Cyanophosphazene Small Molecules and High Polymers: Synthesis and Structure

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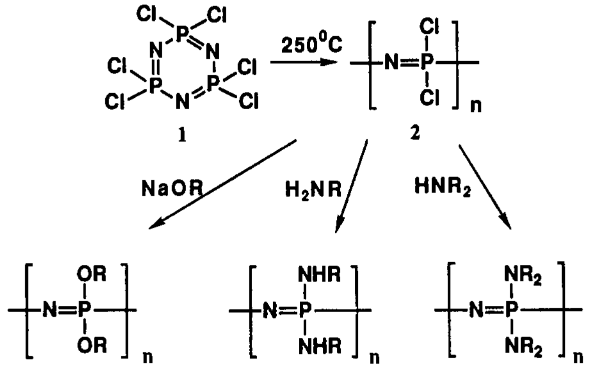
The synthesis and properties of cyclic and high-polymeric cyanophosphazenes were investigated. The interaction of $N_3P_3(OR)_5Cl$ ($OR = OC_6H_5$, OCH_2CF_3, $OCH_2CH_2OCH_2CH_2OCH_3$) with potassium cyanide in the presence of 18-crown-6 ether in acetonitrile yielded small-molecule cyclic cyanophosphazenes, $N_3P_3(OR)_5(CN)$. Reaction of *trans-nongeminal*-$[NP(NMe_2)Cl]_3$ with potassium cyanide in the presence of tetra-*n*-butylammonium bromide in acetonitrile resulted in the formation of *trans-nongeminal*-$[NP(NMe_2)(CN)]_3$. X-ray crystallographic analyses of $N_3P_3(OC_6H_5)_5(CN)$ and *nongeminal*-$[NP(NMe_2)(CN)]_3$ were carried out. $N_3P_3(OC_6H_5)_5(CN)$ crystallized in the monoclinic space group $P2_1/n$. Unit cell parameters were $a = 10.759(4)$ Å, $b = 9.662(3)$ Å, $c = 29.466(4)$ Å, and $\beta = 96.92(3)°$. The structure refined with final $R = 0.045$ and $R_w = 0.047$. *nongeminal*-$[NP(NMe_2)(CN)]_3$ crystallized in the triclinic space group $P\bar{1}$. Unit cell parameters were $a = 6.715(3)$ Å, $b = 8.538(5)$ Å, $c = 14.910(6)$ Å, $\alpha = 92.10(4)°$, $\beta = 105.41(4)°$, and $\gamma = 95.75(4)°$. The structure refined to a final $R = 0.044$ and $R_w = 0.061$. The syntheses of high-polymeric cyanophosphazenes were carried out by the reaction of $[NPR_{1.5}Cl_{0.5}]_n$ ($R = OC_6H_5$ or NMe_2) with potassium cyanide in the presence of 18-crown-6 ether in THF to yield $[NP(OC_6H_5)_{1.53}(CN)_{0.33}Cl_{0.14}]_n$ and $[NP(NMe_2)_{1.5}(CN)_{0.3}Cl_{0.2}]_n$. Attempts to replace the remaining chlorine atoms in $[NP(OC_6H_5)_{1.5}(CN)_{0.33}Cl_{0.17}]_n$ by reaction with $NaOC_6H_5$ resulted in the displacement of both chloro and cyano units to give $[NP(OC_6H_5)_2]_n$. Treatment of $[NP(NMe_2)_{1.5}(CN)_{0.3}Cl_{0.2}]_n$ with excess $HNMe_2$ gave $[NP(NMe_2)_{1.7}(CN)_{0.3}]_n$. The polymers were studied by a combination of NMR, IR, DSC, GPC, TGA, and elemental analysis.

During the past 30 years, the synthesis of new classes of polymers that contain inorganic elements has yielded materials with many combinations of new and unusual properties.[1,2] High-polymeric phosphazenes comprise one of the main classes of inorganic-based polymers.[3-5] The principal synthetic route to phosphazene polymers is shown in Scheme I. It involves the thermal polymerization of hexachlorocyclotriphosphazene (**1**) at 250 °C to form poly(dichlorophosphazene) (**2**). The P–Cl bonds of **1** or **2** can be replaced by reaction with a variety of organic nucleophiles, such as sodium alkoxides, sodium aryloxides, or primary or secondary amines, to generate cyclic or high-polymeric organophosphazene derivatives. In addition to serving as polymerization "monomers", cyclotriphosphazenes are also important as synthetic and structural models for the reactions of the analogous high-polymeric phosphazenes.[6]

In this paper, we discuss a class of phosphazenes that has hitherto received little attention—the cyanophosphazenes. Earlier, in a preliminary communication, we reported the synthesis of two cyclic cyanophosphazene compounds, $N_3P_3(OC_6H_5)_5(CN)$ (**7**) and *trans-nongeminal*-$[NP(NMe_2)(CN)]_3$ (**10**).[7] In the present paper, the chemistry of cyanocyclotriphosphazenes is described in more detail. The discussion is then extended to the synthesis of cyano-substituted macromolecular phosphazenes.

Interest in the synthesis of *macromolecular* cyanophosphazenes stems partly from the knowledge that several technologically important organic polymers bear cyano side groups. For example, the cyano groups in polyacrylonitrile undergo intramolecular cyclization to form a "ladder" polymer, which is a precursor to carbon fibers.

Scheme I



Halogenophosphazene electrophiles such as **1** or **2** might be expected to react with potassium cyanide to generate cyanophosphazenes such as $[NP(CN)_2]_3$ or $[NP(CN)_2]_n$. However, according to "hard/soft, acid/base" principles,[8,9] the ambidentate cyanide anion is a classical "soft" nucleophile, and phosphazenes such as **1** or **2** are "hard" electrophiles due to the strong positive charge at phosphorus. Indeed, electrophilic analogues of chlorophosphazenes, such as sulfonyl chlorides (RSO_2Cl), undergo chloride abstraction reactions with potassium cyanide rather than nucleophilic substitution.[10,11] Thus, it was unclear if halogen replacement reactions would provide a viable route to phosphazenes with cyano side groups.

In fact, several earlier investigations suggested that reactions such as these do not proceed as cleanly as, for example, halogen replacement by amines or alkoxides.[3] An early report indicated that **1** reacts with potassium cyanide to yield partially-substituted cyanochlorophosphazenes, but little characterization data were given.[12] It has also been reported that a mono(*iso*cyanophosphazene), $N_3P_3Cl_5NC$, was formed in the reaction of **1** with

