituted at the carbon position) using Grignard reagents.[7] Studies involving the reaction of related compounds of the type $[NPX_2]_2[NCR]$ (X = Cl; R = CH_3, C_6H_5, $CH_2C_6H_5$, $N(CH_3)_2$) with amines,[8,9] alkoxides,[10] and aryloxides[10] have also been published. We have studied the reaction of **1** with a wider range of nucleophiles.

Hydrolytically sensitive **1** undergoes facile reactions at room temperature with sodium phenoxide, sodium methoxide, and sodium trifluoroethoxide in organic media to give the fully substituted derivatives **2–4** (see Scheme II). The molecular structures of these compounds were examined by the use of ^1H, ^{13}C, and ^{31}P NMR spectroscopy, IR spectroscopy, mass spectrometry, and elemental analysis. The ^{31}P NMR spectra of compounds **1–4** consisted of a singlet resonance in all cases. The chemical shift of **1** was +37 ppm. The organic-derivatized cyclic species **2–4** had chemical shifts that ranged from +20 to +28

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(1) Portions of this work appeared in the doctoral dissertations of Gerhard Renner, University of Bayreuth, Germany, 1991, and of Suzanne Coley and Karyn Visscher, The Pennsylvania State University, 1993.

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ppm. Attempts to preferentially substitute at the carbon site by addition of 1 equiv of the appropriate nucleophile ($NaOC_6H_5$, $NaOCH_3$, or $NaOCH_2CF_3$) to **1** resulted in substitution at both the carbon and phosphorus atoms in all three cases. Thus, the targeted replacement of only the chlorine at carbon in **1** could not be achieved with aryloxide or alkoxide nucleophiles.

The ^{13}C NMR spectrum of compound **1** consists of a triplet centered at ca. +167 ppm with $^2J_{CP}$ = 7.5 Hz. The spectra of compounds **2**–**4** also showed triplets centered at ca. +170 ppm with $^2J_{CP}$ ranging from 20 to 24 Hz. These resonances were assigned to the skeletal carbon atom in the carbophosphazene ring. The ^{13}C NMR spectra of compounds **2**–**4** also contained two different signals that correspond to the aryloxy or alkoxy substituents attached to the carbon and phosphorus atoms in the cyclic skeleton. The relative intensities of these resonances were in a ratio of 1:4, as would be expected for one organic side group linked to the ring carbon versus four organic side groups attached to the phosphorus atoms in the ring.

The proton spectra were also consistent with the expected products. Compound **3** yielded a virtually coupled ABX spin system at +3.6 ppm, which corresponded to the $P–OCH_3$ protons. The virtual coupling arises from an interaction between the methoxy protons and the two phosphorus atoms.[11] A singlet at +3.7 ppm was assigned to the $C–OCH_3$ protons. The integration between the virtually coupled multiplet and the singlet was approximately 1:4, corresponding to a ratio of one methoxy group attached to carbon versus four methoxy groups attached to phosphorus.

The product $N_3P_2C(OC_6H_5)_5$ (**2**) was isolated as a white, crystalline, hydrolytically stable material. However, $N_3P_2C(OCH_3)_5$ (**3**) was a volatile, colorless, hydrolytically sensitive oil and $N_3P_2C(OCH_2CF_3)_5$ (**4**) was also obtained as a colorless, hydrolytically sensitive oil. The analogous classical cyclophosphazenes $N_3P_3(OCH_3)_6$ and $N_3P_3(OCH_2CF_3)_6$ are both crystalline compounds with melting points of 48 and 49–50 °C, respectively.[12] Classical (aryloxy)cyclotriphosphazenes are solids at room temperature due, in part, to a tendency to crystallize with a high degree of intermolecular side group collinearity.[13] Classical alkoxycyclotriphosphazenes, on the other hand, can be solids or nonsolids at room temperature depending, in part, on the degree of free volume generated by the molecule. The free volume of the molecule is related to the steric bulk, linearity, symmetry, and rigidity of the side group. Compounds **3** and **4** may be oils because they possess five substituents per ring versus six substituents for the analogous classical phosphazenes. This leads to an increase in free volume. In the case of **2**, which does crystallize, the planar nature of the phenoxy group may provide enough order for some degree of side group interaction to occur at the carbon position and, thus, for the free volume to be lowered.

The hydrolytic instability of **3** and **4** is in marked contrast to the behavior of $N_3P_3(OCH_3)_6$ and $N_3P_3(OCH_2CF_3)_6$. Both of these compounds are stable toward water.[14–16] On the other hand, alkoxy-substituted *s*-triazines are known to undergo partial and full hydrolysis in the presence of acid or base to give cyanuric acid derivatives and the free alcohol.[17] The presence of an alkyl cyanurate unit (R–CN, R = alkyl) in **3** and **4** may account for this difference in reactivity. Indeed, exposure of **3** and **4** to an approximately 5% by volume water/chloroform emulsion and an approximately 5% by volume water/tetrahydrofuran solution, respectively, resulted in at least partial hydrolysis of the cyclocarbophosphazenes. After several weeks, the ^1H spectrum of **3** showed a broad multiplet ranging from +3.6 to +3.9 ppm. The individual resonances for $P–OCH_3$ and $C–OCH_3$ groups could not be identified. The ^{31}P NMR spectrum showed a small amount of unhydrolyzed **3** and numerous other peaks ranging from +22 to 0 ppm. Mass spectrometry results suggested that $N_3P_2C(OH)(OCH_3)_4$ (mass = 257) and other hydrolysis products are present. The ^1H NMR spectrum of **4** immediately showed a new multiplet at +4.4 ppm. The ^{31}P NMR spectrum showed unhydrolyzed **4** still present and new peaks between +6 and −2 ppm. Mass spectrometry results suggested that $N_3P_2C(OH)(OCH_2CF_3)_4$ (mass = 529) was present. A peak corresponding to $[N_3P_2C(OCH_2CF_3)_5OH]^-$ (mass = 628) was also detected.

