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Transition-Metal Derivatives of Polyphosphazenes: Syntheses of Polyphosphazenes and Cyclic Model Compounds with Iron Cyclopentadienyl Carbonyl Side Groups

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ABSTRACT: The first high polymeric phosphazenes with skeletal phosphorus–transition-metal covalent bonds are reported. These species have been synthesized via two routes: (a) by the interaction of an organometallic iron anion, $[FeCp(CO)_2]^-$, with a mixed-substituent polyphosphazene bearing both chloro- and trifluoroethoxy side groups, and (b) by the reaction of an organometallic halide, $FeCp(CO)_2I$, with a polyphosphazene that bears anionic sites at skeletal phosphorus. The polymers have been characterized by ^{31}P and ^1H NMR and infrared spectroscopy, gel permeation chromatography, and thermal analyses. Spectroscopic comparisons are made with cyclic trimeric model molecules that bear the same substituent groups. The molecular structural characteristics of the polymers have also been probed indirectly by means of a single-crystal X-ray structure study of the small molecule model species, $N_3P_3(OCH_2CF_3)_5FeCp(CO)_2$. Crystals of $N_3P_3(OCH_2CF_3)_5FeCp(CO)_2$ are monoclinic and have the following parameters: space group $P2_1/n$, a = 9.690 (4) Å, b = 20.684 (4) Å, c = 15.082 (2) Å, β = 101.15 (2)°, V = 2965.8 Å^3, Z = 4.

Polyphosphazenes are known that bear a wide variety of organic substituent groups,[1-2] and these macromolecules have been studied in some detail. However, in recent years we have also explored the possibility that analogous polymers may be accessible that contain transition metals in the side group structure.[3-7] Such polymers are prospective electroactive materials or macromolecular catalysts. Except in one case, the advances made up to this point have involved the synthesis and study of systems in which the transition metals are linked to the phosphazene skeleton through organic or carboranyl spacer groups.[4-6] The exception was a platinum derivative in which linkage to the metal was through coordination by the skeletal nitrogen atoms.[7] Our objective in this work was to prepare linear high polymeric phosphazenes in which a metal atom is connected directly to skeletal phosphorus through a covalent bond.

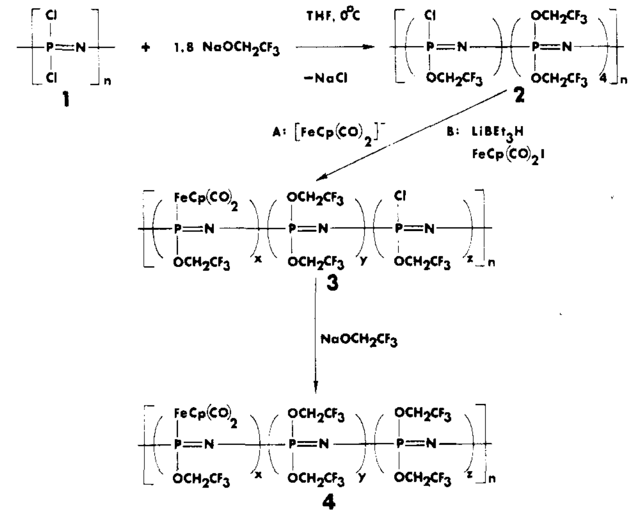
This accomplishment was preceded by a great deal of exploratory synthetic and structural work with small molecule cyclic phosphazenes,[8-15] and the results described here represent an extension of those studies to the more challenging macromolecular level.

Results and Discussion

Synthesis Pathways. Two different pathways have been employed for the synthesis of the polymer shown as 4. These are illustrated in Scheme I. Both pathways begin with poly(dichlorophosphazene) (1) and the replacement of most of the chlorine atoms in 1 by trifluoroethoxy groups to yield polymer 2. In pathway A, the reaction of 2 with sodium dicarbonylcyclopentadienylferrate in THF gave a metallophosphazene polymer (3) in which some P–Cl bonds remained unreacted. Treatment with sodium trifluoroethoxide replaced the remaining chlorine atoms by trifluoroethoxy groups to generate polymer 4.

Alternatively, in pathway B, the phosphorus–chlorine bonds in 2 were allowed to react with lithium or sodium triethylborohydride in THF to form triethylborane stabilized anionic sites along the polymer chain. These reacted with dicarbonylcyclopentadienyliodoiron with attachment of the metal to the polymer chain (3). This polymer was then allowed to react with a slight excess of sodium trifluoroethoxide in THF to replace any remaining chlorine atoms and yield polymer 4. Care must be exercised at this stage to avoid the cleavage of phosphorus–iron bonds by the strong organic nucleophile.

Scheme I



The resultant polymer (4) was a red-brown, tough, film-forming material that was soluble in acetone or tetrahydrofuran.

Characterization of Polymer 4. Polymer 4 was characterized by a combination of ^{31}P, ^1H NMR, and infrared spectroscopies, differential scanning calorimetry, gel permeation chromatography, and elemental microanalysis. The ^{31}P NMR spectrum of 4 in tetrahydrofuran contained a peak at 92.5 ppm $[P(OCH_2CF_3)(FeCp(CO)_2)]$ and peaks in the $P(OCH_2CF_3)_2$ region at −1.2, −8.6, and −14.8 ppm. The ^1H NMR spectrum consisted of a broad singlet at δ 4.52 from the trifluoroethoxy protons and a broadened singlet at δ 5.13 for the cyclopentadienyl protons. Overlap of the signals did not allow an accurate integration of the peak areas to be made. The infrared spectrum of 4, as a thin film on sodium chloride plates, showed peaks in the carbonyl region at 2040 and 2000 cm^{-1}, as well as peaks characteristic of (trifluoroethoxy)phosphazenes.

Gel permeation chromatography (Figure 1) of the poly(metallophosphazenes) prepared via pathway A indicated a slightly lower molecular weight than is typically found for poly[bis(trifluoroethoxy)phosphazene] (Table I). Presumably this is due to small amounts of chain cleavage during the reactions with the iron anion. However, based on the molecular weight values, these materials

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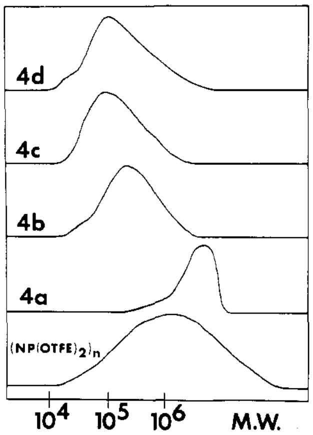


Figure 1. Gel permeation chromatograms of poly(metallophosphazenes) **4a–d** and $[NP(OTFE)_2]_n$ (OTFE = OCH_2CF_3).