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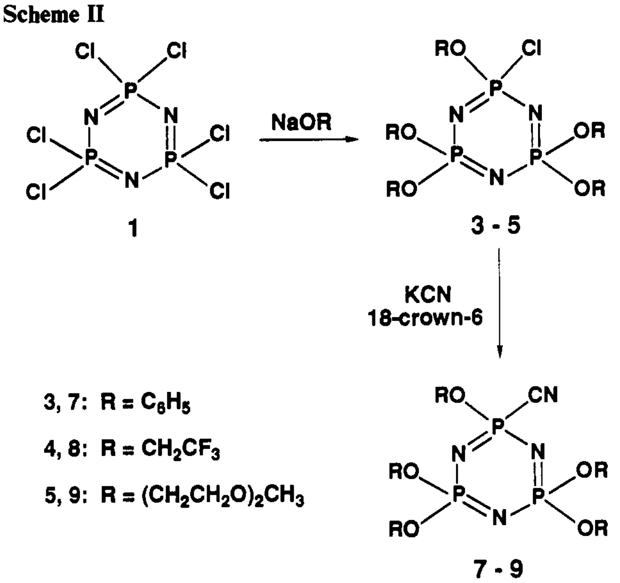
Scheme II



cyanide at low temperature but that the product isomerized and decomposed when warmed.[13] A brief, unsubstantiated report of the synthesis of $[NP(CN)_2]_3$ via the reaction of **1** with cyanide also exists in the patent literature.[14] Finally, the synthesis of the cyanophosphazenes $N_3P_3F_5(CN)$ and $N_4P_4F_7(CN)$ has been reported via the nucleophilic replacement reactions of $N_3P_3F_5Cl$ and $N_4P_4F_7Cl$ with potassium cyanide.[15] However, fluorophosphazenes are extremely sensitive to hydrolysis reactions, particularly at the macromolecular level, and compounds of this type are difficult to use as reaction intermediates or polymerization monomers.

Hence, in this work we have focused on the use of organo*chloro*phosphazenes as substrates for halogen replacement by cyano groups. Specifically, at the small-molecule level we have attempted to deduce if stable cyanophosphazenes are accessible via the initial introduction of organic side groups to leave a limited number of P–Cl bonds available for reaction with cyanide. It was particularly important to establish if such reactions could be transposed to the high-polymer level and to determine the influence of cyano side groups on the properties of the macromolecules.

Results and Discussion

Synthesis of Cyclic Cyanophosphazene Model Compounds. The reactions between chlorophosphazene cyclic trimers and potassium cyanide were found to be influenced by the organic cosubstituents bonded to the ring. Well-characterized cyclic cyanophosphazene compounds were prepared by a two-step process (Schemes II and III), with the critical step being the initial linkage of organic side groups to the cyclotriphosphazene ring to form partially substituted intermediates **3–6** before introduction of the cyano group to form **7–10**. The choice of the organic groups (phenoxy, trifluoroethoxy, 2-(2-methoxyethoxy)ethoxy, and dimethylamino) was determined in part by the importance of these side units in macromolecular phosphazene chemistry.

Cyclic cyanophosphazenes **7–10** were studied by a combination of ^{31}P NMR and IR spectroscopy, mass spectrometry, and elemental analysis (Table I). Compounds **7**, **8**, and **10** were stable over extended periods of time in the atmosphere. However, **9** hydrolyzed slowly in air, sensitized perhaps by the hydrophilic nature of 2-(2-methoxyethoxy)ethoxy side groups. Compound **5** was also sensitive to atmospheric hydrolysis, whereas **3** and **4** were not. This suggested that cyanophosphazene high polymers might be difficult to handle if hydrophilic side groups such as 2-(2-methoxyethoxy)ethoxy units are present.

Scheme III

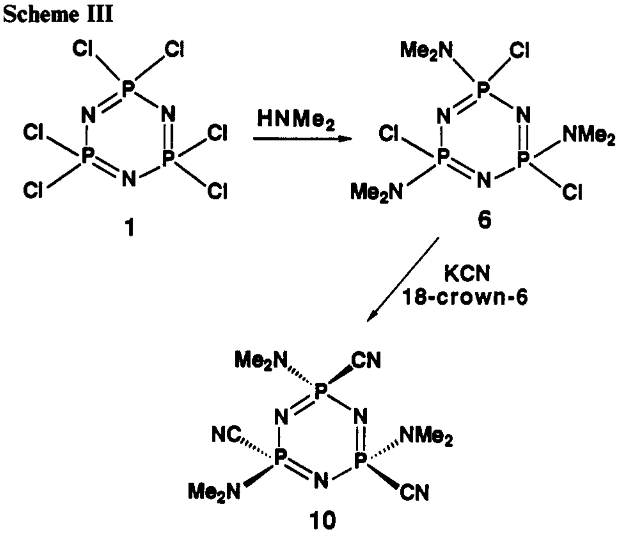


Table I. Characterization Data for Cyclic Cyanophosphazenes

			MS, *m/e*			Anal., %	
compd	^{31}P NMR,[a] ppm	IR,[b] cm^{-1}	calc	found		calc	found
7	$\delta_A(PR_2) = 5.8$	2200	626	626	C	59.42	59.55
	$\delta_B(PRCN) = -9.2$				H	3.99	4.24
	$J = 55$ Hz				N	8.95	8.90
8	$\delta_A(PR_2) = 13.7$	2220	656	656	C	20.14	19.87
	$\delta_B(PRCN) = -7.3$				H	1.54	1.50
	$J = 81$ Hz				N	8.54	8.17
9	$\delta_A(PR_2) = 18.6$	2200	756	*c*	C	41.27	41.17
	$\delta_B(PRCN) = -16.0$				H	7.33	7.39
	$J = 64$ Hz				N	7.41	7.56
10	$\delta = -7.8$	2180	345	345	C	31.30	31.34
					H	5.22	5.25
					N	36.52	36.70

[a] A_2B spin systems were observed for 7–9. [b] The frequency of the cyano stretch is given. [c] No molecular ion was detected in the electron impact mass spectral analysis of 2-(2-methoxyethoxy)ethoxy-substituted phosphazene compounds.

The reactions of **3–6** with potassium cyanide were facilitated by the presence of phase transfer agents such as 18-crown-6 ether or tetra-*n*-butylammonium bromide. Either THF or acetonitrile could be used as the solvent. If the combination of acetonitrile and 18-crown-6 ether was chosen, significantly less forcing conditions (shorter reaction times and smaller amounts of phase-transfer agent) were needed.

The first synthesis of a well-characterized cyclic cyanophosphazene with more than one cyano group attached to the phosphazene ring is illustrated in Scheme III. The dimethylamino group was selected as a cosubstituent due to its strong electron-releasing character. In contrast to the reactions of **3–5**, which were carried out at room temperature, more forcing reaction conditions (longer reaction times and heating to reflux) were needed to replace the chloro units in **6** by cyano groups. This may reflect a high electron density at phosphorus and the influence of steric hindrance.

Infrared spectra of **7-10** and $N_3P_3F_5CN$[15] indicated that the frequency of the cyano absorbance depends on the cosubstituent groups present. Electron-withdrawing cosubstituent groups increased the frequency of the cyano absorbance as illustrated by the following sequence: dimethylamino (2180 cm^{-1}) < 2-(2-methoxyethoxy)ethoxy (2200 cm^{-1}) = phenoxy (2200 cm^{-1}) < trifluoroethoxy (2220 cm^{-1}) < fluoro (2230 cm^{-1}).