Table I. Mass Spectrometry and Elemental Microanalysis Data for Compounds **2**–**4**

compd	MS (calc/found)	EA (% calc/found)
2	581/581	64.03/64.19 C 4.33/4.35 H 7.23/7.29 N
3	271/272[a]	26.66/26.73 C 5.58/5.76 H 15.50/15.87 N
4	611/611	21.62/22.00 C 1.65/1.66 H 6.88/7.24 N

[a] Results obtained by chemical ionization mass spectrometry. The observed peak was from the MH^+ species. A molecular ion could not be obtained for this compound by electron ionization mass spectrometry.

These results suggest that the presence of an alkyl cyanurate unit in the phosphazene ring activates the ring toward hydrolysis. The hydrolytic sensitivity imparted by alkoxy units to cyclocarbophosphazenes is also found in the analogous macromolecular poly(carbophosphazenes). Thus, the attempted isolation of poly[pentakis(trifluoroethoxy)carbophosphazene], $[N_3P_2C(OCH_2CF_3)_5]_n$, by precipitation into water resulted in immediate decomposition of the polymer.[18] Moreover, poly(pentamethoxycarbophosphazene), $[N_3P_2C(OCH_3)_5]_n$, could not be isolated. The macromolecular intermediate $[N_3P_2CCl_5]_n$ was decomposed by the sodium methoxide.[19]

The infrared spectra of cyclic species **2**–**4** contained intense absorptions at 1250–1300 cm^{-1}. These are characteristic of P=N vibrations. In addition, absorptions detected at 1400–1480 cm^{-1} were assigned to C=N vibrations. Mass spectrometry by electron impact (**2**, **4**) and by fast atom bombardment (**3**) showed the appropriate molecular ions. Elemental analyses of **2**–**4** were consistent with assigned structures. These data are summarized in Table I. The NMR data are summarized in Table II.

Reactivity of $N_3P_2CCl_5$ (1) toward Main Group and Transition Metal Nucleophiles. Compound **1** was allowed to react in 1:1 and 1:5 molar ratios in tetrahydrofuran solution under anhydrous conditions with several main group and transition metal nucleophiles. These included $LiP(C_6H_5)_2$, $LiMn(CO)_5$, and NaFe-

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(18) $[N_3P_2CCl_5]_n$ (2.0 g, 6.8 mmol) was dissolved in dry toluene (200 mL), and to the solution was added sodium trifluoroethoxide, prepared from trifluoroethanol (10.0 g, 0.10 mol) and sodium (2.8 g, 0.12 mol) in refluxing THF (50 mL). The reaction mixture was warmed for 12 h. The ^{31}P NMR spectrum of the reaction solution showed a new broad singlet at +0.43 ppm. The solution was filtered, and the filtrate was concentrated. The concentrated polymer solution was precipitated into distilled water (2×), and the mixture was evaporated to dryness under vacuum. The ^{31}P NMR spectrum of the purified polymer showed decomposition.

(19) $[N_3P_2CCl_5]_n$ (1.0 g, 3.4 mmol) was dissolved in dry THF (200 mL), and to the solution was added a suspension of sodium methoxide, prepared from methanol (1.09 g, 34.0 mmol) and sodium (0.9 g, 39.1 mmol) in THF (50 mL). The reaction mixture was stirred at room temperature for 12 h. The ^{31}P NMR spectrum of the reaction solution showed decomposition; no $[N_3P_2CCl_5]_n$ remained (^{31}P = −3.7 ppm in THF).

Table II. ^1H, ^{13}C, and ^{31}P NMR Data for Compounds **2–4**

compd	^{13}C (ppm)	^{31}P (ppm)	^1H (ppm)
2	169.5(t), ring C ($^2J_{CP}$ = 22.6 Hz) 152.2(t), i-COC ($^4J_{CP}$ = 2.7 Hz) 150.0(t), *i*-POC ($^2J_{CP}$ = 4.0 Hz) 129.5(s), *m*-POC 128.9(s), *m*-COC 125.3(s), *p*-POC 125.2(s), *p*-COC 122.3(s), *o*-COC 120.9(s), *o*-POC	20.2 (s)	7.1 (m)
3	170.3(t), ring C ($^2J_{CP}$ = 20.3 Hz) 53.5(t), COC ($^2J_{CP}$ = 3.6 Hz) 52.7(t), POC ($^2J_{CP}$ = 2.7 Hz)	30.7 (s)	3.7 (s) 3.6 (m)
4	170.2(t), ring C ($^2J_{CP}$ = 23.7 Hz) 124.6(q), C–OCH_2CF_3 ($^1J_{CF}$ = 277.2 Hz) 123.9(q), P-OCH_2CF_3 ($^1J_{CF}$ = 277.3 Hz) 63.8(q), P–OCH_2CF_3 ($^2J_{CF}$ = 39.0 Hz) 63.7(q), C–OCH_2CF_3 ($^2J_{CF}$ = 35.8 Hz)	27.8 (s)	4.7 (q) ($^3J_{HF}$ = 8.8Hz) 4.5 (m)

$(C_5H_5)(CO)_2$. In the case of $LiP(C_6H_5)_2$ and $LiMn(CO)_5$, no reaction was detected by ^{31}P NMR spectroscopy. With excess $NaFe(C_5H_5)(CO)_2$ as the nucleophile, ^{31}P NMR spectroscopy indicated that monosubstitution occurred at phosphorus. The ^{31}P NMR spectrum of the reaction solution showed two new doublet resonances centered at +32.4 and −13.8 ppm. Both of these doublets had $^2J_{PP}$ = 25 Hz. After 4 days at room temperature, no unreacted **1** remained. The new product, presumably $[NP(Fe(C_5H_5)(CO)_2)(Cl)][NP(Cl)_2][NCCl]$, was treated with excess sodium phenoxide in an attempt to obtain an easily isolatable product. The ^{31}P NMR spectrum showed a new set of doublet resonances centered at +20.6 and +16.2 ppm, each with $^2J_{PP}$ = 69 Hz. In addition, a resonance at +20.1 ppm, corresponding to **2**, was observed. Apparently, displacement of some $Fe(C_5H_5)(CO)_2$ ligands by sodium phenoxide occurred. Mass spectrometry of the crude products showed a molecular ion for **2** (mass = 581). An ion at a mass of 667 was assigned to $[NP(Fe(C_5H_5)(CO)_2)(OC_6H_5)][NP(OC_6H_5)_2][NC(OC_6H_5)]$ (calculated mass = 665). However, the compound decomposed during attempted isolation and purification by fractional recrystallization.

