Synthesis of Cyclo- and Polyphosphazenes with Pyridine Side Groups

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New types of cyclo- and polyphosphazenes that bear pyridine side groups have been synthesized. The reactions of 2-(2-aminoethyl)pyridine and 2-((2-aminoethyl)amino)-5-nitropyridine with $(NPCl_2)_3$ were complex, with chlorine replacement being complicated by degradation and the formation of mixtures. However, the use of electron-withdrawing cosubstituents, such as phenoxy or trifluoroethoxy groups, allows straightforward chlorine replacement reactions induced by the aminoalkylpyridines to occur. The mono(alkylpyridine)-substituted cyclotriphosphazenes $N_3P_3(OC_6H_5)_5(NHCH_2CH_2(C_5H_4N))$ (**1**) and $N_3P_3(OC_6H_5)_5(NHCH_2CH_2NH(C_5H_3N)NO_2)$ (**2**) were synthesized as model compounds for high polymers. Polyphosphazenes of the general formula $[NP(OCH_2CF_3)_x(NHCH_2CH_2(C_5H_4N))_y]_n$ were prepared by exposing $[NPCl_2]_n$ to sodium trifluorethoxide and 2-(2-aminoethyl)pyridine in a two-step reaction. All compounds were characterized by ^1H, ^{13}C, ^{31}P NMR spectroscopy, and elemental analysis. The cyclic trimers were also identified by mass spectrometry. Molecular weight estimations of the polymers were carried out by gel permation chromatography, and glass transition temperatures were determined by differential scanning calorimetry.

Introduction

Polymers that form metal complexes through N-donor side groups are finding a growing interest due to the wide range of possible applications for those materials such as ion exchangers, carriers or depots for chemotherapeutica, immobilizers of enzymes or catalysts, and electronic conductors.[1−3] A well-investigated organic polymer is, for example, poly(vinylpyridine).[4] Analogous polyphosphazenes with pendent pyridine groups should offer wider opportunities for property modification due to the ease with which the different cosubstituent groups can be introduced. Two types of metalated phosphazenes have been described in the past: those having transition metals as building blocks in the ring or chain[5−8] and others with the metal units attached to side groups.[9−17] Examples of the second group include phosphazene rings or chains with pendent aryl ligands bound to transition metals by π-donor coordination[9−12] and metals linked to skeletal phosphorus atoms by covalent bonds.[13−15] Metals can also be bound to phosphazenes through phosphine containing side groups.[16,17]

When electron-withdrawing groups such as pyrazolyl or imidazolyl are present on a phosphazene, N-donor interactions of side groups are known to occur.[18−22] By contrast, electron donating primary or secondary amines that are bonded to the phosphazene increase the basicity of the ring nitrogen atoms. Coordination of metal ions at these compounds occurs at the electron lone pairs of the phosphazene nitrogen atoms.[23−26] Pyridine-substituted phosphazenes have not been synthesized previously mainly because halogenated phosphazenes exposed