X-ray Structural Characterization of 7 and 10. X-ray structural determinations of **7** and **10** were carried out to examine the influence of the cyano group on the structure of the inorganic ring and, by implication, to provide a starting point for a structural

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Table II. Crystallographic Data for **7** and **10**

	7	**10**
chem formula	$C_{31}H_{25}N_4O_5P_3$	$C_9H_{18}N_9P_3$
a, Å	10.759(4)	6.715(3)
b, Å	9.662(3)	8.538(5)
c, Å	29.466(4)	14.910(6)
α, deg		92.10(4)
β, deg	96.92(3)	105.41(4)
γ, deg		95.75(4)
V, Å^3	3040.7	818.2
Z	4	2
fw	626.5	345.23
space group	$P2_1/n$	$P\bar{1}$
T, °C	20	−133
λ(Mo), Å	0.710 73	0.710 73
ρ_{obsd}, g cm^{-3}	1.368	1.401
μ, cm^{-1}	2.35	3.64
transm coeff	0.976–1.000	0.916–0.999
$R(F_o)$	0.0446	0.044
$R_w(F_o)$	0.0470	0.061

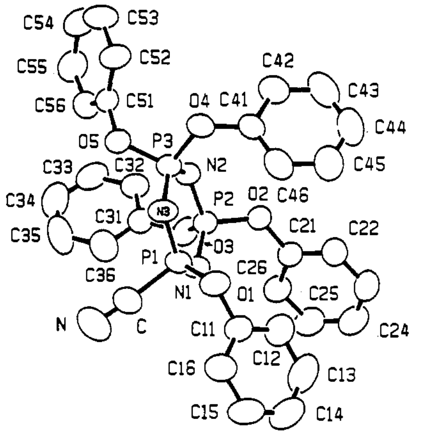

Figure 1. ORTEP diagram for compound **7**, $N_3P_3(OC_6H_5)_5(CN)$.

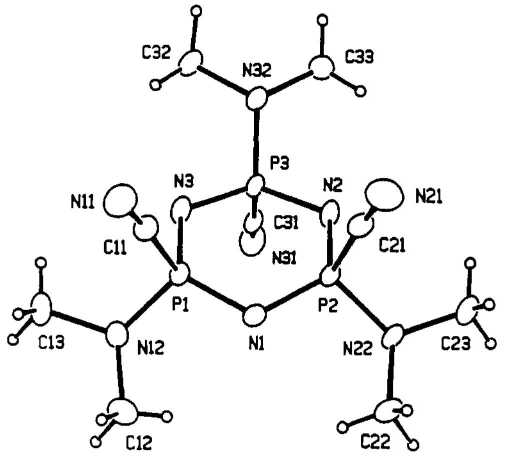

Figure 2. ORTEP diagram for compound **10**, $[NP(NMe_2)(CN)]_3$.

understanding of the high polymers. It was also important to determine if the cyano group was present rather than the isomeric isocyano structure. A summary of cell constants and data collection parameters is given in Table II. ORTEP diagrams are shown in Figures 1 and 2, important bond length and bond angle data are provided in Tables III and IV, and positional parameters are given in Tables V and VI.

The structural chemistry of phosphazenes and cyano compounds has been reviewed.[3,5,16,17] Electron-releasing side groups, such as dimethylamino units linked to phosphazenes, increase the length of both the ring bonds and the exocyclic bonds that link the cyclotriphosphazene unit to other side groups, particularly groups that are geminal to the electron-releasing unit. It is often suggested that electron-releasing side groups will expand the d-orbitals of phosphorus and decrease the dπ–pπ bond overlap within the cyclotriphosphazene ring. Thus, dimethylamino side groups could direct π-electron density from the ring to side groups that are geminal to those dimethylamino units. The strength of π-electron donation from the ring could also depend on the ability of the geminal side group to accept π-electron density. Cyano groups are known for both their electron-withdrawing character and for their π-electron "back-bonding" characteristics.

Table III. Selected Bond Lengths and Estimated Standard Deviations (Å)

	Compound 7		
P(1)–O(1)	1.565(2)	P(3)–O(5)	1.568(2)
P(1)–N(1)	1.564(2)	P(3)–N(2)	1.574(2)
P(1)–N(3)	1.567(2)	P(3)–N(3)	1.577(2)
P(1)–C	1.781(3)	O(1)–C(11)	1.421(3)
P(2)–O(2)	1.577(2)	O(2)–C(21)	1.410(3)
P(2)–O(3)	1.583(2)	O(3)–C(31)	1.398(3)
P(2)–N(1)	1.585(2)	O(4)–C(41)	1.405(3)
P(2)–N(2)	1.570(2)	O(5)–C(51)	1.413(3)
P(3)–O(4)	1.578(2)	N–C	1.134(3)
	Compound 10		
P(1)–N(1)	1.583(2)	P(3)–N(2)	1.589(2)
P(1)–N(3)	1.585(2)	P(3)–N(3)	1.590(2)
P(1)–N(12)	1.623(2)	P(3)–N(32)	1.625(2)
P(1)–C(11)	1.815(2)	P(3)–C(31)	1.819(2)
P(2)–N(1)	1.583(2)	N(11)–C(11)	1.145(3)
P(2)–N(2)	1.590(2)	N(21)–C(21)	1.139(3)
P(2)–N(22)	1.628(2)	N(31)–C(31)	1.145(3)
P(2)–C(21)	1.812(2)		

Table IV. Selected Bond Angles and Estimated Standard Deviations (deg)

	Compound 7		
P(1)–N(1)–P(2)	120.9(1)	O(5)–P(3)–O(4)	100.69(9)
P(2)–N(2)–P(3)	122.6(1)	P(1)–O(1)–C(11)	123.9(1)
P(1)–N(3)–P(3)	121.4(1)	P(2)–O(2)–C(21)	126.0(2)
N(1)–P(1)–N(3)	119.3(1)	P(2)–O(3)–C(31)	122.6(1)
N(1)–P(2)–N(2)	117.4(1)	P(3)–O(4)–C(41)	120.9(1)
N(2)–P(3)–N(3)	117.4(1)	P(3)–O(5)–C(51)	124.0(1)
O(1)–P(1)–C	101.6(1)	P(1)–C–N	177.1(3)
O(3)–P(2)–O(2)	99.64(9)		
	Compound 10		
N(1)–P(1)–N(3)	118.58(9)	P(3)–C(31)–N(31)	176.7(2)
N(12)–P(1)–C(11)	103.82(9)	P(1)–N(12)–C(12)	120.5(1)
N(1)–P(2)–N(2)	117.86(8)	P(1)–N(12)–C(13)	117.4(1)
N(22)–P(2)–C(21)	104.40(9)	C(12)–N(12)–C(13)	113.4(2)
N(2)–P(3)–N(3)	119.71(9)	P(2)–N(22)–C(22)	120.0(1)
N(32)–P(3)–C(31)	103.58(8)	P(2)–N(22)–C(23)	117.7(1)
P(1)–N(1)–P(2)	119.5(1)	C(22)–N(22)–C(23)	113.3(2)
P(2)–N(2)–P(3)	119.6(1)	P(3)–N(32)–C(32)	118.6(1)
P(1)–N(3)–P(3)	119.4(1)	P(3)–N(32)–C(33)	118.3(1)
P(1)–C(11)–N(11)	176.0(2)	C(32)–N(32)–C(33)	113.8(2)
P(2)–C(21)–N(21)	176.3(2)		

The C–N triple bond in **7** [1.134(3) Å] was slightly shorter than the three C–N triple bonds in **10** [1.145(3), 1.139(3), and 1.145(3) Å]. However, the P–CN bond in **7** [1.781(3) Å] was significantly shorter than the three exocyclic P–CN bonds in **10** [1.815(2), 1.812(2), and 1.819(2) Å], and this is consistent with the electron-releasing character of the dimethylamino group. In addition, the two shortest endocyclic P–N bonds of **7** were bonded to the phosphorus atom bearing the cyano side group. This is in sharp contrast to the expected effects of π-back-bonding.