The reaction of transition metal compounds with $N_3P_3Cl_6$ in classical phosphazene chemistry is complex and results either in no reaction or in the formation of a wide range of products. When reaction does occur, two processes appear to be favored: monosubstitution and halide–cation exchange.[20] The cyclocarbophosphazene **1** appears to be less reactive than $N_3P_3Cl_6$ with respect to main group and transition metal nucleophiles.

X-ray Structure Determination of $N_3P_2CCl_5$ (1) and $N_3P_2C(OC_6H_5)_5$ (2). The X-ray structure determination of **1** was undertaken in an attempt to explain its thermal behavior. The molecular structure of **1** is shown in Figure 1. A summary of cell constants and data collection parameters is given in Table III. Selected bond lengths, bond angles, and final fractional atomic coordinates are shown in Tables IV–VI, respectively. The crystal was refined to 7.3%, and crystal decay was only 2.1%.

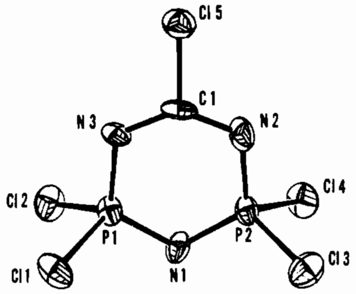

Figure 1. Molecular structure (ORTEP) of $N_3P_2CCl_5$ (**1**).

Table III. Summary of Crystal Data and Intensity Collection Parameters for $N_3P_2CCl_5$ (**1**)

formula	$CCl_5N_3P_2$
fw	293.24
space group	*Pbca*
a (Å)	7.7(1)
b (Å)	29.35(3)
c (Å)	16.79(5)
α (deg)	90.00
β (deg)	90.00
γ (deg)	90.00
V (Å^3)	3840
Z	16
d(calcd) (mg/m^3)	2.028
θ limits (deg)	5–60
μ (cm^{-1})	169.46
radiation	Cu Kα
T (K)	293(1)
scan method	$\omega/2\theta$
ω-scan width (deg)	1.00 + 0.35 tan θ
cryst decay (%)	2.1
empirical abs cor	
min cor factor	0.3152
max cor factor	0.9988
no. of unique data measd	3265
no. of data used [$I > 3\sigma(I)$]	1476
data:param	7.41
R, R_w ($=(\Sigma\Delta^2/\Sigma wF_o^2)^{0.5}$)	0.0728, 0.9945
$(\Delta/\sigma)_{max}$ in last cycle	0.01
Δp in final ΔF map (e Å^{-3})	0.926
final *p* (weighting factor)	0.200
error in weights	0.958

Table IV. Selected Bond Distances (Å) for $N_3P_2CCl_5$ (**1**)

conformation A		conformation B	
Cl(1)–P(1)	1.987(5)	Cl(6)–P(3)	1.979(5)
Cl(2)–P(1)	1.983(5)	Cl(7)–P(3)	1.982(5)
Cl(3)–P(2)	1.976(5)	Cl(8)–P(4)	1.983(5)
Cl(4)–P(2)	1.986(5)	Cl(9)–P(4)	1.982(5)
Cl(5)–C(1)	1.75(1)	Cl(10)–C(2)	1.75(1)
P(1)–N(1)	1.58(1)	P(3)–N(4)	1.59(1)
P(1)–N(3)	1.60(1)	P(3)–N(6)	1.59(1)
P(2)–N(1)	1.57(1)	P(4)–N(4)	1.58(1)
P(2)–N(2)	1.62(1)	P(4)–N(5)	1.61(1)
N(2)–C(1)	1.31(2)	N(5)–C(2)	1.33(2)
N(3)–C(1)	1.31(2)	N(6)–C(2)	1.32(2)

Table V. Selected Bond Angles (deg) for $N_3P_2CCl_5$ (**1**)

conformation A		conformation B	
N(1)–P(1)–N(3)	117.2(6)	N(4)–P(3)–N(6)	117.1(6)
N(1)–P(2)–N(2)	117.5(6)	N(4)–P(4)–N(5)	117.8(7)
P(1)–N(1)–P(2)	116.0(8)	P(3)–N(4)–P(4)	115.6(8)
P(2)–N(2)–C(1)	117(1)	P(4)–N(5)–C(2)	117.1(9)
P(1)–N(3)–C(1)	117.7(9)	P(3)–N(6)–C(2)	118(1)
N(2)–C(1)–N(3)	134(1)	N(5)–C(2)–N(6)	133(1)

Single-crystal X-ray analysis of **1** confirmed that the molecule contains an approximately planar ring of alternating phosphorus or carbon and nitrogen atoms. Furthermore, two ring conformers were identified in the unit cell (Figure 2). It is possible that the existence of these conformers is an artifact, attributable to excessive thermal motion of the crystal during analysis. However, three additional X-ray analyses yielded the same solution. An attempt to solve the X-ray crystal structure of **1** via a low-temperature data collection was unsuccessful due to decomposition of the crystal.

The average P–N bond distance is 1.59 Å, compared with the average C–N bond distance of 1.32 Å. These values are similar to the average P–N bond distance of 1.58 Å in hexachlorocyclotriphosphazene and the average C–N bond distance of 1.33

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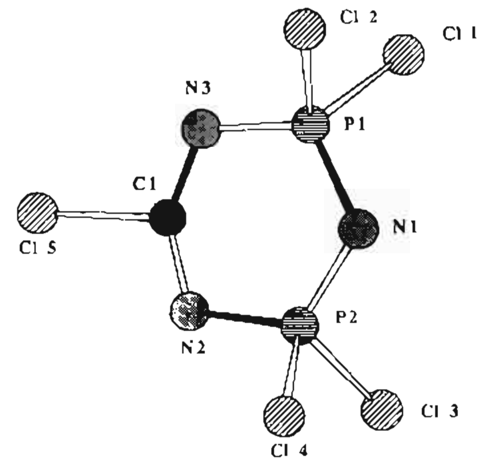

Conformation A

Conformation B

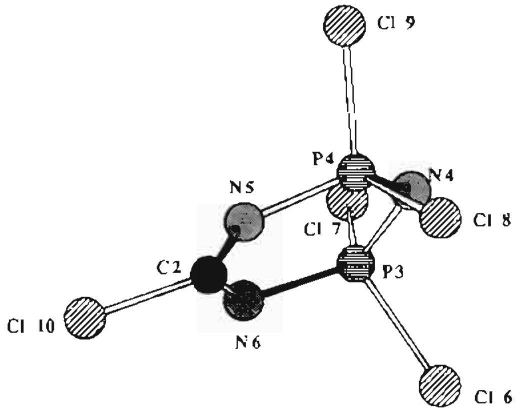

Figure 2. Conformers A and B of $N_3P_2CCl_5$ (**1**).