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(1) Allcock, H. R.; Desorcie, J. L.; Riding, G. H. *Polyhedron* **1987**, *6*, 119.
(2) Andrews, H. P.; Ozin, G. A. *Chem. Mater.* **1989**, *1*, 474.
(3) Sheats, J. E.; Carraher, C. E., Jr.; Pittman, C. U., Jr., Eds. *Metal-Containing Polymeric Systems*; Plenum: New York: **1985**.
(4) Lyons, A. M.; Pearce, E. M.; Vasile, M. J.; Mujsce, A. M.; Waszczak, J. V. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988.
(5) Roesky, H. W.; Katti, K. V.; Seske, U.; Witt, M.; Egert, E.; Sheldrick, G. M. *Angew. Chem.* **1986**, *98*, 447; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 477.
(6) Hasselbring, R.; Roesky, H. W.; Noltemeyer, M. *Angew. Chem.* **1992**, *104*, 613; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 601.
(7) Roesky, H. W. *Synlett* **1990**, 651.
(8) Pandey, S. K.; Steiner, A.; Roesky, H. W.; Stahlke, D. *Inorg. Chem.* **1993**, *32*, 5444.
(9) Allcock, H. R.; Dodge, J. A.; Manners, I.; Riding, G. H. *J. Am. Chem. Soc.* **1991**, *113*, 9596.
(10) Allcock, H. R.; Dembek, A. A.; Klingenberg, E. H. *Macromolecules* **1991**, *24*, 5208.
(11) Allcock, H. R.; Dodge, J. A.; Manners, I.; Parvez, M.; Riding, G. H.; Visscher, K. B. *Organometallics* **1991**, *10*, 3098.
(12) Allcock, H. R.; Dembek, A. A.; Bennett, J. L.; Manners, I.; Parvez, M. *Organometallics* **1991**, *10*, 1865.
(13) Allcock, H. R.; Mang, M. N.; McDonnell, G. S.; Parvez, M. *Macromolecules* **1987**, *20*, 2060.
(14) Allcock, H. R.; Riding, G. H.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 5561.
(15) Allcock, H. R.; Greigger, P. P.; Wagner, L. J.; Bernheim, M. Y. *Inorg. Chem.* **1981**, *20*, 716.
(16) Allcock, H. R.; Manners, I.; Mang, M. N.; Parvez, M. *Inorg. Chem.* **1990**, 522.
(17) Allcock, H. R.; Lavin, K. D.; Tollefson, N. M.; Evans, T. L. *Organometallics* **1983**, *2*, 267.
(18) Gallicano, K. D.; Paddock, N. L.; Rettig, S. J.; Trotter, J. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 417.
(19) Chandrasekaran, A.; Krishnamurthy, S. S.; Methaji, M. *Inorg. Chem.* **1993**, *32*, 6102.
(20) Justin Thomas, K. R.; Chandrasekhar, V.; Pal, P.; Scott, S. R.; Hallford, R.; Cordes, A. W. *Inorg. Chem.* **1993**, *32*, 606.
(21) Allcock, H. R.; Greigger, P. P.; Gardner, J. E.; Schmutz, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 606.
(22) Allcock, H. R.; Neenan, T. X.; Boso, B. *Inorg. Chem.* **1985**, *24*, 2656.
(23) Trotter, J.; Whitlow, S. H. *J. Chem. Soc. A* **1970**, 455.
(24) Allcock, H. R.; Allen, R. W.; O'Brien, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 3984.
(25) Allen, R. W.; O'Brien, J. P.; Allcock, H. R. *J. Am. Chem. Soc.* **1977**, *99*, 3987.
(26) Schmidtpeter, A.; Blanck, K.; Ahmed, F. R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 488.

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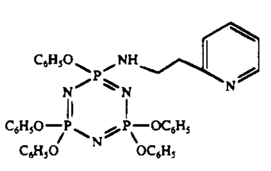
to pyridine derivatives are known to form adducts and to decompose.[27,28]

This work is the first step of a systematic investigation of the reaction behavior of pyridine derivatives with cyclo- and polyphosphazenes. We describe here the syntheses of the pyridine-substituted phosphazene trimers **1** and **2** as well as the polyphosphazenes **3**–**6**.



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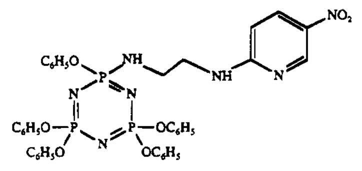

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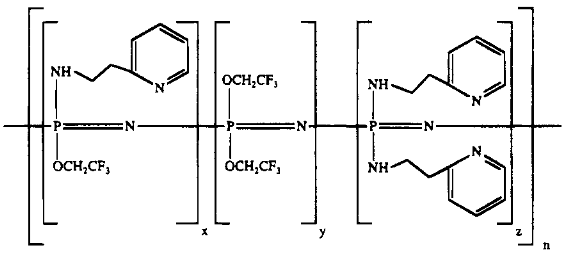