The four P–C–N angles in **7** [177.1(3)°] and **10** [176.0(2), 176.3(2), and 176.7(2)°] suggest that the hybridization at the cyano carbon atom is essentially of the sp type.

The average exocyclic P–NMe_2 bond length in **10** (1.626 Å) is nearly identical to the average bond length in *trans-nongeminal*-$N_3P_3(NMe_2)_3Cl_3$ (1.623 Å).[18] This is evidence that the cyano

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Table V. Positional Parameters (Non-Hydrogen Atoms) for 7[a]

atom	x	y	z	B_{eq},[b] Å^2
P(1)	1.06741(8)	0.0923(1)	0.43149(3)	3.90(2)
P(2)	1.00008(8)	0.1981(1)	0.34578(3)	3.65(2)
P(3)	0.81890(8)	0.1297(1)	0.40063(3)	3.71(2)
O(1)	1.1352(2)	0.1769(3)	0.4725(1)	4.66(6)
O(2)	1.0220(2)	0.3568(2)	0.3371(1)	4.42(5)
O(3)	1.0214(2)	0.1385(2)	0.2973(1)	4.63(6)
O(4)	0.7326(2)	0.2428(2)	0.4195(1)	4.42(5)
O(5)	0.7266(2)	0.0037(2)	0.3947(1)	4.31(6)
N	1.1754(3)	−0.1830(4)	0.4463(1)	7.6(1)
N(1)	1.1033(2)	0.1406(3)	0.3841(1)	3.95(6)
N(2)	0.8593(2)	0.1800(3)	0.3538(1)	3.64(6)
N(3)	0.9258(2)	0.0823(3)	0.4388(1)	4.20(7)
C	1.1354(3)	−0.0746(4)	0.4415(1)	5.05(1)
C(11)	1.2641(3)	0.2128(4)	0.4770(1)	4.18(8)
C(12)	1.2997(4)	0.3270(4)	0.4549(1)	6.0(1)
C(13)	1.4257(4)	0.3645(5)	0.4623(2)	7.2(1)
C(14)	1.5083(4)	0.2906(5)	0.4911(1)	6.8(1)
C(15)	1.4700(4)	0.1784(5)	0.5128(2)	6.7(1)
C(16)	1.3451(3)	0.1370(4)	0.5059(1)	5.4(1)
C(21)	1.1390(3)	0.4219(4)	0.3363(1)	4.2(1)
C(22)	1.1544(3)	0.5471(4)	0.3584(1)	5.5(1)
C(23)	1.2654(4)	0.6184(4)	0.3570(2)	7.0(1)
C(24)	1.3575(4)	0.5632(5)	0.3338(2)	7.5(1)
C(25)	1.3413(3)	0.4375(5)	0.3126(1)	6.4(1)
C(26)	1.2308(3)	0.3651(4)	0.3136(1)	5.01(9)
C(31)	0.9680(3)	0.0142(4)	0.2802(1)	4.09(8)
C(32)	0.8763(3)	0.0231(4)	0.2437(1)	4.99(9)
C(33)	0.8258(3)	−0.0967(5)	0.2245(1)	6.1(1)
C(34)	0.8660(4)	−0.2211(4)	0.2408(1)	6.8(1)
C(35)	0.9577(5)	−0.2285(4)	0.2775(2)	7.9(1)
C(36)	1.0097(4)	−0.1090(4)	0.2978(1)	6.1(1)
C(41)	0.7652(3)	0.3836(4)	0.4195(1)	4.19(8)
C(42)	0.6858(4)	0.4724(4)	0.3953(2)	6.3(1)
C(43)	0.7153(4)	0.6109(5)	0.3958(2)	7.9(1)
C(44)	0.8235(4)	0.6585(4)	0.4198(2)	7.0(1)
C(45)	0.9008(4)	0.5698(4)	0.4433(2)	7.1(1)
C(46)	0.8732(4)	0.4302(4)	0.4439(1)	6.1(1)
C(51)	0.6162(3)	0.0008(3)	0.3634(1)	4.01(8)
C(52)	0.5078(3)	0.0522(4)	0.3768(1)	5.24(9)
C(53)	0.3984(3)	0.0389(5)	0.3466(2)	6.7(1)
C(54)	0.3998(4)	−0.0236(5)	0.3052(2)	7.1(1)
C(55)	0.5108(4)	−0.0745(4)	0.2924(1)	6.2(1)
C(56)	0.6199(3)	−0.0629(4)	0.3219(1)	4.81(9)

[a] Numbers in parentheses are estimated standard deviations. [b] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table VI. Positional Parameters (Non-Hydrogen Atoms) for 10[a]

atom	x	y	z	B_{eq},[b] Å^2
P(1)	0.84437(8)	0.40678(6)	0.73607(4)	1.38(1)
P(2)	0.96294(8)	0.69170(7)	0.83582(4)	1.37(1)
P(3)	0.63742(8)	0.66110(6)	0.67677(4)	1.29(1)
N(1)	1.0172(3)	0.5242(2)	0.8071(1)	1.67(4)
N(2)	0.7818(3)	0.7662(2)	0.7646(1)	1.61(4)
N(3)	0.6563(3)	0.4774(2)	0.6676(1)	1.71(4)
N(11)	0.6467(3)	0.1830(3)	0.8423(2)	2.60(5)
N(12)	0.9560(3)	0.2915(2)	0.6805(1)	1.77(4)
N(21)	0.8266(4)	0.6678(3)	1.0077(2)	2.73(5)
N(22)	1.1747(3)	0.8141(2)	0.8686(1)	1.72(4)
N(31)	0.7437(3)	0.7971(3)	0.5131(1)	2.49(4)
N(32)	0.3958(3)	0.6923(2)	0.6597(1)	1.54(4)
C(11)	0.7200(4)	0.2738(3)	0.8024(2)	1.74(4)
C(12)	1.1736(4)	0.2616(3)	0.7216(2)	2.34(5)
C(13)	0.8256(4)	0.1557(3)	0.6239(2)	2.35(5)
C(21)	0.8751(4)	0.6724(3)	0.9402(2)	1.76(4)
C(22)	1.3753(4)	0.7548(3)	0.9085(2)	2.34(5)
C(23)	1.1604(4)	0.9702(3)	0.9087(2)	2.03(5)
C(31)	0.7085(3)	0.7433(3)	0.5772(2)	1.62(4)
C(32)	0.2354(4)	0.5924(3)	0.5871(2)	1.96(5)
C(33)	0.3491(4)	0.8552(3)	0.6696(2)	1.95(5)

[a] Numbers in parentheses are estimated standard deviations. [b] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

side group has a similar overall electron-withdrawing capacity to that of a chloro side unit when bonded to a phosphazene ring. The average P–N exocyclic bond length for $[\mathrm{NP(NMe_2)_2}]_3$ (1.652 Å)[19] is relatively long compared to that of **10**, suggesting also that the cyano group withdraws electron density from the phosphazene ring. The average exocyclic P–O bond length for $[\mathrm{NP(OC_6H_5)_2}]_3$ (1.582 Å)[20] is slightly longer than that for **7** (1.574 Å), and the shortest exocyclic P–O bond [1.565(2) Å] in **7** is for the phenoxy side group geminal to the cyano group.