Table VI. Final Fractional Atomic Coordinates for $N_3P_2CCl_5$ (**1**)

atom	x	y	z
Cl(1)	0.3745(5)	0.1308(1)	−0.0513(2)
Cl(2)	0.2208(5)	0.2147(1)	−0.1358(2)
Cl(3)	0.3771(6)	0.2062(1)	0.2035(2)
Cl(4)	0.2184(5)	0.2933(1)	0.1340(2)
Cl(5)	−0.2251(5)	0.1622(1)	0.0815(2)
Cl(6)	0.2318(6)	0.5836(1)	0.2555(2)
Cl(7)	0.3983(5)	0.5719(1)	0.0899(2)
Cl(8)	0.1931(6)	0.4086(1)	0.2595(2)
Cl(9)	0.3584(5)	0.4113(1)	0.0937(2)
Cl(10)	−0.2227(5)	0.5016(1)	0.0721(2)
P(1)	0.2342(5)	0.1859(1)	−0.0292(2)
P(2)	0.2359(5)	0.2269(1)	0.1126(2)
P(3)	0.2408(5)	0.5406(1)	0.1649(2)
P(4)	0.2202(5)	0.4497(1)	0.1666(2)
N(1)	0.329(2)	0.2186(4)	0.0309(6)
N(2)	0.046(2)	0.2051(4)	0.1240(7)
N(3)	0.044(1)	0.1697(4)	−0.0060(6)
N(4)	0.321(2)	0.4934(4)	0.1931(7)
N(5)	0.034(1)	0.4566(4)	0.1267(6)
N(6)	0.056(1)	0.5390(4)	0.1253(6)
C(1)	−0.015(2)	0.1813(4)	0.0644(8)
C(2)	−0.018(2)	0.4991(4)	0.1147(8)

Å in trichloro-*s*-triazine.[21,22] Because the average P–N and C–N bond lengths of **1** differ by 0.27 Å, the ring structure is distorted from a perfect hexagon. This distortion is also apparent in the bond angles of **1**. The average N–P–N and C–N–P bond angles are 117.4°, while the P–N–P angle opposite from the carbon atom is only 115.8°. In addition, the average N–C–N angle is 134°. Therefore, the P–N–P angle of **1** deviates by 5.5° from the related angle in hexachlorocyclotriphosphazene (121.3°).[21] Furthermore, the N–C–N angle is 14° larger than would be expected for an sp^2-hybridized carbon atom. Thus, the distortion caused by the replacement of a phosphorus atom in hexachlorocyclotriphosphazene by a much smaller carbon atom appears to generate a significant amount of ring strain. Increased ring strain is one possible explanation for the observed decrease in the temperature required for ring-opening polymerization of **1** (120 °C) compared to hexachlorocyclotriphosphazene (250 °C).

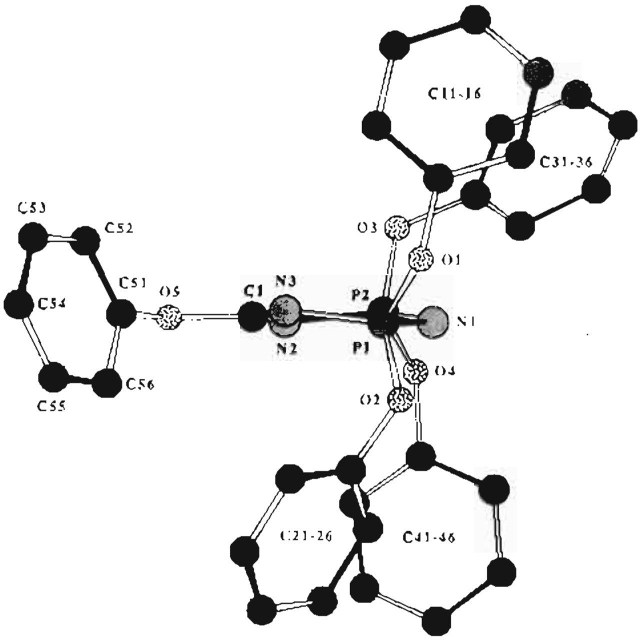

Figure 3. Molecular structure (CHEM-3D) of $N_3P_2C(OC_6H_5)_5$ (**2**).

The X-ray structure determination of **2** was undertaken in order to determine the effect of large, bulky side groups, such as the phenoxy units, on the ring structure. The molecular structure of **2** is shown in Figure 3. A summary of cell constants and data collection parameters is given in Table VII. Selected bond lengths, bond angles, and final fractional atomic coordinates are shown in Tables VIII–X, respectively. The crystal was refined to 4.6%, and crystal decay was 17.3%.

Single-crystal X-ray analysis of **2** showed that the central ring is noticeably puckered. This result is consistent with the structural data available for classical cyclotriphosphazenes. For example, replacement of the chloro units of hexachlorocyclotriphosphazene by phenoxy units causes the hitherto approximately planar ring to pucker.[23]

The average P–N bond distances in **1** and **2** are equivalent (1.60 Å vs 1.59 Å). Furthermore, the average C–N bond distances in **1** and **2** are both 1.32 Å. However, more substantial changes can be seen by a comparison of the bond angles in the ring. Specifically, the N–P–N bond angles show a narrowing of 2.5–2.8 Å when a chloro side unit is replaced by a phenoxy group. The average N–P–N angles in **1** are 117.2 and 117.6°, while the N–P–N angles in **2** are 115.2(2) and 114.8(1)°. In addition, the P–N–P bond angle furthest from the carbon atom is widened by 2.4 Å. The average of this angle is 115.8° in **1** and 118.2(3)° in **2**. The wider P–N–P angle in **2** probably reflects the steric requirements of the bulky phenoxy groups. An increase in the P–N–P angle maximizes the distance between side units and minimizes unfavorable steric interactions.