3-6

	3	4	5	6
OCH_2CF_3	75.0 %	48.5 %	24.5 %	0.0 %
$NH(CH_2)_2C_5H_4N$	25.0 %	51.5 %	75.5 %	100 %

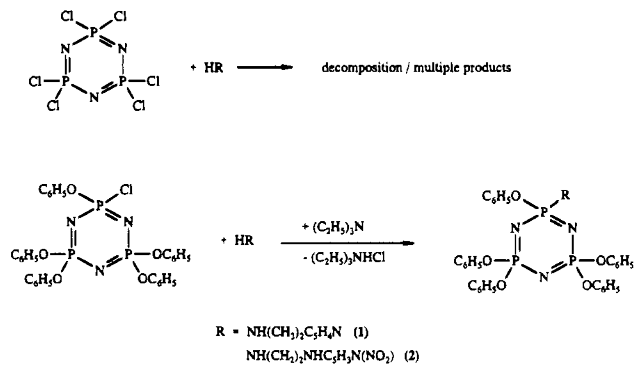
Results and Discussion

Synthesis and Characterization of Cyclotriphosphazenes 1 and 2. The functionalized pyridines 2-(2-aminoethyl)pyridine and 2-((2-aminoethyl)amino)-5-nitropyridine react with hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) to form a mixture of substitution products with differing numbers of organic substituents as well as decomposition products and some unidentified side products. These products could be detected by ^{31}P NMR spectroscopy but were difficult to isolate and identify specifically.

However, unlike the hexachlorinated species the monofunctional cyclotriphosphazene pentaphenoxymonochlorocyclotriphosphazene ($N_3P_3(OC_6H_5)_5Cl$) reacts directly with the same pyridine derivatives to give the monopyridine-substituted products **1** and **2** (Scheme 1). This reaction was monitored by ^{31}P NMR spectroscopy. No side products were detected. Apparently, the electron-withdrawing and sterically protecting phenoxy groups are able to protect the phosphazene system from degradation and side product formation.

The reaction mixtures were subjected to column chromatography and recrystallization, and **1** was isolated as a colorless crystalline solid. Compound **2** is a dark yellow oil that crystallizes slowly to give a yellow solid. The characterization of **1** and **2** was performed by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, mass spectrometry, and elemental analysis. The NMR spectroscopic data are summarized in Table 1.

Scheme 1



The ^{31}P NMR spectra of both compounds show A_2B patterns with chemical shifts of 9.4 (**1**) and 9.3 ppm (**2**) for the phenoxy-substituted phosphorus atoms. The resonance frequencies for those phosphorus atoms that bear one pyridine and one phenoxy group are 18.1 (**1**) and 18.2 ppm (**2**) (J_{AB} = 74 Hz). The ^1H NMR spectra also confirm the composition of compounds **1** and **2**. Figure 1 shows the ^1H NMR spectrum of **2**. Comparison with literature data allowed the assignment of the resonance frequencies for each of the different protons.[29]

The ^{13}C NMR spectra of **1** and **2** show the expected resonance signals for the phenoxy and pyridine groups. The signals of three different kinds of phenoxy groups could be distinguished. Two of the groups are positioned cis respectively trans to the pyridine group relative to the phosphazene ring plane, and one phenoxy group is attached to the same phosphorus atom as the pyridine substituent.

Synthesis of Polymers 3–6. In theory two synthetic methodologies could lead to polyphosphazenes that bear two different substituents at the phosphorus atoms of the chain such as trifluoroethoxy and the 2-(2-aminoethyl)pyridine groups. For example, the first step of the substitution could involve initial exposure of the poly(dichlorophosphazene) either to the aminoalkylpyridine or to the sodium trifluorethoxide. Because primary amines are known to follow a geminal substitution pathway, whereas alkoxy- or aryloxy groups attack phosphazenes in a nongeminal sequence,[30,31] different types of polymers could be expected depending on the nucleophile introduced first.