Table I
Polymer Properties

polymer	$\bar{M}_n$	$\bar{M}_w$	T_g, °C
$[NP(OCH_2CF_3)_{1.86}(FeCp(CO)_2)_{0.14}]_n$, **4a**	$>1 \times 10^6$	$>1 \times 10^6$	−47
$[NP(OCH_2CF_3)_{1.95}(FeCp(CO)_2)_{0.05}]_n$, **4b**	1.4×10^5	2.9×10^5	−56
$[NP(OCH_2CF_3)_{1.94}(FeCp(CO)_2)_{0.06}]_n$, **4c**	8.6×10^4	3.5×10^5	−46
$[NP(OCH_2CF_3)_{1.95}(FeCp(CO)_2)_{0.05}]_n$, **4d**	1×10^5	3.6×10^5	−53

can still be considered high polymers.

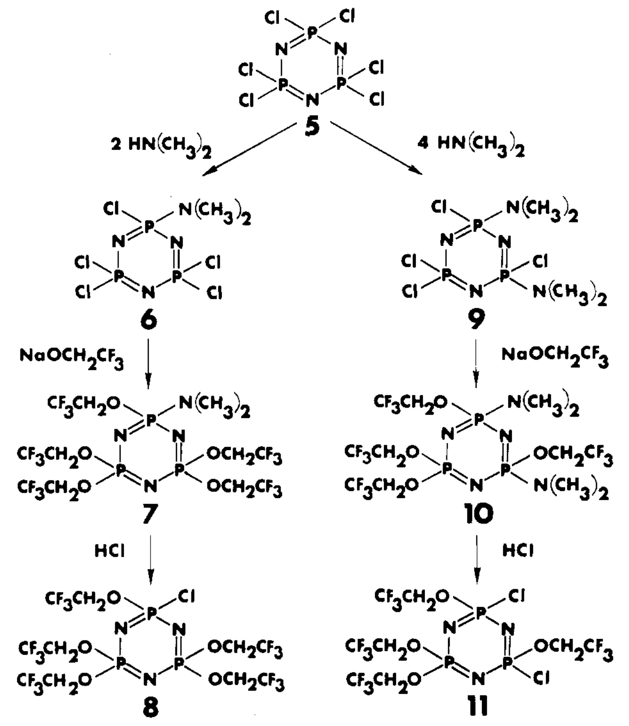
Differential scanning calorimetry indicates that the glass transition temperatures of the poly(metallophosphazenes) are slightly higher than that of poly[bis(trifluoroethoxy)phosphazene] (T_g = −66 °C) (Table I). Thus, the bulky organometallic groups may restrict the torsional mobility of some of the phosphazene backbone bonds. No other thermal transitions were detected at temperatures up to 200 °C.

Optical microscopy of thin polymer films demonstrated that the polymers were completely amorphous: no birefringence was detected through crossed polarizers.

Synthesis of Small Molecule Model Compounds. Macromolecular substitution reactions of this type are difficult to study at the fundamental mechanistic level because of the structural complexity of the precursor polymers, intermediates, and products. Hence, much of the known mechanistic and structural information for polyphosphazenes has in fact been obtained from small molecule, model compound studies. This is true for the present work also. Our general experience from past work indicates that the reactions of such small molecule model compounds often mimic the reactions of the high polymer, for example, in the substitution of chlorine atoms in phosphazenes by sodium trifluoroethoxide. However, when differences do exist, they can often be attributed to the flexibility of the polymer chain compared to the cyclic species. The small molecule compounds used in the present work are good models in the sense that they mimic the overall reaction pathways involved, i.e., substitution vs. cleavage or metal–halogen exchange. However, there is no evidence that they are effective models for the *pattern* of substitution at the macromolecular level, for example, whether substitutions are geminal, non-geminal, distal, cis, or trans.

Compound **8** (Scheme II) was synthesized as a model species for high polymeric phosphazenes that contain —$N{=}P(OCH_2CF_3)Cl$— repeating units flanked by —$N{=}P(OCH_2CF_3)_2$— units. Small molecule species **11** is a model for polymers that contain two adjacent —$N{=}P(OCH_2CF_3)Cl$— repeating units. The syntheses of **8** and **11** are outlined in Scheme II. In earlier work, **8** and **11** were isolated from the reaction of **5** with sodium trifluoroethoxide,[16] but this method yielded complex mixtures of products that were difficult to separate. In this present work we have developed the alternative synthetic procedure shown in Scheme II. This method allows the large scale, high yield preparation of **8** and **11** without contamination by related impurities.

Scheme II



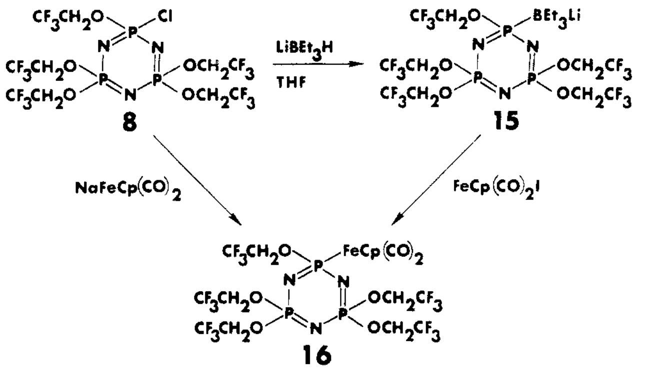
Thus, species **8** was prepared by the interaction of **5** with 2 equiv of dimethylamine in an ether–water mixture at 0 °C.[17] Separation of product **6** from compound **9** or unreacted **5** was achieved by careful fractional distillation. Species **6** reacted with sodium trifluoroethoxide to replace all the chlorine atoms by trifluoroethoxy groups.[16] Deaminolysis was accomplished by treatment of **7** with hydrogen chloride gas in a sealed tube at 110 °C.[18]

Similarly, **11** was prepared by the reaction of **5** with 4 equiv of anhydrous dimethylamine in diethyl ether at −78 °C.[18] Species **9** reacted with sodium trifluoroethoxide to give **10**. Species **10** interacted with hydrogen chloride in a sealed tube at 110 °C to give **11**.