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Table VII. Summary of Crystal Data and Intensity Collection Parameters for $N_3P_2C(OC_6H_5)_5$ (**2**)

formula	$C_{31}H_{25}N_3O_5P_2$
fw	581.49
space group	$P\bar{1}$
a (Å)	10.249(2)
b (Å)	12.290(4)
c (Å)	14.437(2)
α (deg)	84.65(2)
β (deg)	85.57(1)
γ (deg)	70.82(2)
V (Å^3)	1708.08
Z	2
d(calcd) (mg/m^3)	1.131
θ limits (deg)	2–25
μ (cm^{-1})	1.596
radiation	Mo Kα
T (K)	293(1)
scan method	$\omega/2\theta$
ω-scan width (deg)	$1.00 + 0.35 \tan\theta$
cryst decay (%)	17.4
empirical abs cor	
min cor factor	0.9852
max cor factor	0.9985
no. of unique data measd	6010
no. of data used [$I > 3\sigma(I)$]	4051
data:param	7.701
R, R_w ($=(\sum\Delta^2/\sum wF_o^2)^{0.5}$)	0.04563, 0.05189
$(\Delta/\sigma)_{max}$ in last cycle	0.16
Δp in final ΔF map (e Å^{-3})	0.261
final p (weighting factor)	0.070
error in weights	5.151

Table VIII. Selected Bond Distances (Å) for $N_3P_2C(OC_6H_5)_5$ (**2**)

P(1)–N(1)	1.576(3)	P(2)–N(2)	1.614(3)
P(1)–N(3)	1.607(3)	N(2)–C(1)	1.305(4)
P(2)–N(1)	1.579(3)	N(3)–C(1)	1.331(5)

Table IX. Selected Bond Angles (deg) for $N_3P_2C(OC_6H_5)_5$ (**2**)

N(1)–P(1)–N(3)	115.2(2)	P(2)–N(2)–C(1)	119.0(3)
N(1)–P(2)–N(2)	114.8(1)	P(1)–N(3)–C(1)	118.0(2)
P(1)–N(1)–P(2)	118.2(3)	N(2)–C(1)–N(3)	132.3(4)

Table X. Final Fractional Atomic Coordinates for $N_3P_2C(OC_6H_5)_5$ (**2**)

atom	x	y	z
P(1)	0.53702(9)	0.20974(8)	0.80330(7)
P(2)	0.8068(1)	0.09479(8)	0.83320(7)
O(1)	0.4687(2)	0.1904(2)	0.7147(2)
O(2)	0.4044(2)	0.2480(2)	0.8718(2)
O(3)	0.9033(2)	−0.0190(2)	0.7892(2)
O(4)	0.8811(3)	0.0692(2)	0.9286(2)
O(5)	0.7490(2)	0.3988(2)	0.7297(2)
N(1)	0.6510(3)	0.0983(2)	0.8437(2)
N(2)	0.8312(3)	0.2080(2)	0.7792(2)
N(3)	0.5889(3)	0.3185(2)	0.7732(2)
C(1)	0.7245(3)	0.3000(3)	0.7634(3)
C(11)	0.4112(4)	0.1012(3)	0.7096(3)
C(12)	0.4816(5)	0.0137(4)	0.6547(3)
C(13)	0.4219(6)	−0.0726(4)	0.6477(4)
C(14)	0.3009(6)	−0.0696(4)	0.6921(4)
C(15)	0.2331(5)	0.0194(5)	0.7441(5)
C(16)	0.2858(4)	0.1092(4)	0.7539(4)
C(21)	0.4093(4)	0.2701(3)	0.9653(3)
C(22)	0.4185(4)	0.1820(4)	1.0333(3)
C(23)	0.4157(5)	0.2050(5)	1.1245(4)
C(24)	0.4022(6)	0.3132(6)	1.1469(4)
C(25)	0.3929(6)	0.3996(5)	1.0791(4)
C(26)	0.3947(5)	0.3804(4)	0.9846(3)
C(31)	0.8740(4)	−0.0595(3)	0.7079(3)
C(32)	0.8725(4)	0.0028(4)	0.6239(3)
C(33)	0.8481(5)	−0.0403(4)	0.5450(3)
C(34)	0.8287(5)	−0.1469(5)	0.5511(3)
C(35)	0.8336(5)	−0.2113(4)	0.6359(4)
C(36)	0.8554(4)	−0.1666(3)	0.7169(3)
C(41)	0.8852(4)	0.1578(3)	0.9823(3)
C(42)	1.0019(4)	0.1895(4)	0.9730(3)
C(43)	1.0079(5)	0.2734(4)	1.0305(4)
C(44)	0.8991(6)	0.3202(4)	1.0922(4)
C(45)	0.2120(6)	0.7140(5)	0.9010(4)
C(46)	0.7783(5)	0.2044(5)	1.0438(4)
C(51)	0.8853(4)	0.4000(3)	0.7142(3)
C(52)	0.9383(5)	0.3964(4)	0.6245(3)
C(53)	1.0709(6)	0.4049(5)	0.6070(4)
C(54)	1.1426(5)	0.4172(4)	0.6777(5)
C(55)	0.0885(5)	0.4223(4)	0.7671(4)
C(56)	0.9549(4)	0.4136(4)	0.7875(3)

The average C–N bond distances in **1** and **2** are identical (1.32 Å). However, the angles around carbon do change. The N–C–N bond angle becomes narrower when the chloro unit is replaced by a phenoxy group. The average N–C–N angles are 134° in **1** and 132.3(4)° in **2**. A narrower angle at the carbon atom would minimize the steric repulsion of the attached phenoxy group with the other side groups and perhaps with the ring itself.

Finally, the N–C–O angles are unusual because they are not equivalent. These angles have values of 109.9(3) and 117.7(3)°. This large deviation may be caused by a molecule of phenol which cocrystallized with **2**. The phenol is situated with its oxygen atom pointing into the niche formed by the 117.7(3)° N–C–O angle. The steric interaction of the phenol with **2** may cause the N–C–O angles to be nonequivalent in the solid state.