The phosphazene rings of **7** and **10** are slightly nonplanar and have χ^2 values (deviation from planarity) of 602 and 2310, respectively. The ring in **7** occupies a half-chair conformation; the P(2) atom of **7** is 0.108 Å out of the plane of the ring. The phosphazene ring in **10** assumes a slight boat conformation. The distal atoms of the ring, N(1) and P(3), lie out of the plane of the ring (+0.17 and +0.20 Å, respectively).

The bond length alternation detected for the six endocyclic P–N bonds of **7** is consistent with the structures of other cyclotriphosphazenes that have one inequivalent phosphorus atom in the trimeric ring. The two shortest endocyclic P–N bonds of **7** are adjacent to each other and are bonded to the phosphorus atom that bears the electron-withdrawing cyano side group. Adjacent to each of these two short bonds are the two longest bonds in the ring. The average endocyclic P–N bond length for **7** (1.573 Å) is shorter than that for **10** (1.587), which reflects the greater electron-releasing capacity of the dimethylamino side group. In contrast to the endocyclic bonds of **7**, each of the endocyclic P–N bonds in **10** is almost identical in length, reflecting the greater equivalency of the phosphorus atom in **10**.

Finally it should be noted that the X-ray structural analysis of **10** indicates that the side group configuration is trans rather than cis. Trans–cis isomerization reactions of dimethylamino-substituted phosphazene compounds are possible.[21] In addition, the X-ray structures of **7** and **10** support the infrared data, which suggested that the *cyano* isomer was present rather than the isocyano form. For example, when the structure of **10** was allowed to refine with an assumed isocyano structure, the final R value was 0.058, significantly higher than the R value calculated for a defined cyano structure (0.044). However, the final R value for **7** with an assumed isocyano arrangement (0.049) was only slightly higher than that for **7** with an assumed cyano structure (0.045).

Synthesis of Polymeric Cyanophosphazenes. (a) Reactions of Poly(dichlorophosphazene) (2) and (Trifluoroethoxy)chlorophosphazene Polymers. The reactions of small-molecule cyclic phosphazenes often provide a useful starting point for predicting the outcome of similar reactions at the high-polymer level.[6] This is true of the systems discussed here, where the small-molecule reactions just described anticipate some of the problems encountered at the macromolecular level.

For example, the treatment of poly(dichlorophosphazene) (**2**) with potassium cyanide yielded a complex mixture of unstable products that were difficult to identify. Similarly, polyphosphazenes with both trifluoroethoxy and chloro side units underwent chlorine replacement by cyano groups in the initial stages of the reaction (on the basis of ^{31}P NMR analysis) but yielded a complicated mixture of products that were unstable after prolonged treatment with potassium cyanide. These reactions were so complex that the pattern of substitution and decomposition could not be determined.

(b) Phenoxychlorophosphazene Polymers. An assumption was made that bulky, hydrophobic, aromatic side groups might shield the phosphazene backbone sufficiently to retard skeletal cleavage reactions. Hence, a series of polyphosphazenes were prepared in which different ratios of phenoxy to chloro side units were present,

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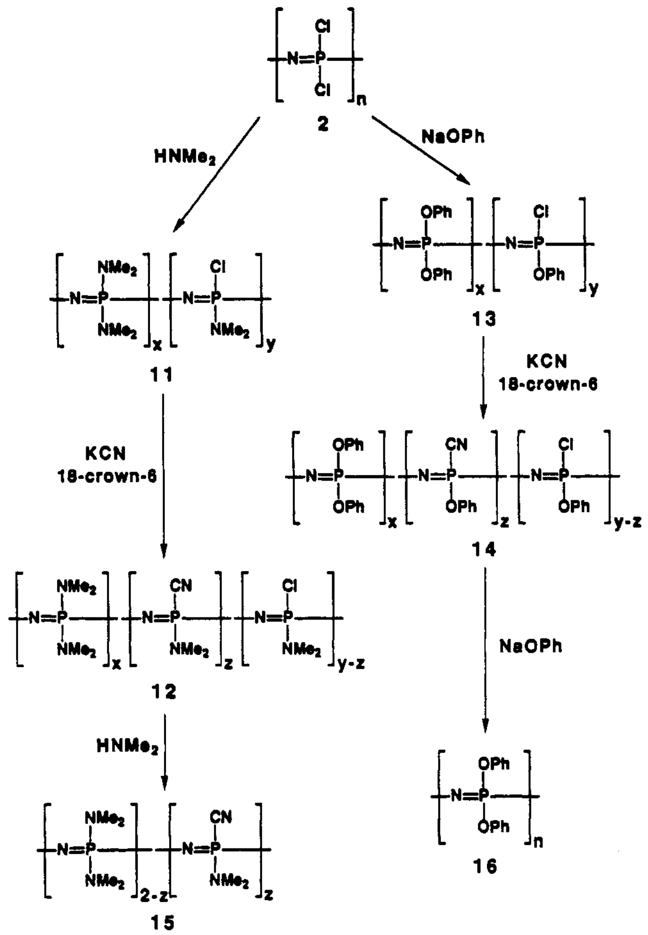
(19) Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1973**, *51*, 1295.

(20) Marsh, W. C.; Trotter, J. *J. Chem. Soc. A* **1971**, 169.

(21) Keat, R.; Shaw, R. A. *J. Chem. Soc.* **1965**, 4067.

Scheme IV



and each polymer was treated with potassium cyanide. A polymer with 50% phenoxy and 50% chloro side groups underwent apparent cross-linking and decomposition when treated with potassium cyanide and 18-crown-6 ether. This is consistent with the model compound chemistry in which *nongeminal*-$N_3P_3(OPh)_4Cl_2$ decomposed in the presence of the same reagent.

However, as illustrated in Scheme IV, a polyphosphazene with 75% of the side groups as phenoxy and 25% as chloro units (**13**) (prepared by the reaction of **2** with NaOPh in THF at 66 °C) reacted with excess potassium cyanide in THF at 66 °C in the presence of 18-crown-6 ether to form a hydrolytically stable phenoxycyanophosphazene polymer, **14**. This was a light brown, film-forming material. ^{31}P NMR spectroscopy indicated that some unreacted P–Cl bonds remained in this polymer, and elemental analyses suggested a formula close to $[NP(OC_6H_5)_{1.53}(CN)_{0.33}Cl_{0.14}]_n$.[22] Further treatment of this polymer with potassium cyanide in THF resulted in the formation of insoluble and possibly cross-linked materials. Some evidence was obtained from infrared analysis that *iso*cyano groups may participate in this process. Attempts to replace the remaining chloro side units in **13** by treatment with sodium phenoxide in THF at 25 °C resulted in complete displacement of both the chloro and cyano groups by phenoxy to yield $[NP(OC_6H_5)_2]_n$ (**16**). The ability of the phenoxide anion to displace cyano units was confirmed by a model reaction of **6** with sodium phenoxide (THF, 25 °C) to form $[NP(OC_6H_5)_2]_3$. This illustrates that the cyano group is a labile unit in the presence of a strong nucleophile.