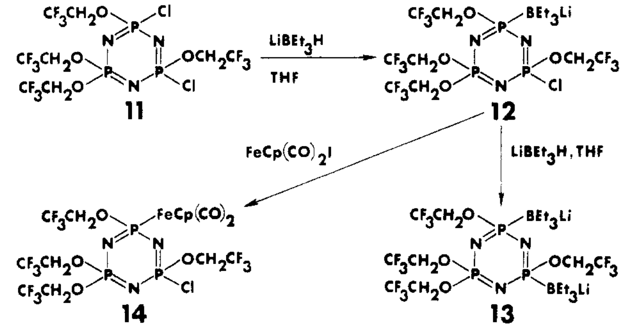
Mechanistic Questions Probed via Small Molecule Studies. Two mechanistic questions about the macromolecular reactions are of particular interest. First, why do attempts to replace all the remaining chlorine atoms in **2** by the organometallic species result instead in only partial replacement, to give **3**? Second, does the treatment of **3** with sodium trifluoroethoxide result in displacement of metal atoms from the polymer or modification of the organometallic side group?

In order to answer these questions, analogous reactions to those with **2** or **3** were carried out with the use of the small molecule models, **8** and **11**. Use of these model compounds permitted a study of the influence of a trifluoroethoxy group in the ease of replacement of a geminal chlorine atom by either triethylborohydride or the ferrate anions. In addition, compounds **8** and **11** allowed the role of flanking $P(OCH_2CF_3)Cl$ or $P(OCH_2CF_3)_2$ units to be assessed.

Scheme III



Scheme IV



It is known from earlier work that $(NPCl_2)_3$ (5) reacts with $LiBEt_3H$[19] at only one phosphorus atom of the ring. $NaFeCp(CO)_2$ reacts with $(NPF_2)_3$ in a similar manner.[20] Geminal dimetallo derivatives can be prepared with the use of $NaFe(Cp)(CO)_2$ or $NaRu(Cp)(CO)_2$ but the nongeminal sites appear to be deactivated to further attack.[10] Formation of a bis(triethylborohydride) derivative has not yet been demonstrated from $(NPCl_2)_3$.

The influence of trifluoroethoxy cosubstituent groups on these organometallic reactions was examined through the behavior of compound 8 (Scheme III). Thus, species 8 was allowed to react with $LiBEt_3H$ in THF to yield 15. Intermediate 15 was not isolated but was allowed to react with $FeCp(CO)_2I$ under a high pressure of carbon monoxide (to prevent carbonyl displacement reactions)[15] to yield 16. Compound 16 is a hydrolytically stable, yellow crystalline solid. The same compound was prepared independently by the direct reaction of 8 with $NaFeCp(CO)_2$. However, this latter pathway is less efficient than the first, since the complete conversion of 8 to 16 could not be accomplished. Clearly, if the reactivity of the cyclic trimer mimics that of the high polymer, it suggests that the incomplete replacement of chlorine by $NaFeCp(CO)_2$ occurs with high polymer 2 because of the inefficiency of the organometallic substitution process. However, the alternative pathway via the triethylborohydride derivatives, is highly efficient, and in principle, total replacement of chlorine in 2 by the iron units should be possible by this route.

Next, species 11 was allowed to react with a large excess of $LiBEt_3H$ in tetrahydrofuran at 25 °C. After 24 h of reaction, species 12 (Scheme IV) was detected by ^{31}P NMR analysis of the reaction mixture. The spectrum consisted of an ABX pattern with $\nu_A = 11.8$ ppm, m, $P(OCH_2CF_3)_2$; $\nu_B = 21.1$ ppm, m, $P(OCH_2CF_3)Cl$; and $\nu_X = 87.0$ ppm, br, $P(OCH_2CF_3)(BEt_3Li)$. Residual 11 was not detected. The mixture was then heated to reflux for 10 days. Species 13 was now present, as detected from the ^{31}P NMR spectrum. This spectrum was an AX_2 pattern with $\nu_A = 16.5$ ppm, m, $P(OCH_2CF_3)_2$; and $\nu_{X2} = 56$ ppm, $P(OCH_2CF_3)(BEt_3Li)$. Compound 12 was no longer detected. The ^{31}P NMR spectra recorded as the reaction progressed showed a gradual decrease in the concentration of 12 and a concurrent increase in the concentration of 13. We conclude from these results that the presence of one triethylborohydride unit in 12 deactivates the PCl bond at the nongeminal phosphorus to reaction with $LiBEt_3H$ but that this chlorine atom can be replaced under forcing conditions. However, treatment of 13 with an excess of $FeCp(CO)_2I$ in THF brought about decomposition of the phosphazene ring.

In a related experiment, 12 was allowed to react with an excess of $FeCp(CO)_2I$ to yield 14. Species 14 was identified on the basis of its ^{31}P NMR spectrum, which consisted of an ABX pattern with $\nu_A = 18$ ppm, $P(OCH_2CF_3)Cl$; $\nu_B = 7.5$ ppm, $P(OCH_2CF_3)_2$; and $\nu_X = 118$ ppm, $P(OCH_2CF_3)FeCp(CO)_2$. However, treatment of 14 with excess $LiBEt_3H$ in boiling THF brought about decomposition of the phosphazene. It can be implied that, once an iron-containing unit is present, it deactivates the nongeminal site to attack both by $NaFeCp(CO)_2$ and by $LiBEt_3H$. These observations provide some clues to why polymer 3 is formed from 2 and why total replacement of the P–Cl bonds by P–$FeCp(CO)_2$ units does not occur.

Finally, it was shown that treatment of 16 with sodium trifluoroethoxide (under mild conditions) did not bring about displacement of $FeCp(CO)_2$ groups by trifluoroethoxy units. Species 16 was recovered unchanged. Thus, if the small molecule reactions are good models for the corresponding high polymer, it would appear that the conversion of high polymer 3 to polymer 4 can be accomplished without loss of the iron-containing side groups.