In conclusion, when small side groups such as chloro groups are replaced by sterically hindered units such as phenoxy groups, the cyclocarbophosphazene ring structure alters significantly: the ring twists from a pseudoplanar structure, and the angle P(1)–N(1)–P(2) widens by 2.4 Å.

^{31}P NMR Investigation of the Thermal Behavior of $N_3P_2CCl_5$ (1). ^{31}P NMR studies were undertaken to monitor the thermal polymerization of **1**. The studies were carried out at 110, 120, and 130 °C (120 °C has been found to be the most convenient temperature for polymerization of **1** in the melt).

Figure 4 shows the ^{31}P NMR spectra recorded at 110 °C over a 5-h period. The initial spectrum contained a singlet from compound **1**, at +37 ppm. After 1 h at 110 °C, new peaks were visible at −0.5 and −3.9 ppm. These peaks continued to grow until the reaction was terminated after 5 h. After 2 h, peaks were also visible at −3.0, −3.6, −3.7, and −3.8 ppm. The intensities of these signals remained approximately constant once they appeared during the second hour of the reaction until the reaction was terminated. The large signal at −3.9 ppm corresponds to poly(pentachlorocarbophosphazene). The peaks between −0.5 and −3.8 ppm are probably generated by cyclic carbophosphazenes with rings larger than that of species **1**. Similar cyclic compounds are formed in the thermal polymerization of hexachlorocyclotriphosphazene, where the homologous cylic tetramer, pentamer, hexamer, heptamer, and octamer are formed in addition to poly(dichlorophosphazene).[24]

Figure 5 shows the ^{31}P NMR spectra of **1** recorded at 120 °C over a 4-h period. The initial spectrum shows only **1**. After 1 h at this temperature, new peaks are visible in the −0.5 to −3.9 ppm region of the spectrum. These are the same peaks formed after 2 h in reactions of 110 °C (Figure 4). It is interesting to note that at 110 °C the intensity of the signal for **1** declines and the intensities of the signals increase for the polymer and for the higher molecular weight cyclic species as the reaction proceeds. At 120 °C, however, the signals for the higher molecular weight cyclics between −0.5 and −3.8 ppm decreased after 2 h.

Figure 6 shows the ^{31}P NMR spectra recorded at 130 °C over 2 h. After 1 h at this temperature, the polymerization of **1** is approximately 50% completed. The same peaks that appeared in the −0.5 to −3.8 ppm region of the spectrum at lower temperatures appeared here as well. The intensities of these signals decreased after 1 h. The signal at −0.5 ppm, in particular, decreased by about 30%.

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[24] Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic Press: New York, 1972; Chapter 15.

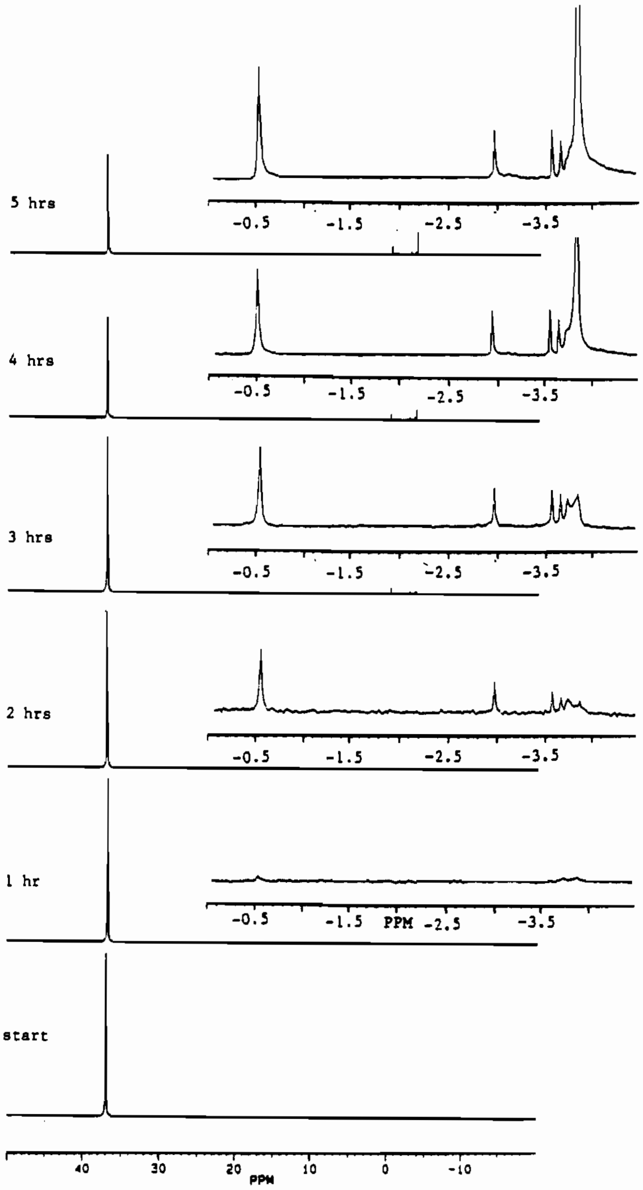

Figure 4. 145.8-MHz ^{31}P NMR spectra of the polymerization of $N_3P_2CCl_5$ (**1**) at 110 °C in $CDCl_3$.

Evidence was obtained in support of the existence of higher cyclic carbophosphazenes. Compound **1** was polymerized in the melt at 120 °C for 3 h. The tube contents were treated with sodium phenoxide in order to replace the chlorine and obtain hydrolytically stable products. The isolated products included poly(pentaphenoxycarbophosphazene), **2**, and a small amount of a compound identified by FAB mass spectrometry as $N_6P_4C_2(OC_6H_5)_{10}$ (mass = 1162). The analogous chloro-substituted compound, $N_6P_4C_2Cl_{10}$, probably gives rise to the ^{31}P NMR signal at −0.5 ppm: this signal corresponds to the major product in the −0.5 to −3.8 ppm region of the spectrum at 110, 120, and 130 °C.