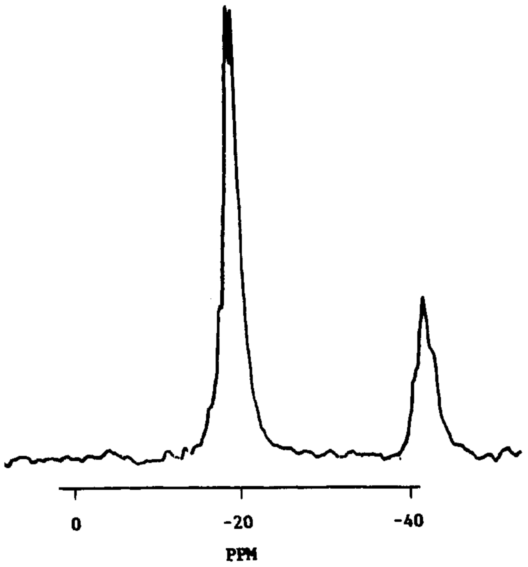


Figure 3. ^{31}P NMR spectrum of polymer **14**. The peaks at −20 ppm were assigned to $P(OPh)_2$ and P(OPh)(Cl) units and those at −43 ppm to P(OPh)(CN) units.

An analogue of **13** with 90% of the side units as phenoxy groups, $[NP(OC_6H_5)_{1.8}Cl_{0.2}]_n$, did not react with potassium cyanide in the presence of 18-crown-6 ether in THF at 66 °C during 7 days. This unreactivity probably reflects shielding of the chlorine atoms by the bulky phenoxy groups. The P–Cl units were also unreactive to atmospheric moisture.

(c) (Dimethylamino)chlorophosphazene Polymers. By analogy with the model reaction used to prepare **10**, polymer **11** (prepared from **2** and dimethylamine in THF at 0 °C in the presence of triethylamine) was allowed to react with excess potassium cyanide in the presence of 18-crown-6 ether (THF, 66 °C) to yield polymer **12** as a hydrolytically stable, light brown, film-forming polymer. Again, ^{31}P NMR spectra were consistent with the replacement of only two-thirds of the chlorine atoms by cyano units. However, treatment of this polymer with excess dimethylamine (toluene, Et_3N, 25 °C) resulted in the replacement of the remaining chlorine atoms by dimethylamino units, without loss of the cyano groups, to yield $[NP(NMe_2)_{1.7}(CN)_{0.3}]_n$ (**15**).

Structure Proof for Polymeric Cyanophosphazenes. Polymers **14** and **15** were examined by a combination of ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy, elemental analysis, IR spectroscopy, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC).

The ^{31}P NMR spectrum of **14** consisted of a major, double-peaked resonance at $\delta = -20$ ppm from the nonequivalent phosphorus atoms in $P(OC_6H_5)_2$ and $P(OC_6H_5)Cl$ units and a minor resonance at $\delta = -43$ ppm ($P(OC_6H_5)(CN)$ units) (Figure 3). Although the ^{13}C NMR spectrum of **14** showed four aromatic carbon resonances (δ = 122, 127, 131, and 152 ppm) from the phenoxy side groups, the carbon atoms of the cyano groups could not be detected. Similarly, the cyano carbon atoms of small-molecule cyclic species **6** could not be detected by ^{13}C NMR analysis. This was attributed to the low concentration of cyano carbon atoms, the poor ability of cyano carbon atoms to relax in the NMR experiment due to a lack of C–H bonding, and the overlap of cyano and phenoxy resonances.

The ^{31}P NMR spectrum of **15** consisted of a major resonance at $\delta = -2$ ppm from $P(NMe_2)_2$ groups and a minor resonance at $\delta = -43$ ppm attributed to $P(NMe_2)(CN)$ units. The ^{13}C NMR spectrum of **15** showed a small doublet (δ = 121 ppm, J_{PC} = 128 Hz) associated with the carbon atoms of the cyano groups and a major resonance at 37.9 ppm from the carbon atoms of the dimethylamino groups.

The IR spectra of **14** and **15** contained cyano absorptions at 2200 and 2180 cm^{-1}, respectively. These values were identical

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(22) Analysis of polymers prepared in different runs suggested slightly different compositions, such as $[NP(OPh)_{1.5}(CN)_{0.33}Cl_{0.17}]_n$. The discrepancies between calculated and found analyses are often larger for high polymers than for small molecules because of the difficulties involved in purification of the macromolecules.

to those of the cyclic cyanophosphazene model compounds and indicate that the cyano group was present rather than the isocyano structure.

Gel permeation chromatography (GPC) analysis of **14** and **15** confirmed that the compounds were moderate molecular weight macromolecules (**14**, $M_n = 7 \times 10^4$, $M_w = 7 \times 10^5$; **15**, $M_n = 2 \times 10^5$, $M_w = 9 \times 10^5$). The molecular weight of **15** is similar to those of other aminophosphazene polymers, but the value for **14** is lower than the normal molecular weight of phenoxyphosphazene polymers, which are typically in excess of 1×10^6. The possibility was considered that this was due to hydrolysis and chain cleavage during purification, but no corroborating evidence for this view could be obtained from the analytical data. In addition, no further change in molecular weight was detected after prolonged exposure of the polymer to wet solvents or additional precipitations into water.

Differential scanning calorimetry (DSC) analysis of **14** showed a glass transition at −6 °C. No transitions for **15** were detected by DSC analysis.

Thermolysis of the Polymers. As mentioned earlier, organic cyano polymers such as poly(acrylonitrile) are widely used as precursors for pyrolysis to carbon fibers, a reaction which depends critically on internal addition and perhaps cross-linking reactions via the nitrile side groups. Thus a preliminary assessment was made of the thermal behavior of polymers **14** and **15** by means of thermogravimetric analysis (TGA) and thermogravimetric analysis coupled with mass spectrometry (TGA/MS).

Thermogravimetric analysis of polymer **15** showed that no weight loss occurred below 150 °C and that only a 1.5% weight loss occurred below 300 °C. TGA/MS analysis indicated that very small amounts of hydrogen cyanide and trimethylamine were evolved between 200 and 350 °C. A significant weight loss (~60%) at 380 °C was associated with extensive cross-linking and volatilization of the amino side groups. The resultant nonvolatile residue showed no change in weight between 450 and 900 °C. Above 900 °C, rapid volatilization of the backbone components[23,24] occurred to leave only 9% of the original weight in the form of a nonvolatile material by 1000 °C.

By contrast, polymer **14** underwent slow cross-linking reactions when heated at 100 °C to give a material that swelled in THF but did not dissolve. Samples of **14** evolved hydrogen cyanide ($m/e = 27$) at approximately 100 °C, with a sharp increase in the amount of hydrogen cyanide evident at 115 °C. The TGA–MS data suggested that loss of chloro or phenoxy side groups did not occur at 115 °C. Thus, the mechanism of the low-temperature cross-linking appears to involve loss of cyano side groups rather than chloro or phenoxy units. Further evidence for this was the fact that $[NP(OC_6H_5)_2]_n$ and $[NP(OC_6H_5)_{1.8}Cl_{0.2}]_n$ did not cross-link when heated at 100 °C under vacuum for 24 h. The low-temperature cross-linking of **14** was accompanied by the formation of a strong adhesive bond to glass. Above 400 °C, thermal elimination of side groups and cyclic phosphazene residues proceeded until only 38% of the original weight remained at 750 °C and only 10% remained at 1000 °C. The cross-links formed at the lower temperatures appeared to reduce the decomposition rate in the medium temperature range (400–750 °C) but had no significant effect when compared to $[NP(OPh)_2]_n$ at 1000 °C.[23]

Conclusions. Overall, the conclusions from the small-molecule work are that (1) the cyano form of this side group is present rather than the isocyano, (2) the influence of the cyano group on the phosphazene skeleton reflects an electron-withdrawing effect similar to that of the chlorine atoms it replaces, and (3), by inference, π-back-bonding from the phosphorus atoms to cyano is not a significant contributor to the stability of these molecules.