Structural Characterization of the Model Compounds 16. (a) Spectroscopic Analysis. The structural analysis of 16 is described as an example of the general techniques employed. Compound 16 was characterized by a combination of ^1H, ^{13}C, and ^{31}P NMR and infrared spectroscopies, mass spectrometry, and elemental microanalysis. The ^{31}P NMR spectrum consisted of an AX_2 pattern. The A portion, an unresolved triplet, had a chemical shift of 118.1 ppm in $CDCl_3$ and was assigned to the phosphorus-linked to the iron atom. This downfield shift is typical of an iron-substituted phosphazene. The X_2 portion of the spectrum was a doublet ($J_{PNP} = 3.9$ Hz) with a chemical shift of 10.4 ppm and was attributed to the bis(trifluoroethoxy)-linked phosphorus atoms. The ^1H NMR spectrum consisted of a doublet at 5.06 ppm ($J_{PFeH} = 0.8$ Hz) assigned to C_5H_5, a multiplet at 4.25 ppm from $P(OCH_2CF_3)_2$, and a pentet at 4.09 ppm assigned to the trifluoroethoxy protons adjacent to the transition-metal substituent. The ^{13}C NMR spectrum of 16 consisted of a doublet at 210.56 ppm ($J_{PFeC} = 40.3$ Hz) for the carbonyl carbon atoms and a singlet at 86.48 ppm assigned to the cyclopentadienyl carbon atoms. The trifluoroethoxy group geminal to the iron substituent yielded a quartet of doublets at 123.53 ppm ($J_{FC} = 269.78$ Hz) from the CF_3 carbon atom and a quartet at 62.51 ppm ($J_{FCC} = 37.84$ Hz) from the CH_2 carbon atom. The remaining trifluoroethoxy groups yielded a quartet of doublets at 118.36 ppm ($J_{FC} = 277.10$ Hz), from the CF_3 carbon atoms, and a quartet of doublets at 59.54 ppm ($J_{FCC} = 36.01$ Hz), from the CH_2 carbon atoms. The infrared spectrum in the carbonyl region of 16 in dichloromethane solution consisted of two strong absorbances at 2031 and 1995 cm^{-1}. This spectrum is similar in appearance to other $FeCp(CO)_2$-substituted phosphazenes. The EI mass spectrum did not show the parent ion (m/z 807), but peaks corresponding to the parent less one carbonyl unit were detected (m/z 779).

Table II
Summary of Crystal and Data Collection Parameters for Compound 16

crystal size (mm)	0.30 × 0.24 × 0.18
fw (amu)	807.08
space group	$P2_1/n$
a (Å)	9.690 (4)
b (Å)	20.684 (4)
c (Å)	15.082 (2)
β (deg)	101.15 (2)
vol (Å^3)	2965.8
Z	4
d_{calcd} (g cm^{-3})	1.81
2θ max (deg)	50
scan width	$0.50 + 0.35 \tan \theta$
unique measd data	5212
obsd data [$I > 3\sigma(I)$]	3666
μ (cm^{-1})	8.0
R, R_w	0.063, 0.098
p (weighting factor)	0.05
error in weights	3.11
data/parameter	8.83
max shift/error	0.24
largest peak (e Å^{-3})	0.45

Elemental microanalysis was consistent with the proposed structure.

(b) X-ray Structural Determination of 16. The X-ray crystallographic study of compound **16** was carried out to confirm the molecular geometry and to obtain structural data that might be transferable to the high polymer.

A summary of cell constants and data collection parameters are included in Table II. Bond lengths and angles are included in Table III. Observed and calculated structure factor amplitudes are listed in Table IV in the supplementary material. Atomic positional and thermal parameters are included in Table V. Least-squares planes are listed in Table VI in the supplementary material.

The solution of the crystal structure of **16** confirmed that the molecule consists of a cyclotriphosphazene ring with five trifluoroethoxy substituents, and one dicarbonylcyclopentadienyliron substituent attached through a phosphorus–iron covalent bond. All features of the structure of **16** were determined. An ORTEP view of **16** is included in Figure 2.

The iron–phosphorus bond distance is 2.20 Å, which is comparable to that found in other iron-substituted cyclic phosphazenes.[14,15] The cyclopentadienyl ring is planar and is separated from the iron atom by an average distance of 2.10 Å. The carbonyl groups are normal, with an average iron–carbon distance of 1.77 Å, an average carbon–oxygen distance of 1.13 Å, and an average iron–carbon–oxygen angle of 178.6°. These values are expected to be directly transferable to the linear high polymeric analogue.

The most critical feature of **16** is in the structure of the phosphazene ring. The average P(1)–nitrogen bond distance is 1.63 Å, while the remaining phosphorus–nitrogen distances are equal (1.57 Å), with the exception of P(3)–N(2) which is 1.59 Å in length. The resultant nonregularity of the endocyclic N–P–N and P–N–P angles is also notable. Most metallophosphazenes are characterized by a variation in ring angles symmetrical about the P(1)–N(2) plane. In compound **16**, the N(1)–P(1)–N(3) angle is narrowed to 113.1°, while N(1)–P(2)–N(2) is 118.3° and N(1)–P(3)–N(2) is 120.9°. The P–N–P angles range from 120.1° to 124.1° with no apparent relationship to one another. One more striking feature is the near planarity of the ring. Atom P(1) is located 0.23 Å from a plane formed by the five remaining ring atoms. Other metallocyclophosphazenes exhibit far greater distortions in ring planarity. Apparently the presence of the trifluoroethoxy groups moderates the effect of the organometallic group on the structural parameters of the ring. Clearly, many of these peculiarities are associated with the structural and conformational restraints imposed by a six-membered ring. They may not exist in the linear high polymer. However, the data for **16** do indicate a strong electronic influence by the transition metal on the phosphazene skeleton, and it appears likely that this influence exists also in a high polymer.

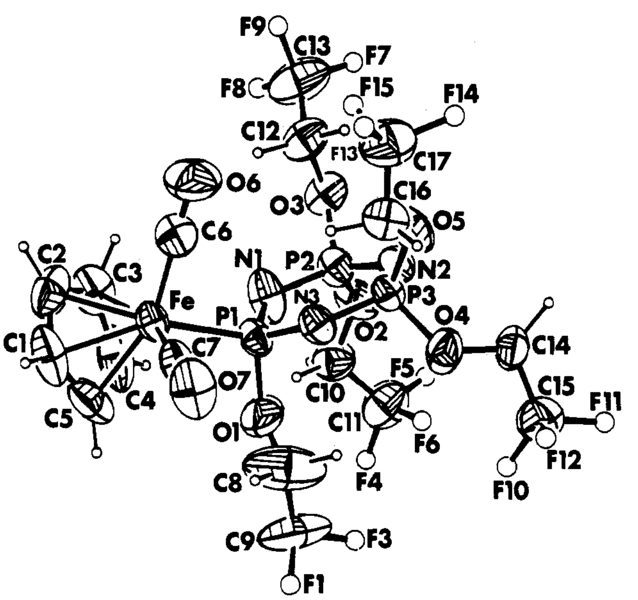


Figure 2. ORTEP view of **16**.