Although both methodologies are worth investigating, the main disadvantage expected from the exposure of the poly(dichlorophosphazene) directly to the pyridine derivative is adduct formation and partial depolymerization which can be detected by ^{31}P NMR, depending on the reaction conditions. Therefore, polymers **3**–**5** were synthesized by treatment of different samples of the starting material, $[NPCl_2]_n$, with 0.5 (**3**), 1.0 (**4**) and 1.5 (**5**) equiv of sodium trifluorethoxide first. The second step was the addition of an excess of 2-(2-aminoethyl)pyridine to the boiling solution.

Species **6** was obtained by exposure of the poly(dichlorophosphazene) to an excess of the pyridine derivative. Although it was possible to synthesize the fully pyridine-substituted polymer **6**, this reaction was accompanied by a breakdown of the polymer chain to yield a significantly lower molecular weight polymer than in the case of the trifluorethoxy-substituted derivatives **3**–**5**. In all cases, the reactions must be carried out at reflux temperature in an extremely dry atmosphere, because the breakdown of the phosphazene chain can be reduced significantly under these conditions. Product formation versus

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(27) Audrieth, L. F.; Steinmann, R.; Toy, A. D. F. *Chem. Rev.* **1943**, *32*, 109.

(28) Migachev, G. I.; Stepanov, B. I. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1966**, *11*, 929.

(29) *Aldrich Library of NMR Spectra*, 1st ed.; Aldrich: Milwaukee, WI; Vol. 3, p 289.

(30) Allen, C. W. In *The Chemistry of Homo and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic Press: New York, 1987; Vol. 2, p 501 and references therein.

(31) Allen, C. W. *Chem. Rev.* **1991**, *91*, 119 and references therein.

Table 1. NMR Characterization Data of **1**−**6**[a]