From a reaction chemistry point of view, the results also emphasize the similarity between the hydrolytic sensitivity of cyano- and chlorophosphazenes, especially at the high-polymer level, and the tendency of cyano groups to be displaced from phosphorus by nucleophiles such as phenoxide. However, cyanophosphazene polymers differ from their chlorophosphazene counterparts with respect to their thermal behavior. At elevated temperatures, P–Cl units favor depolymerization whereas P–CN units appear to facilitate cross-linking reactions.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (**1**), supplied by the Ethyl Corp., was purified by recrystallization from hot hexane and by vacuum sublimation. Poly(dichlorophosphazene) (**2**) was prepared by the thermal polymerization of **1** at 250 °C.[3] Compounds **3**,[25] **4**,[26] and **6**[27] were prepared by literature procedures. Phenol (Aldrich) was sublimed and dried by azeotropic distillation from benzene. Trifluoroethanol and 2-(2-methoxyethoxy)ethanol (Aldrich) were distilled from barium oxide and stored over molecular sieves. Potassium cyanide (Aldrich) was dried in a vacuum oven at 110 °C for 24 h and was stored in an inert-atmosphere glovebox. (*Caution! Strong poison! Neutralize with bleach and adjust to neutral pH after use!*) 18-Crown-6 ether (Aldrich) was recrystallized from acetonitrile and stored in an inert-atmospheric glovebox. Tetra-*n*-butylammonium bromide (Aldrich) was dried by azeotropic distillation from benzene followed by storage in an inert-atmosphere glovebox. Sodium metal (Aldrich) was stored in an inert-atmosphere glovebox. THF was distilled from sodium benzophenone. Acetonitrile was first distilled from calcium hydride and then redistilled from P_2O_5. Manipulations and storage of the materials were carried out under inert atmosphere.

Instrumentation and Methods. The ^{31}P NMR (^1H decoupled) spectra were recorded with a JEOL FX90Q spectrometer operating at 36.23 MHz. The chemical shifts are relative to 85% phosphoric acid with positive shifts downfield from the reference. The high-field ^{13}C NMR spectra were recorded with a Bruker WP-360 spectrometer operating at 90.56 MHz. Chemical shifts are relative to TMS. Infrared spectra of the cyclotriphosphazenes were recorded with a Perkin-Elmer 283B spectrometer. Infrared spectra of polymer films were obtained with the use of a Perkin-Elmer 1710 FTIR spectrometer. Oils were examined as thin films on NaCl disks, while solids were analyzed as KBr pellets. Thin films of the polymers were cast on NaCl disks. Electron impact mass spectra were obtained with an AEI MS 950 mass spectrometer.

Molecular weights were determined by means of a Hewlett-Packard HP1090 gel permeation chromatograph equipped with a refractive index detector. The samples were eluted with a 0.1% by weight solution of tetra-*n*-butylammonium bromide in THF through Polymer Laboratories PLgel columns (10^6, 10^6, 10^3 Å). Approximate molecular weight calibrations were obtained using narrow molecular weight distribution polystyrene standards. Poly[bis(trifluoroethoxy)phosphazene] samples (provided by Drs. R. Singler and G. Hagnauer of the Army Materials Technology Laboratories) were used as controls for the GPC work. These fractionated samples were of known molecular weights as determined by GPC and light-scattering measurements. Good agreement between our GPC data and the standards was obtained.

DSC analysis was performed with a Perkin-Elmer DSC-7 differential scanning calorimeter equipped with a PE7500 computer. Each polymer sample was analyzed in a crimped aluminum pan under a flow of dry helium gas. Calibration of the DSC-7 was carried out before analysis. The TGA–MS data were obtained with the use of a Du Pont 951 thermal analyst instrument that was connected to a VG quadrupole mass spectrometer. A helium gas flow was employed with a purge rate of 5–10 mL/min to carry the volatile products to the mass spectrometer. The TGA data were also recorded with a Perkin-Elmer TGA-7 thermogravimetric analyzer. The TGA instruments were calibrated before use. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN 37921.

Synthesis of $N_3P_3(OCH_2CH_2OCH_2CH_2OCH_3)_5Cl$ (5). Compound **1** (20 g, 0.057 mol) was allowed to react with 5.1 equiv of the sodium salt of 2-(2-methoxyethoxy)ethanol in THF for several hours at 25 °C. The ^{31}P NMR spectral analysis of the reaction mixture indicated that the main product of this reaction was **5**, together with small amounts of $N_3P_3(OCH_2CH_2OCH_2CH_2OCH_3)_4Cl_2$ and $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_3$. After removal of solvent, **5** was isolated by column chro-

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[24] Allcock, H. R.; Welker, M. F.; Parvez, M. *Chem. Mater.* **1992**, *4*, 296.

[25] McBee, E. T.; Okuhara, K.; Morton, C. J. *Inorg. Chem.* **1966**, *5*, 450.

[26] Allcock, H. R.; Mang, M. N.; McDonnell, G. S.; Parvez, M. *Macromolecules* **1987**, *20*, 2060.

[27] Keat, R.; Shaw, R. A. *J. Chem. Soc.* **1965**, 2215.

matography of the residue on silica gel with a hexane, methylene chloride, and acetone gradient elution. The first compound to elute was the tetrasubstituted product, followed by the penta- and hexasubstituted products. The ^{31}P NMR spectrum of **5** consisted of an AB_2 spin system: $\delta_A = 28.0$ ppm, $\delta_B = 18.8$ ppm, and $J = 66$ Hz. IR analysis showed aliphatic C–H stretches (2800–3000 cm^{-1}) and C–O bending (1050–1150 cm^{-1}). Elemental analysis confirmed the proposed composition. Anal. Calc: C, 39,19; N, 5.49; H, 7.18. Found: C, 38.99; N, 5.20; H, 7.11. Yield: 44%. Compound **5** hydrolyzed slowly in the atmosphere but could be stored in a drybox.

Syntheses of 7–9. A typical procedure follows. Compound **3** (5.0 g, 7.9 mmol), potassium cyanide (5.0 g, 76 mmol), and 18-crown-6 ether (0.1 g, 0.3 mmol) were dissolved in acetonitrile (100 mL). The reaction mixture was stirred at 25 °C for several days, until ^{31}P NMR analysis showed that complete substitution had occurred. Solvent was removed by rotary evaporation, and the residue was extracted with methylene chloride. The methylene chloride extract was filtered through Fuller's earth, and removal of solvent by rotary evaporation yielded product **7**, which was recrystallized from hexane. Analogous procedures were used for the syntheses of **8** and **9**. THF solvent and tetra-*n*-butylammonium bromide were also employed in these reactions. When THF was used as a solvent, longer reaction times, larger amounts of phase-transfer agent, and higher temperatures were necessary to induce the cyanide substitution reaction. The yields of **7–9** were typically 60–80%. Compounds **8** and **9** were oils.