The structural information for the trifluoroethoxy side units (Table II) is expected to be directly applicable to the high polymers. The high thermal factors found for several of the CF_3 units are consistent with the ease of conformational reorientation normally found in fluoroalkoxyphosphazene high polymers.[21]

Experimental Section

Materials and Equipment. Hexachlorocyclotriphosphazene (5) was kindly provided by Ethyl Corp. and was sublimed before use. Poly(dichlorophosphazene) (1),[2] sodium potassium alloy,[22] $FeCp(CO)_2I$,[23] and 9[24] were prepared according to a previously published procedure. Sodium metal, lithium triethylborohydride, sodium triethylborohydride, potassium triethylborohydride, and dimethylamine hydrochloride were used as received from Aldrich. Tetracarbonyldicyclopentadienyldiiron was obtained from Alfa and was used as received. Dimethylamine, hydrogen chloride, and carbon monoxide were used as received from Matheson. Trifluoroethanol (Halocarbon) was distilled from activated 3-Å molecular sieves under dry argon before use. Tetrahydrofuran was distilled from sodium benzophenone ketyl under dry argon. All manipulations were performed by standard Schlenk-line techniques under an atmosphere of dry argon unless otherwise indicated. NMR spectra were recorded on a JEOL FX90Q spectrometer operating in the Fourier transform mode. Infrared spectra were recorded on a Perkin-Elmer 283B spectrophotometer as KBr disks for crystalline solids, as thin films on sodium chloride plates for oils and polymers, or as dichloromethane solutions in sodium chloride solution cells. Electron impact mass spectra were recorded on a KRATOS MS9/50 spectrometer. Polymer molecular weights were determined on a Hewlett-Packard HP1090 gel permeation chromatograph equipped with Polymer Laboratories PL Gel columns and using tetrahydrofuran as eluent. Approximate molecular weight calibrations were performed with use of narrow molecular weight polystyrene standards. Thermal analyses were performed by using a Perkin-Elmer DSC-7 differential scanning calorimeter. Elemental microanalyses were obtained by Galbraith Laboratories, Knoxville, TN.

Synthesis of ($NP(OCH_2CF_3)_{1.8}Cl_{0.2})_n$ (2). Polymer 1 (5.00 g, 43 mmol) was dissolved in THF (200 mL). Sodium trifluoroethoxide, prepared from the reaction of trifluoroethanol (7.77 g,

Table III
Bond Distances and Angles for 16

bond	distance, Å	bond	distance, Å	bond	distance, Å
Fe–P(1)	2.196 (1)	P(3)–N(2)	1.589 (3)	O(1)–C(8)	1.258 (7)
Fe–C(1)	2.103 (4)	P(3)–N(3)	1.568 (3)	O(2)–C(10)	1.398 (5)
Fe–C(2)	2.126 (4)	F(1)–C(9)	1.277 (8)	O(3)–C(12)	1.431 (5)
Fe–C(3)	2.099 (4)	F(2)–C(9)	1.123 (7)	O(4)–C(14)	1.448 (4)
Fe–C(4)	2.078 (4)	F(3)–C(9)	1.311 (10)	O(5)–C(16)	1.430 (5)
Fe–C(5)	2.080 (4)	F(4)–C(11)	1.277 (7)	O(6)–C(6)	1.139 (5)
Fe–C(6)	1.763 (5)	F(5)–C(11)	1.350 (6)	O(7)–C(7)	1.122 (4)
Fe–C(7)	1.786 (4)	F(6)–C(11)	1.318 (6)	C(1)–C(2)	1.328 (7)
P(1)–O(1)	1.605 (3)	F(7)–C(13)	1.309 (7)	C(1)–C(5)	1.417 (7)
P(1)–N(1)	1.628 (3)	F(8)–C(13)	1.300 (7)	C(2)–C(3)	1.399 (7)
P(1)–N(3)	1.630 (3)	F(9)–C(13)	1.337 (6)	C(3)–C(4)	1.398 (7)
P(2)–O(2)	1.599 (3)	F(10)–C(15)	1.241 (6)	C(4)–C(5)	1.416 (7)
P(2)–O(3)	1.588 (3)	F(11)–C(15)	1.368 (6)	C(8)–C(9)	1.489 (9)
P(2)–N(1)	1.565 (3)	F(12)–C(15)	1.337 (6)	C(10)–C(11)	1.428 (6)
P(2)–N(2)	1.570 (3)	F(13)–C(17)	1.374 (6)	C(12)–C(13)	1.440 (7)
P(3)–O(4)	1.577 (3)	F(14)–C(17)	1.357 (7)	C(14)–C(15)	1.481 (6)
P(3)–O(5)	1.575 (3)	F(15)–C(17)	1.261 (6)	C(16)–C(17)	1.442 (7)