compd	^{1}H NMR	^{13}C NMR	^{31}P NMR
1	8.48 (d, $J = 5.4$ Hz, 1 H, $\mathrm{CH_{pyr}}$), 7.30−6.0 (m, 26 H, Ar, $\mathrm{CH_{pyr}}$), 7.08 (t, $J = 9.0$ Hz, 1 H, $\mathrm{CH_{pyr}}$), 6.78 (d, $J = 9.0$ Hz, 1 H, $\mathrm{CH_{pyr}}$), 3.15 (b, 1 H, NH), 3.10 (m, 2H, $\mathrm{NHC}H_2$), 2.75 (t, 2H, $\mathrm{NHCH_2C}H_2$, $J = 7.5$)	159.4, 148.9, 136.8, 123.8, 116.9 (5s, $\mathrm{C_{pyr}}$), 151.3−150.6 (3d), 129.4 (3s), 124.5 (3s), 121.3 (3d) (Ar C), 39.9 (s, $\mathrm{NHCH_2}C\mathrm{H_2}$), 38.6 (d, $\mathrm{NH}C\mathrm{H_2}$, $J_{\mathrm{CP}} = 11$ Hz)	18.1 (t), 9.4 (d), $J = 74.0$ Hz
2	8.96 (d, $J = 2.2$ Hz, 1H, $\mathrm{CH_{pyr}}$), 7.96 (d of d, $J_{\mathrm{CHCH}} = 9.3$ Hz, $J_{\mathrm{CHCCH}} = 2.2$ Hz, 1H, $\mathrm{CH_{pyr}}$), 7.40−6.80 (m, 25H, Ar H), 6.12 (b, NH), 6.02 (d, $J = 8.3$ Hz, 1H, $\mathrm{CH_{pyr}}$), 3.28 (d, $J = 4$ Hz, 1H, NH), 2.94 (m, 2H, $\mathrm{NHC}H_2$), 2.71 (q, 2H, $\mathrm{NHCH_2C}H_2$)	161.0, 147.0, 135.7, 132.2, 118.5 (5s, $\mathrm{C_{pyr}}$), 150.8 (3d), 129.5 (3s), 125.0 (3s), 121.0 (3s) (Ar C), 43.2 (s), 40.0 (s) ($\mathrm{CH_2}$)	18.2 (t), 9.3 (d), $J = 74.0$ Hz
3	8.4, 7.5, 7.0 ($\mathrm{CH_{pyr}}$), 4.2 (*gem*-$\mathrm{OCH_2CF_3}$), 4.1 (non-*gem*-$\mathrm{OCH_2CF_3}$), 3.8 (NH), 3.2 (non-*gem*-$\mathrm{NHC}H_2\mathrm{CH_2C_5H_4N}$), 3.1 (*gem*-$\mathrm{NHC}H_2\mathrm{CH_2C_5H_4N}$), 2.8 ($\mathrm{NHCH_2C}H_2\mathrm{C_5H_4N}$)	160.0, 148.9, 136.4, 123.2, 121.3 (5s, $\mathrm{C_{pyr}}$), 124.2 (m, $\mathrm{CF_3}$), 62.5 (m, $\mathrm{OCH_2}$), 40.8 (s, $\mathrm{NHCH_2}C\mathrm{H_2}$), 39.1 (s, $\mathrm{NH}C\mathrm{H_2}$)	1.4 ($\mathrm{P(NH{\cdot}{\cdot})_2}$), 0.3 ($\mathrm{P(NH{\cdot}{\cdot})(O{\cdot}{\cdot})}$), −7.6 ($\mathrm{P(O{\cdot}{\cdot})_2}$)
4	8.3, 7.5, 7.0 ($\mathrm{CH_{pyr}}$), 4.4 (*gem*-$\mathrm{OCH_2CF_3}$), 4.2 (non-*gem*-$\mathrm{OCH_2CF_3}$), 3.4 (NH), 3.2 (non-*gem*-$\mathrm{NHC}H_2\mathrm{CH_2C_5H_4N}$), 3.1 (*gem*-$\mathrm{NHC}H_2\mathrm{CH_2C_5H_4N}$), 2.8 ($\mathrm{NHCH_2C}H_2\mathrm{C_5H_4N}$)	160.0, 149.1, 136.2, 123.3, 121.8 (5s, $\mathrm{C_{pyr}}$), 124.5 (m, $\mathrm{CF_3}$), 62.2 (m, $\mathrm{OCH_2}$), 40.9 (s, $\mathrm{NHCH_2}C\mathrm{H_2}$), 39.9 (s, $\mathrm{NH}C\mathrm{H_2}$)	2.6 ($\mathrm{P(NH{\cdot}{\cdot})_2}$), 0.6 ($\mathrm{P(NH{\cdot}{\cdot})(O{\cdot}{\cdot})}$), −7.7 ($\mathrm{P(O{\cdot}{\cdot})_2}$)
5	8.2, 7.2, 6.9 ($\mathrm{CH_{pyr}}$), 4.2 (*gem*-$\mathrm{OCH_2CF_3}$), 4.1 (non-*gem*-$\mathrm{OCH_2CF_3}$), 3.4 (NH), 3.2 (non-*gem*-$\mathrm{NHC}H_2\mathrm{CH_2C_5H_4N}$), 3.1 (*gem*-$\mathrm{NHC}H_2\mathrm{CH_2C_5H_4N}$), 2.8 ($\mathrm{NHCH_2C}H_2\mathrm{C_5H_4N}$)	160.5, 149.1, 136.1, 123.2, 121.0 (5s, $\mathrm{C_{pyr}}$), 124.8 (m, $\mathrm{CF_3}$), 62.5 (m, $\mathrm{OCH_2}$), 41.0 (s, $\mathrm{NHCH_2}C\mathrm{H_2}$), 40.0 (s, $\mathrm{NH}C\mathrm{H_2}$)	3.1, 2.3 ($\mathrm{P(NH{\cdot}{\cdot})_2}$), 0.7 ($\mathrm{P(NH{\cdot}{\cdot})(O{\cdot}{\cdot})}$), −8.3 ($\mathrm{P(O{\cdot}{\cdot})_2}$)
6	8.3, 7.3, 6.9, 6.8 ($\mathrm{CH_{pyr}}$), 3.8 (NH), 3.1 ($\mathrm{NHC}H_2\mathrm{CH_2C_5H_4N}$), 2.8 ($\mathrm{NHCH_2C}H_2\mathrm{C_5H_4N}$)	160.1, 148.8, 136.0, 123.2, 120.9 (5s, $\mathrm{C_{pyr}}$), 41.1 (s, $\mathrm{NHCH_2}C\mathrm{H_2}$), 40.1 (s, $\mathrm{NH}C\mathrm{H_2}$)	3.5, 2.9 ($\mathrm{P(NH{\cdot}{\cdot})_2}$)