These results suggest that the thermal behavior of **1** involves two processes: ring expansion and polymerization. Ring expansion products are formed along with polymer at 110, 120, and 130 °C, perhaps by means of the growing chain end biting back on itself. However, as the reaction proceeds at the higher temperatures, these ring expansion products probably undergo ring-opening polymerization themselves. Such behavior would explain the observed decrease in intensity of the NMR signals in the −0.5 to −3.8 ppm region of the ^{31}P NMR spectra at 120 and 130 °C as the polymerization reaction neared completion. Classical phosphazene cyclics with rings larger than that of $N_3P_3Cl_6$ undergo ring-opening polymerization to give poly(dichlorophosphazene), albeit at slower rates.[24]

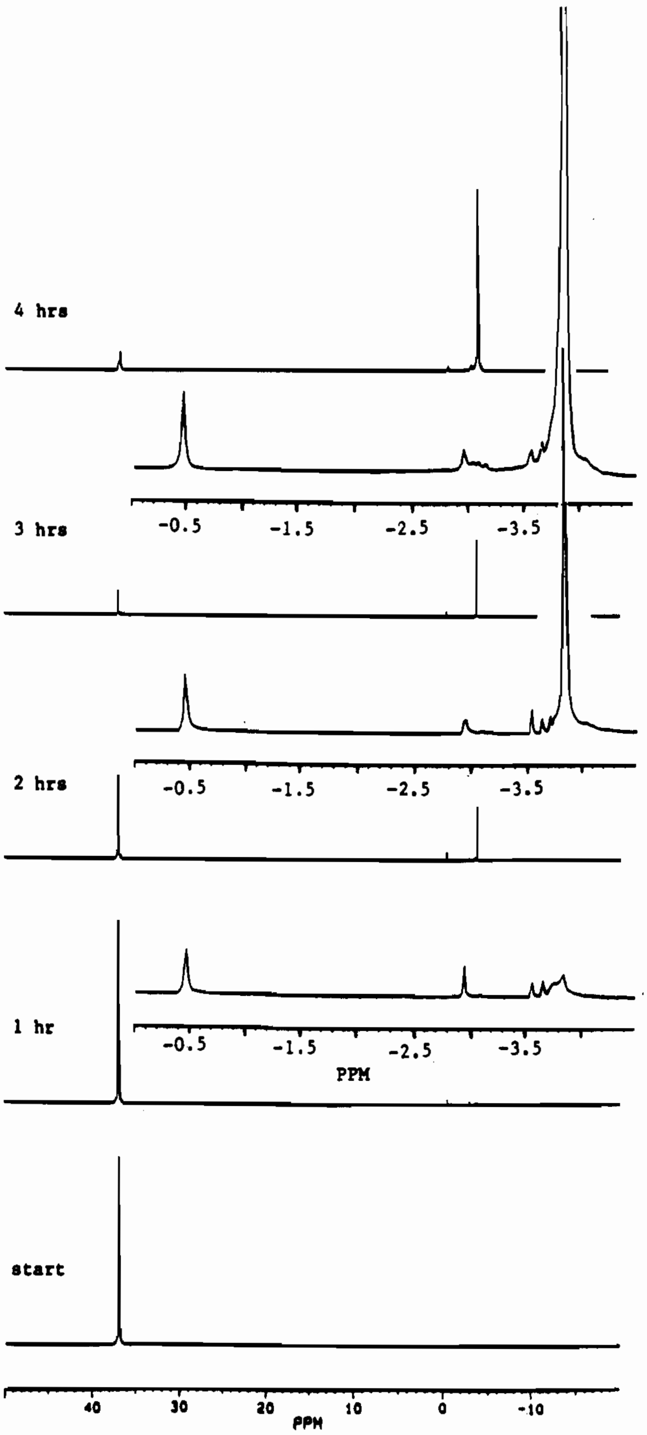

Figure 5. 145.8-MHz ^{31}P NMR spectra of the polymerization of $N_3P_2CCl_5$ (**1**) at 120 °C in $CDCl_3$.

Experimental Section

Equipment and Materials. The cyclocarbophosphazene was synthesized by a modification of the method of Fluck et al.[6] A four-step route was employed, as described below, using phosphorus pentachloride, ammonium chloride, and cyanamide, which were obtained from Aldrich. Cyanamide was recrystallized from anhydrous diethyl ether before use and was stored at −55 °C under an argon atmosphere. 1,1,2,2-Tetrachloroethane, 1,2-dichloroethane, and nitrobenzene were dried over molecular sieves (Davison 4 Å). Tetrahydrofuran and diethyl ether were purified by distillation from sodium benzophenone ketyl. Hexane, methylene chloride, and $CDCl_3$ were purified by distillation from calcium hydride. Literature procedures were used to prepare lithium diphenylphosphide, lithium

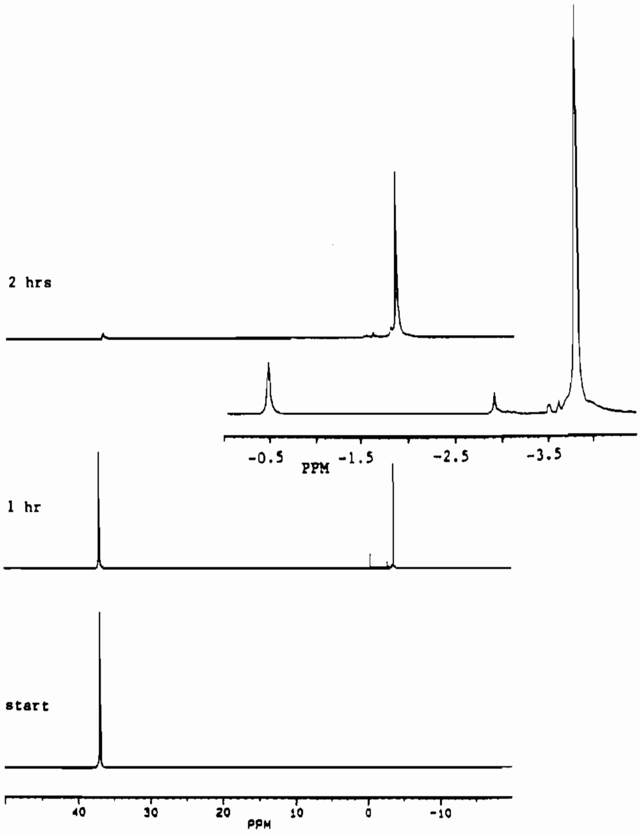

Figure 6. 145.8-MHz ^{31}P NMR spectra of the polymerization of $N_3P_2CCl_5$ (**1**) at 130 °C in $CDCl_3$.