bond	angle, deg	bond	angle, deg
P(1)–Fe–C(1)	147.2 (2)	C(2)–C(1)–C(5)	109.2 (4)
P(1)–Fe–C(2)	144.9 (2)	Fe–C(2)–C(1)	70.8 (3)
P(1)–Fe–C(3)	106.3 (1)	Fe–C(2)–C(3)	69.6 (2)
P(1)–Fe–C(4)	88.1 (1)	C(1)–C(2)–C(3)	111.2 (5)
P(1)–Fe–C(5)	107.6 (2)	Fe–C(3)–C(2)	71.7 (2)
P(1)–Fe–C(6)	89.7 (1)	Fe–C(3)–C(4)	69.6 (3)
P(1)–Fe–C(7)	90.2 (1)	C(2)–C(3)–C(4)	105.0 (4)
C(1)–Fe–C(2)	36.6 (2)	Fe–C(4)–C(3)	71.2 (3)
C(1)–Fe–C(5)	39.6 (2)	Fe–C(4)–C(5)	70.2 (2)
C(1)–Fe–C(6)	121.8 (2)	C(3)–C(4)–C(5)	109.7 (4)
C(1)–Fe–C(7)	95.6 (2)	Fe–C(5)–C(1)	71.1 (3)
C(2)–Fe–C(3)	38.7 (2)	Fe–C(5)–C(4)	70.0 (2)
C(2)–Fe–C(6)	93.9 (2)	C(1)–C(5)–C(4)	104.7 (5)
C(2)–Fe–C(7)	124.1 (2)	Fe–C(6)–O(6)	178.1 (4)
C(3)–Fe–C(4)	39.1 (2)	Fe–C(7)–O(7)	179.1 (4)
C(3)–Fe–C(6)	96.0 (2)	O(1)–C(8)–C(9)	116.6 (5)
C(3)–Fe–C(7)	160.3 (2)	F(1)–C(9)–F(2)	113.7 (8)
C(4)–Fe–C(5)	39.8 (2)	F(1)–C(9)–F(3)	102.4 (7)
C(4)–Fe–C(6)	131.2 (2)	F(1)–C(9)–C(8)	106.0 (7)
C(4)–Fe–C(7)	134.1 (2)	F(2)–C(9)–F(3)	98.4 (9)
C(5)–Fe–C(6)	158.2 (2)	F(2)–C(9)–C(8)	119.8 (7)
C(5)–Fe–C(7)	98.4 (2)	F(3)–C(9)–C(8)	115.4 (9)
C(6)–Fe–C(7)	94.6 (2)	O(2)–C(10)–C(11)	112.2 (4)
Fe–P(1)–O(1)	109.4 (2)	F(4)–C(11)–F(5)	107.7 (5)
Fe–P(1)–N(1)	112.5 (2)	F(4)–C(11)–F(6)	105.6 (5)
Fe–P(1)–N(3)	113.4 (2)	F(4)–C(11)–C(10)	113.9 (5)
O(1)–P(1)–N(1)	100.1 (2)	F(5)–C(11)–F(6)	107.0 (5)
O(1)–P(1)–N(3)	107.4 (2)	F(5)–C(11)–C(10)	111.1 (5)
N(1)–P(1)–N(3)	113.1 (2)	F(6)–C(11)–C(10)	111.2 (5)
O(2)–P(2)–O(3)	94.1 (1)	O(3)–C(12)–C(13)	105.5 (4)
O(2)–P(2)–N(1)	111.8 (2)	F(7)–C(13)–F(8)	103.0 (5)
O(2)–P(2)–N(2)	111.2 (2)	F(7)–C(13)–F(9)	107.0 (6)
O(3)–P(2)–N(1)	110.0 (2)	F(7)–C(13)–C(12)	115.5 (6)
O(3)–P(2)–N(2)	108.8 (2)	F(8)–C(13)–F(9)	105.9 (6)
N(1)–P(2)–N(2)	118.3 (2)	F(8)–C(13)–C(12)	115.9 (6)
O(4)–P(3)–O(5)	103.1 (2)	F(9)–C(13)–C(12)	108.9 (5)
O(4)–P(3)–N(2)	109.8 (2)	O(4)–C(14)–C(15)	103.2 (3)
O(4)–P(3)–N(3)	106.3 (2)	F(10)–C(15)–F(11)	105.8 (5)
O(5)–P(3)–N(2)	104.3 (2)	F(10)–C(15)–F(12)	106.5 (5)
O(5)–P(3)–N(3)	111.1 (2)	F(10)–C(15)–C(14)	114.5 (5)
N(2)–P(3)–N(3)	120.9 (2)	F(11)–C(15)–F(12)	107.5 (5)
P(1)–O(1)–C(8)	126.8 (4)	F(11)–C(15)–C(14)	108.5 (4)
P(2)–O(2)–C(10)	124.1 (2)	F(12)–C(15)–C(14)	113.5 (5)
P(2)–O(3)–C(12)	118.5 (2)	O(5)–C(16)–C(17)	106.1 (4)
P(3)–O(4)–C(14)	122.1 (2)	F(13)–C(17)–F(14)	104.1 (5)
P(3)–O(5)–C(16)	121.8 (3)	F(13)–C(17)–F(15)	107.9 (5)
P(1)–N(1)–P(2)	124.1 (2)	F(13)–C(17)–C(16)	110.2 (5)
P(2)–N(2)–P(3)	120.1 (2)	F(14)–C(17)–F(15)	105.3 (6)
P(1)–N(3)–P(3)	121.1 (2)	F(14)–C(17)–C(16)	112.2 (5)
Fe–C(1)–C(2)	72.6 (3)	F(15)–C(17)–C(16)	116.3 (5)
Fe–C(1)–C(5)	69.30 (2)		

78 mmol) and sodium (2.75 g, 0.19 mol) in THF (100 mL) at 66 °C for 18 h, was added dropwise to the cooled (0 °C) solution of polymer. The mixture was allowed to warm to room temperature and was stirred for 3 h. The ^{31}P NMR spectrum of the reaction mixture consisted of a broad singlet at −9.8 ppm, which is indicative of incomplete P–Cl substitution. The polymer was not isolated because of the presence of hydrolytically sensitive P–Cl bonds but was used immediately in the following reactions.

Synthesis of $(NP(OCH_2CF_3)_{1.86}(FeCp(CO)_2)_{0.14})_n$ (4a) from the Reaction of 2 with LiBEt$_3$H and FeCp(CO)$_2$I. Di-

Table V
Atomic Positional and Thermal Parameters for 16[a]