[a] In $\mathrm{CDCl_3}$ solvent.

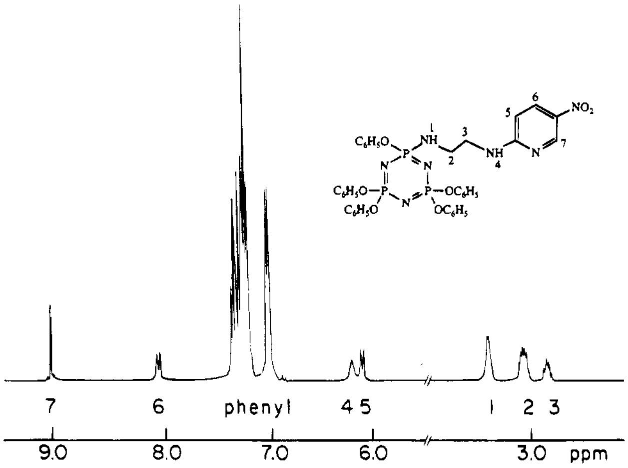

Figure 1. ^{1}H NMR spectrum of **2** in $\mathrm{CDCl_3}$.

Table 2. Analytical Data of the Polymers **3**−**6**

polymer		elem anal.					
		% C	% H	% N	% Cl	M_{w}	T_{g}, °C
3	calcd	30.71	2.95	11.02	0	*a*	−30.5
	found	31.23	3.41	11.42	<1		
4	calcd	41.33	4.22	16.13	0	2.2×10^6	−14.1
	found	41.39	4.44	16.01	<1		
5	calcd	50.00	5.25	20.29	0	2.8×10^6	−12.7
	found	50.17	5.27	20.37	<1		
6	calcd	24.39	6.27	58.54	0	3.1×10^5	−4.7
	found	23.19	5.95	57.23	1.62		

[a] The molecular weight is higher than the calibration range.

depolymerization/side product formation at room temperature and in boiling THF was monitored by ^{31}P NMR spectroscopy.

The new polymers were separated from sodium chloride and the HCl salt of excess 2-(2-aminoethyl)pyridine by filtration of the solution and by dialysis. They were subsequently purified by reprecipitation from highly concentrated THF or $\mathrm{CH_2Cl_2}$ solutions into hexane. The characterization was performed by ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy, microanalysis, GPC, and DSC measurements. The data are given in Tables 1 and 2.

The ^{31}P NMR spectra of **3**−**6** contain a broad singlet resonance at approximately −7.8 ppm for the phosphorus atoms that bear two trifluorethoxy groups and a second resonance at around 0.5 ppm for the phosphorus atoms that are attached to one trifluorethoxy and one pyridine group. The spectra of the polymers with 75% and 100% pyridine group substitution (**5** and **6**) show either one ($\mathrm{CD_3OD}$, $\mathrm{D_2O}$) or two ($\mathrm{CDCl_3}$) signals in the range between 1.5 and 3 ppm for the phosphorus atoms with two pyridine groups. Only a small singlet resonance at 1.4 and 2.6 ppm is observed for **3** and **4** respectively which contain smaller amounts of the geminal dipyridine-substituted phosphorus atoms. Figure 2 shows the ^{31}P NMR spectrum of **4** as a characteristic example for this type of polymer. The ^{1}H and ^{13}C NMR spectra also support the compositions of the polymers **3**−**6**. The chemical shifts are in good agreement with literature data and those found for the trimeric compounds **1** and **2**.[29]