Synthesis of 10. Compound **6** (10.0 g, 26.9 mmol), potassium cyanide (20 g, 310 mmol), and tetra-*n*-butylammonium bromide (20 g, 62 mmol) were dissolved in acetonitrile (100 mL). Two drops of distilled, deionized water (0.1%) were added to the flask, and the reaction mixture was refluxed until the ^{31}P NMR analysis showed that substitution was complete (at least 1 week). No reaction was detected without the addition of water. Solvent was removed by rotary evaporation, and the residue was extracted with methylene chloride. The extract was filtered through Fuller's earth, and removal of solvent yielded an oil. Compound **10** was extracted from this oil with diethyl ether. The ethereal phase was extracted several times with water and dried over magnesium sulfate. Ether was removed under vacuum, and the product was purified by recrystallization from hexane. The yield was 10%.

X-ray Crystallographic Analysis. Single crystals of **7** suitable for X-ray crystallograpic studies were grown by the slow cooling of a saturated solution of the compound in hexane. Single crystals of **10** were obtained by the slow evaporation of a hexane solution. For both crystals, accurate cell constants were determined by least-squares treatment of the setting angles of 25 reflections within the θ range 10–15°. Intensity data for both compounds were collected on an Enraf-Nonius CAD4 diffractometer by the $\omega/2\theta$ scan method using graphite-monochromatized radiation (Mo Kα) employing variable scan speeds in the range $4° < 2\theta < 50°$. The intensities of three reflections, chosen as standards in both cases, were monitored at regular intervals and decreased in a linear fashion by 0.4 and 9.9% for **7** and **10**, respectively, over the course of data collection. These decays were corrected for by approximate scaling. Data were also corrected for Lorentz–polarization factors and for empirical absorption.

The structures were solved by direct methods using MULTAN 82[28] and were refined by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic thermal parameters. H atoms for **7** were included in geometrically idealized positions (C–H = 0.95 Å) with overall isotropic temperature factors. In the refinement cycles, weights were derived from the counting statistics. Scattering factors were those of Cromer and Mann[29] and Stewart, Davidson, and Simpson,[30] and allowance was made for anomalous dispersion. The difference maps at the conclusion of the refinement had no chemically significant features. All computer programs used were part of the Enraf-Nonius Structure Determination Package (SDP Plus, version 3.0) and were implemented on a PDP 11/44 computer.[31]

Synthesis of 14. Polymer **2** (4.74 g, 0.0409 mol) was dissolved in THF (150 mL) in a 500-mL three-necked flask equipped with a fritted addition funnel and a reflux condenser. A solution of sodium phenoxide was prepared in THF (100 mL) from sodium (1.26 g, 0.0548 mol) and phenol (5.15 g, 0.0548 mol). The salt solution was added dropwise at room temperature to the polymer solution via the addition funnel. The reaction mixture was heated to reflux for 16 h and was then allowed to cool to room temperature. At this point, ^{31}P NMR analysis indicated that **13** had formed and that the reaction had ceased. Integration of the resultant spectrum was consistent with the structure $[NP(OPh)_{1.5}Cl_{0.5}]_n$. A mixture of 18-crown-6 ether (6.2 g, 0.023 mol) and potassium cyanide (15.3 g, 0.0235 mol) was added to the reaction mixture, and the resultant mixture was heated to reflux. After 24 h, the reaction mixture had become light brown. The reaction mixture was allowed to cool to room temperature and was then was gravity-filtered. The filtrate was concentrated to 100 mL by rotary evaporation, and the polymer was recovered by precipitation into water. The polymer was purified by repeated precipitations from THF into distilled water (×3), diethyl ether (2×), and hexane (1×). Finally, the polymer was further purified by Soxhlet extraction with diethyl ether for 7 days and with acetonitrile for 1 day to remove residual 18-crown-6 ether. The final yield of polymer **14** after drying under vacuum (2×10^{-6} mmHg, 24 h) was 2.8 g (36%). Elemental microanalysis suggested a molecular formula of $[NP(OPh)_{1.53}(CN)_{0.33}Cl_{0.14}]_n$. Anal. Calc: C, 56.92; H, 3.84; N, 9.28; Cl, 2.47. Found: C, 56,44; H, 4.23; N, 8.28; Cl, 2.73. Other preparations of the same polymer gave slightly different compositions (see ref 22).

Synthesis of 15. Polymer **2** (5.00 g, 0.0431 mol) was dissolved in THF (500 mL) in a 1000-mL three-necked flask equipped with an addition funnel cooled by a dry ice/acetone bath and a reflux condenser. The polymer solution was cooled to 0 °C, and a solution of dimethylamine (2.72 g, 0.0603 mol) in THF (200 mL) and triethylamine (10 mL) was added dropwise via the addition funnel. After complete addition of the dimethylamine solution, the reaction mixture was allowed to warm to room temperature. The solution was subsequently heated to reflux for 6 h and then allowed to cool to room temperature. Analysis by ^{31}P NMR indicated that **11** had formed and that the reaction had ceased. Integration of the resultant spectrum was consistent with the structure $[NP(NMe_2)_{1.4}Cl_{0.6}]_n$. The reaction solution was concentrated using heat and reduced pressure under airless conditions to 350 mL. The amine hydrochloride salts were removed by suction filtration through a course glass frit directly into a 500-mL three-necked flask (equipped with a reflux condenser) containing a mixture of 18-crown-6 ether (10.0 g, 0.0371 mol) and potassium cyanide (25.4 g, 0.0390 mol). This reaction mixture was heated to reflux for 72 h. After the system had cooled to room temperature, the solids were removed from the light brown reaction mixture by suction filtration through a course glass frit under airless conditions. The solution was concentrated using heat and reduced pressure to 100 mL, and the polymer was recovered by precipitation into distilled hexane under a dry atmosphere. The recovered polymer was redissolved in freshly distilled toluene (300 mL) in a 500-mL three-necked flask equipped with a dry ice/acetone cold finger. A large excess of dimethylamine (approximately 50 g) was added dropwise to the polymer solution via evaporation, and the amine hydrochloride salts were removed by gravity filtration. Polymer **15** was recovered by further concentration of the polymer solution to 100 mL and precipitation into hexane. Purification of **15** was carried out by repeated precipitations from THF into water (4×), diethyl ether (2×), and hexane (2×). The purified polymer was dried under vacuum (2×10^{-6} mmHg) for 24 h to give 1.8 g (32% yield) of a light brown elastomer. Elemental microanalysis confirmed the molecular formula as $[NP(NMe_2)_{1.70}(CN)_{0.30}]_n$. Anal. Calc: C, 34.79; H, 8.05; N, 32.91; Cl, 0. Found: C, 34.56; H, 8.06; N, 32.09; Cl, 0.17.

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Supplementary Material Available: Tables of hydrogen atom coordinates, general temperature factors (*U*'s), and bond distances and angles for **7** and **10**, a listing of least-squares planes for **10**, and a complete list of cell constants and data collection parameters for both compounds (13 pages). Ordering information is given on any current masthead page. Copies of the structure factor tables may be obtained directly from H.R.A. within 1 year of the publication date.

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