atom	x	y	z	$U(1,1)$	$U(2,2)$	$U(3,3)$	$U(1,2)$	$U(1,3)$	$U(2,3)$
Fe	0.48475 (8)	0.10981 (4)	0.69484 (5)	0.0374 (4)	0.0547 (4)	0.0553 (4)	0.0028 (3)	0.0116 (3)	0.0098 (4)
P1	0.3363 (2)	0.1251 (1)	0.7859 (1)	0.0422 (6)	0.0457 (7)	0.0635 (8)	0.0008 (6)	0.0186 (6)	0.0043 (7)
P2	0.0436 (2)	0.1088 (1)	0.7705 (1)	0.0383 (7)	0.0619 (9)	0.0663 (8)	0.0053 (7)	0.0143 (6)	0.0011 (8)
P3	0.2252 (1)	0.0492 (1)	0.9078 (1)	0.0432 (7)	0.0511 (8)	0.0536 (7)	−0.0060 (6)	0.0131 (6)	−0.0004 (7)
F1	0.5425 (7)	0.2913 (3)	0.9867 (5)	0.198 (5)	0.125 (4)	0.195 (6)	−0.061 (4)	−0.068 (5)	−0.012 (4)
F2	0.3854 (12)	0.3177 (3)	0.8855 (6)	0.47 (1)	0.063 (3)	0.244 (7)	0.005 (6)	−0.173 (7)	−0.004 (4)
F3	0.3356 (11)	0.2867 (6)	0.9897 (8)	0.303 (8)	0.35 (1)	0.36 (1)	0.135 (7)	0.152 (7)	−0.055 (9)
F4	−0.0255 (7)	0.3246 (3)	0.8613 (4)	0.160 (5)	0.103 (3)	0.187 (5)	−0.013 (3)	0.025 (4)	−0.071 (3)
F5	−0.1966 (5)	0.2599 (3)	0.8574 (5)	0.091 (3)	0.169 (5)	0.251 (5)	0.006 (3)	0.075 (3)	−0.067 (4)
F6	0.0098 (9)	0.2390 (4)	0.9328 (1)	0.234 (7)	0.213 (7)	0.080 (3)	0.055 (6)	−0.001 (4)	−0.023 (4)
F7	−0.2553 (5)	−0.0191 (3)	0.6209 (4)	0.085 (3)	0.163 (5)	0.192 (6)	−0.018 (3)	0.005 (4)	−0.048 (4)
F8	−0.1734 (7)	0.0297 (4)	0.5253 (4)	0.151 (5)	0.220 (6)	0.086 (3)	0.035 (5)	−0.029 (3)	−0.025 (4)
F9	−0.1030 (7)	−0.0651 (3)	0.5581 (5)	0.146 (5)	0.215 (5)	0.259 (6)	0.048 (4)	−0.027 (5)	−0.161 (4)
F10	0.2263 (7)	0.1670 (3)	1.1261 (4)	0.172 (5)	0.095 (3)	0.181 (5)	−0.035 (3)	0.064 (4)	−0.042 (3)
F11	0.1047 (6)	0.1124 (3)	1.1981 (3)	0.148 (4)	0.200 (6)	0.093 (2)	−0.007 (4)	0.065 (2)	−0.036 (3)
F12	0.3198 (6)	0.0854 (3)	1.1906 (3)	0.111 (4)	0.187 (5)	0.078 (3)	0.006 (4)	−0.003 (3)	−0.021 (3)
F13	0.4180 (6)	−0.1661 (3)	0.8818 (5)	0.157 (5)	0.082 (3)	0.210 (5)	0.023 (3)	0.045 (4)	−0.027 (3)
F14	0.2222 (7)	−0.1583 (3)	0.9284 (5)	0.193 (5)	0.070 (3)	0.266 (7)	−0.039 (3)	0.077 (5)	−0.005 (4)
F15	0.2347 (8)	−0.1255 (4)	0.7998 (4)	0.186 (6)	0.221 (7)	0.110 (4)	0.004 (5)	−0.031 (4)	−0.058 (4)
O1	0.3591 (7)	0.1960 (2)	0.8294 (3)	0.190 (5)	0.060 (3)	0.083 (3)	−0.030 (3)	0.060 (3)	−0.022 (2)
O1	−0.0623 (4)	0.1672 (2)	0.7767 (3)	0.048 (2)	0.060 (2)	0.120 (3)	−0.001 (2)	0.026 (2)	−0.007 (3)
O3	−0.0637 (4)	0.0714 (2)	0.6947 (3)	0.048 (2)	0.084 (3)	0.067 (2)	0.016 (2)	0.006 (2)	−0.010 (2)
O4	0.2513 (4)	0.0714 (3)	1.0097 (3)	0.052 (2)	0.119 (4)	0.051 (2)	−0.014 (2)	0.012 (2)	−0.008 (2)
O5	0.2242 (5)	−0.0267 (2)	0.9148 (4)	0.078 (3)	0.051 (2)	0.125 (3)	−0.002 (2)	0.039 (2)	0.013 (2)
O6	0.3848 (7)	−0.0222 (2)	0.6662 (4)	0.146 (5)	0.059 (3)	0.122 (4)	−0.010 (3)	0.024 (4)	−0.014 (3)
O7	0.7054 (5)	0.0791 (3)	0.8490 (3)	0.054 (2)	0.127 (4)	0.079 (3)	0.014 (3)	−0.001 (2)	0.035 (3)
N1	0.1744 (5)	0.1314 (3)	0.7318 (4)	0.045 (2)	0.090 (4)	0.091 (3)	0.016 (3)	0.021 (2)	0.036 (3)
N2	0.0695 (5)	0.0672 (3)	0.8593 (3)	0.043 (2)	0.072 (3)	0.062 (3)	−0.011 (2)	0.011 (2)	−0.005 (2)
N3	0.3551 (5)	0.0734 (2)	0.8690 (3)	0.040 (2)	0.058 (3)	0.060 (3)	−0.001 (2)	0.008 (2)	0.005 (2)
C1	0.6182 (7)	0.1521 (4)	0.6165 (5)	0.055 (3)	0.121 (5)	0.095 (4)	0.000 (4)	0.027 (3)	0.048 (4)
C2	0.5175 (9)	0.1210 (4	0.5603 (4)	0.118 (5)	0.089 (5)	0.054 (3)	0.017 (4)	0.029 (3)	0.012 (3)
C3	0.3843 (7)	0.1438 (4)	0.5675 (5)	0.065 (4)	0.090 (5)	0.073 (4)	0.005 (4)	−0.000 (3)	0.026 (4)
C4	0.4102 (7)	0.1949 (4)	0.6293 (5)	0.094 (4)	0.087 (4)	0.126 (4)	0.043 (3)	0.062 (3)	0.066 (3)
C5	0.5565 (8)	0.2001 (4)	0.6634 (5)	0.085 (4)	0.077 (4)	0.094 (4)	−0.034 (3)	0.006 (4)	0.029 (4)
C6	0.4262 (7)	0.0292 (3)	0.6779 (4)	0.068 (4)	0.066 (4)	0.073 (4)	0.004 (3)	0.015 (3)	0.002 (3)
C7	0.6210 (6)	0.0913 (3)	0.7893 (4)	0.046 (3)	0.068 (4)	0.067 (3)	0.001 (3)	0.020 (2)	0.013 (3)
C8	0.4369 (12)	0.2110 (5)	0.9034 (8)	0.158 (8)	0.080 (6)	0.164 (8)	−0.005 (6)	−0.083 (6)	0.005 (6)
C9	0.4247 (12)	0.2784 (4)	0.9355 (6)	0.21 (1)	0.067 (5)	0.103 (6)	−0.011 (6)	−0.046 (6)	−0.031 (4)
C10	−0.0237 (7)	0.2324 (3)	0.7800 (5)	0.074 (4)	0.066 (4)	0.079 (4)	0.007 (3)	0.017 (3)	−0.008 (3)
C11	−0.0579 (9)	0.2647 (4)	0.8567 (5)	0.089 (5)	0.105 (6)	0.085 (5)	0.015 (4)	0.017 (4)	−0.012 (4)
C12	−0.0206 (7)	0.0114 (4)	0.6618 (5)	0.067 (4)	0.085 (4)	0.065 (3)	0.014 (3)	0.001 (3)	−0.015 (3)
C13	−0.1369 (9)	−0.0094 (4)	0.5933 (6)	0.100 (5)	0.106 (5)	0.115 (6)	0.031 (5)	−0.004 (5)	−0.043 (5)
C14	0.1407 (7)	0.0710 (4)	1.0619 (4)	0.066 (3)	0.091 (5)	0.052 (3)	−0.009 (3)	0.024 (3)	−0.004 (3)
C15	0.2008 (9)	0.1100 (4)	1.1426 (6)	0.092 (5)	0.092 (5)	0.096 (5)	−0.013 (4)	0.030 (4)	−0.024 (4)
C16	0.3492 (7)	−0.0642 (3)	0.9186 (5)	0.067 (4)	0.062 (4)	0.076 (4)	−0.001 (3)	0.005 (3)	−0.001 (3)
C17	0.3041 (10)	−0.1216 (4)	0.8796 (6)	0.117 (6)	0.073 (5)	0.104 (6)	0.008 (5)	0.012 (5)	−0.011 (4)
H1	0.7207	0.1347	0.6250	*					
H2	0.5352	0.0814	0.5156	*					
H3	0.2773	0.1152	0.5410	*					
H4	0.3320	0.2148	0.6445	*					
H5	0.6093	0.2324	0.7070	*					
H81	0.4066	0.1807	0.9568	*					
H82	0.5419	0.2012	0.9038	*					
H101	−0.0839	0.2675	0.7285	*					
H102	0.0820	0.2343	0.7695	*					
H121	0.0755	0.0181	0.6345	*					
H122	−0.0006	−0.0236	0.7178	*					
H141	0.1093	0.0175	1.0820	*					
H142	0.0546	0.1015	1.0195	*					
H161	0.4179	−0.0488	0.8750	*					
H162	0.3906	−0.0664	0.9804	*					