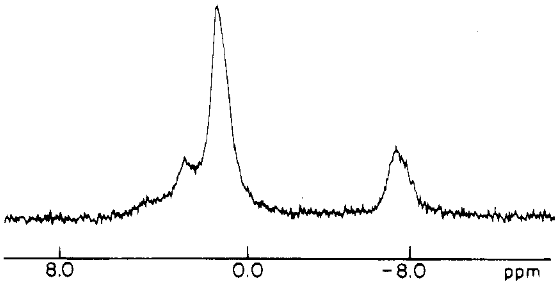

Figure 2. {^{1}H} ^{31}P NMR spectrum of **4** in $\mathrm{CDCl_3}$.

Polymers **3**−**6** are soluble in methylene chloride, THF, and methanol. The solubility in water increases with an increasing number of pyridine groups attached to the phosphazene chain. The polymers are also soluble in aqueous acids, due to the basicity of the pyridine side groups.

The glass transition temperatures (T_{g}) are also related to the ratios of the two different substituents. Increasing amounts of pyridine groups generate more leathery properties, whereas the polymer with only 25% pyridine groups is an elastomeric material.

Conclusions. A synthetic route to pyridine-substituted phosphazenes is described. Both cyclo- and polyphosphazenes can be stabilized against the pyridine-induced adduct formation and degradation of the PN system by electron-withdrawing cosubstituents and moderately high reaction temperatures.

Mono((aminoalkyl)pyridine)-substituted cyclotriphosphazenes are not accessible directly from $\mathrm{N_3P_3Cl_6}$, but they can be prepared by reacting ($\mathrm{N_3P_3(OC_6H_5)_5Cl}$) with the (aminoalkyl)pyridine. The two-step reaction of $[\mathrm{NPCl_2}]_n$ with sodium trifluorethoxide and the pyridine derivative yielded high molecular weight mixed-substituent copolymers, whereas direct exposure of the poly(dichlorophosphazene) to the pyridine-induced partial chain cleavage to yield a homopolymer with significantly lower molecular weight.

Experimental Section

Reagents and Equipment. All reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. Hexachlorocyclotriphosphazene was provided by Ethyl. Corp. Before use it was recrystallized from hexane and sublimed (30 °C, 0.05 mmHg). Pentaphenoxymonochlorocyclotriphosphazene and poly(dichlorophosphazene) were prepared by published procedures.[32,33] 2-(2-Aminoethyl)pyridine was distilled and 2-((2-aminoethyl)amino)-5-nitropyridine (Aldrich) used as received. 2,2,2-Trifluorethanol was distilled from calcium hydride and stored over 3-Å molecular sieves. Phenol was recrystallized from pentane and sublimed. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketal, and hexane was distilled from calcium hydride.

^{31}P (145 MHz), ^{13}C (90 MHz), and ^{1}H (360 MHz) NMR spectra were obtained by the use of a Bruker WM 360 spectrometer. ^{31}P shifts were referenced to external 85% H_3PO_4 with positive shifts downfield from the reference. ^{1}H NMR spectra were referenced to external tetramethylsilane. Electron impact mass spectra were obtained with use of a Kratos MS9/50 spectrometer. Glass transition temperatures were measured with a Perkin-Elmer DSC 7 instrument and TAS 7 software. The molecular weights of the polymers were estimated by gel permation chromatography with use of a Hewlett-Packard 1090 liquid chromatography unit using a polystyrene stationary phase. Polystyrene standards of known molecular weight were used to calibrate the columns. Sample concentrations were ca. 1.5% in THF. Elemental analyses were obtained either by Galbraith Laboratories (Knoxville, TN) or at the Institute for Inorganic and Analytical Chemistry of the Free University Berlin using a CHN-Analyzer 240 (Perkin-Elmer).