pentcarbonylmanganate, and sodium dicarbonyl(η^5-2,4-cyclopentadien-1-yl)ferrate.[25–27] All manipulations and reactions were carried out in a drybox or under an atmosphere of dry argon using standard Schlenk techniques. Compound **1** was sublimed twice before use and was stored in a drybox (Vacuum Atmospheres). ^{31}P (^{1}H decoupled) NMR spectra were obtained with a JEOL FX-90Q NMR spectrometer operating at 36.2 MHz and with a Bruker WP-360 NMR spectrometer operating at 145.8 MHz. ^{31}P NMR chemical shifts are relative to 85% phosphoric acid as external reference, with positive shift values downfield from the reference. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker WP-360 NMR spectrometer operating at 360 and 90 MHz, respectively. Chemical shifts are relative to external TMS. Infrared spectra were obtained with a Perkin-Elmer 283B grating spectrometer. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN.

Synthesis of $N_3P_2CCl_5$ (1). Step 1. NP_2Cl_7 was synthesized by following the literature procedure (^{31}P = +19.6 ppm in methylene chloride; overall yield 61%).[28]

Step 2. NP_2Cl_7 (15.0 g, 46.2 mmol) was dissolved in methylene chloride (300 mL) with vigorous stirring. A solution of cyanamide (2.0 g, 47.6 mmol) in diethyl ether (150 mL) was added dropwise under argon to the stirred solution which was cooled to 0 °C. The reaction mixture was allowed to warm to room temperature after the addition was completed and was then warmed at 35 °C for 3 days. The reaction liquors were transferred to another flask via canula. The solvent was removed under vacuum, and white, crystalline **1** was isolated from the resultant oil by two vacuum sublimations; yield 5.9 g, 42% (^{31}P = +36.2 ppm in THF).

Synthesis of $N_3P_2C(OC_6H_5)_5$ (2). Compound **1** (0.50 g, 1.7 mmol) was dissolved in THF (20 mL), and to the solution was added dropwise a solution of sodium phenoxide in THF, prepared from phenol (2.4 g, 25.5 mmol) and sodium (0.69 g, 30.0 mmol) in refluxing THF (50 mL). The reaction mixture was warmed for 2 h, after which the ^{31}P NMR spectrum indicated that complete substitution had occurred. The reaction mixture was filtered, the reaction solvent was removed, and the product, **2**, was purified by washing with distilled water and recrystallization from a THF/hexane solution; yield 0.87 g, 88%.

Synthesis of $N_3P_2C(OCH_3)_5$ (3). Compound **1** (0.50 g, 1.7 mmol) was dissolved in diethyl ether (20 mL), and to the solution was added sodium methoxide, prepared from methanol (0.82 g, 25.5 mmol) and sodium (0.69 g, 30.0 mmol) in diethyl ether (100 mL). The mixture was cooled to 0 °C. After 12 h, the ^{31}P NMR spectrum indicated that full substitution had occurred. The reaction mixture was filtered, and the solvent was removed from the ice-cooled flask under vacuum using a double trap (liquid N_2 cooled). The pure product was obtained as a volatile, colorless oil; yield 0.32 g, 69%.

Synthesis of $N_3P_2C(OCH_2CF_3)_5$ (4). Compound **1** (0.50 g, 1.7 mmol) was dissolved in THF (20 mL), and to the solution was added sodium trifluoroethoxide, prepared from trifluoroethanol (0.85 g, 8.5 mmol) and sodium (0.23 g, 10.0 mmol) in refluxing THF (30 mL). The reaction mixture was stirred at room temperature for 12 h, after which the ^{31}P NMR spectrum indicated that full substitution had occurred. The mixture was centrifuged under argon (5000 rpm, 40 min) to remove NaCl. The solvent was removed from the centrifuged solution under vacuum. The pure product was obtained as a colorless oil; yield 0.83 g, 80%.

X-ray Structure Determination Technique. The general technique is described elsewhere.[29] Only details related to the present work are given here. Crystals of **1** and **2** were grown by the slow diffusion of hexane into a THF solution at 0 °C. A summary of important crystallographic data is presented in Tables III and VII.

The structures were solved by direct methods (using MULTAN 82)[30] and Fourier methods. Both structures were refined by full-matrix, least-squares calculations with anisotropic thermal parameters for the non-hydrogen atoms.

^{31}P NMR Studies Procedure. Samples of compound **1** (0.5 g each) were sealed in 15 5-mm NMR tubes under argon. Five of the tubes were placed in an oil bath at 110 °C. The tubes were removed from the oil bath after 1–5 h. The tubes were opened under an argon atmosphere, $CDCl_3$ was added, and ^{31}P NMR spectra were obtained. The same procedure was repeated with five sealed NMR tubes at 120 °C (the fifth tube contained cross-linked polymer that would not dissolve in $CDCl_3$) and five sealed NMR tubes at 130 °C (the third, fourth, and fifth tubes all contained cross-linked polymer).

Acknowledgment. This work was supported by the U.S. Army Research Office (HRA, SMC, IM, KBV, MP) and by Bayer AG and the FRG Ministry of Science Technology (ON, GR). All work was carried out at The Pennsylvania State University.

Registry Numbers (supplied by author): **1**, 57332-66-8; **2**, 121440-63-9; PCl_5, 10026-13-8; NH_4Cl, 12125-02-9; H_2NCN, 420-04-2; NP_2Cl_7, 57646-88-5; $LiP(C_6H_5)_2$, 4541-02-0; $LiMn(CO)_5$, 15689-01-7; $NaFe(C_5H_5)(CO)_2$, 12152-20-4; phenol, 108-95-2; methanol, 67-56-1; 2,2,2-trifluoroethanol, 75-89-8; $[N_3P_2CCl_5]_n$, 132492-02-5.

Supplementary Material Available: Tables of complete bond distances, bond angles, and anisotropic thermal parameters for **1** and **2** (8 pages). Ordering information is given on any current masthead page.

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