Synthesis of $N_3P_3(OC_6H_5)_5(NH(CH_2)_2C_5H_4N)$ (1). Pentaphenoxymonochlorocyclotriphosphazene ($N_3P_3(OC_6H_5)_5Cl$) (2 g, 0.003 mol) and triethylamine (0.5 g, 0.005 mol) were dissolved in 100 mL of tetrahydrofuran (THF). A solution of 2-(2-aminoethyl)pyridine in 20 mL of THF was added dropwise to the stirred solution of the phosphazene. The reaction mixture was heated to reflux for 72 h. It was then filtered through a fritted funnel to remove the triethylamine hydrochloride that had precipitated from the solution. After removal of the solvent and unreacted base from the filtrate by evaporation, a colorless oil was obtained. Purification by column chromatography using aluminum oxide as the stationary phase and an eluent mixture of diethyl ether and hexane (1:1) yielded **1** as a colorless oil. After recrystallization from diethyl ether/hexane mixtures, colorless crystals were obtained (1.8 g, 83%) (mp = 68–72 °C).

MS (M(**1**) = 721): *m/e* 721 (M^+), 629, 429, 414, 360, 121, 94, 78, 65, 28. Anal. Calcd: C, 61.53; H, 4.71; N, 9.70. Found: C, 61.13; H, 4.85; N, 9.46.

Synthesis of $N_3P_3(OC_6H_5)_5((NH(CH_2)_2NH)C_5H_3N(NO_2))$ (2). 2-((2-Aminoethyl)amino)-5-nitropyridine (0.55 g, 0.003 mol) was dissolved in 50 mL of THF and then added dropwise to a stirred solution of pentaphenoxymonochlorocyclotriphosphazene ($N_3P_3(OC_6H_5)_5Cl$) (2 g, 0.003 mol) and triethylamine (0.5 g, 0.005 mol) in 100 mL of THF. The reaction was monitored by ^{31}P NMR spectroscopy and was complete after heating the reaction mixture to reflux for 3 weeks. The solids which precipitated from the solution were filtered off. Solvent and unreacted base were removed, and the crude product, a yellow oil, was obtained. Purification was carried out by column chromatography on aluminum oxide using dichloromethane/hexane mixtures as solvents. Recrystallization from dichloromethane/hexane and diethyl ether/hexane mixtures yielded the pure compound **2** as a dark yellow oil which crystallized slowly (1.8 g, 76.6%).

MS (M(**2**) = 781.6): *m/e* 781.5 (M^+), 629, 617, 600, 524, 508, 431, 414, 338, 321, 94, 77, 65. Anal. Calcd: C, 56.81; H, 4.35; N, 12.54. Found: C, 56.64; H, 4.25; N, 12.09.

Synthesis of $[NP(OCH_2CF_3)_x(NH(CH_2)_2C_5H_4N)_y]_n$ (3–6). The syntheses of polymers **3**–**6** were carried out in a similar manner. The procedure for the synthesis of **4** is given as a typical example. Poly(dichlorophosphazene), $[NPCl_2]_n$ (2,86 g, 0.025 mol), was dissolved in 500 mL of THF. A solution of sodium trifluorethoxide (3.0 g, 0.025 mol) in 50 mL of THF was added dropwise to the stirred solution of the phosphazene. The reaction mixture was allowed to reflux for about 5 h. Then, 2-(2-aminoethyl)pyridine (9.2 g, 0.075 mol) dissolved in 50 mL THF was added to the boiling solution. (For the synthesis of the fully pyridine-substituted polymer **6**, the 2-(2-aminoethyl)pyridine was added directly to the boiling poly(dichlorophosphazene) solution.) After another 72 h at reflux temperature the reaction mixture was concentrated and then transferred into cellulose tubing (12000–14000 molecular weight cutoff). The solution was then dialyzed against methanol (48 h), deionized water (48 h), THF (48 h), and dichloromethane (48 h). The polymer solution was again concentrated and precipitated into hexane (2×). The pure polymer was obtained after removal of traces of solvents for 48 h on a vacuum line.

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(32) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.

(33) McBee, E. T.; Okuhara, K.; Morton, C. J. *Inorg. Chem.* **1966**, *5*, 450.