[a] Starred atoms were included in refinements with an overall isotropic temperature factor $B = 4.0$ Å^2. The form of the anisotropic thermal parameter is $\exp[-2PI^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + 12c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)\}]$ where a, b, and c are reciprocal lattice constants.

carbonylcyclopentadienyliodoiron (4.19 g, 14 mmol) was dissolved in tetrahydrofuran (15 mL) and was transferred to a stirred solution of **2** (17.3 mmol) in tetrahydrofuran. Lithium triethylborohydride (14 mL of a 1.0 M tetrahydrofuran solution) was added via syringe, and the mixture was heated to reflux overnight. A solution of sodium trifluoroethoxide was prepared from trifluoroethanol (1.5 g, 15 mmol) and sodium (0.32 g, 14 mmol) in boiling tetrahydrofuran (15 mL). Both solutions were cooled to room temperature, and 5 mL of the sodium trifluoroethoxide solution was added to the polymer solution via syringe. The mixture was stirred at room temperature for 3.5 h. The polymer solution was concentrated and the polymer was isolated by precipitation into dilute acid. Further purification was achieved by additional precipitations into water and hexane. The product was collected and dried in vacuo, yielding 2.81 g of a dark-red polymer (65% yield). The polymer was soluble in tetrahydrofuran and acetone and was insoluble in hexanes and methanol. Anal. Calcd for $(NP(OCH_2CF_3)_{1.86}(FeCp(CO)_2)_{0.14})_n$: C, 22.22; H, 1.74; N, 5.51; Fe, 3.07; Cl, 0. Found: C, 20.92; H, 2.11; N, 5.45; Fe, 3.04; Cl, 0.18.

Synthesis of $(NP(OCH_2CF_3)_x(FeCp(CO)_2)_y)_n$ (4b–d) from Metal Anions. Sodium triethylborohydride (6.2 mL of a 1.0 M solution) was added via syringe to a solution of tetracarbonyldicyclopentadienyldiiron (1.10 g, 3.11 mmol) in tetrahydrofuran (100 mL), and the mixture was stirred at room temperature for 4.5 h. A color change from dark red to bright red was observed. The anion solution was transferred to an addition funnel and added dropwise to a solution of **2** (17.4 mmol). The mixture was then stirred for 7–9 days at room temperature. A solution of sodium trifluoroethoxide, prepared from sodium (0.52 g, 23 mmol) and trifluoroethanol (2.7 mL, 27 mmol) in tetrahydrofuran (20 mL), was added to the reaction solution. The mixture was then stirred at room temperature for 1 h. The solution was concentrated and the polymer was isolated by precipitation into dilute acid. The polymer was further purified by three additional precipitations from tetrahydrofuran into water and hexanes. The purified polymer was obtained in 50–60% yield. Anal. Calcd for $(NP(OCH_2CF_3)_{1.95}(FeCp(CO)_2)_{0.05})_n$ (system **4b**): C, 20.60; H, 1.70; N, 5.67; Fe, 1.13; Cl, 0. Found: C, 20.06; H, 1.86; N, 5.40; Fe, 1.06; Cl, 0.2.

This polymer can also be prepared by the reaction of **2** with the iron anion generated by cleavage of tetracarbonyldicyclopentadienyldiiron with either potassium triethylborohydride (system **4c**) or sodium–potassium alloy (system **4d**). Anal. Calcd for $[NP(OCH_2CF_3)_{1.94}(FeCp(CO)_2)_{0.06}]_n$ (**4c**): C, 20.80; H, 1.69; N, 5.56; Fe, 1.36; Cl, 0. Found: C, 20.47; H, 1.73; N, 5.67; Fe, 1.25; Cl, 0.31. Anal. Calcd for $[NP(OCH_2CF_3)_{1.95}(FeCp(CO)_2)_{0.05}]_n$ (**4d**): C, 20.60; H, 1.70; N, 5.67; Fe, 1.13; Cl, 0. Found: C, 20.96; H, 1.87; N, 5.65; Fe, 1.03; Cl, 0.46.

Synthesis of $N_3P_3(OCH_2CF_3)_5(FeCp(CO)_2)$ (16) from Phosphazene Anions. Compound **8** (2.00 g, 3.0 mmol) was dissolved in tetrahydrofuran solution (40 mL). Lithium triethylborohydride (9.0 mL of a 1.0 M tetrahydrofuran solution) was added via syringe and was stirred overnight. The solution of **15** was placed in a stainless steel Parr bomb which contained dicarbonylcyclopentadienyliodoiron (1.00 g, 3.3 mmol). The bomb was charged with carbon monoxide (500 psi), sealed, and placed in an oil bath at 60 °C for 48 h. The bomb was allowed to cool and was vented in a hood. The solvents were removed by rotary evaporation. The residue was dissolved in dichloromethane and was filtered through a short column of alumina. Column chromatography on neutral alumina with hexane–dichloromethane mixtures as eluents yielded **16** as a yellow crystalline solid after removal of solvents: obtained 1.20 g (50% yield). Anal. Calcd for $C_{17}H_{15}F_{15}FeN_3O_7P_3$: C, 25.30; H, 1.87; N, 5.21. Found: C, 25.40; H, 2.09; N, 4.93.

Synthesis of $N_3P_3(OCH_2CF_3)_5FeCp(CO)_2$ (16) from Metal Anions. Sodium triethylborohydride (2.0 mL of a 1.0 M solution) was added via syringe to a solution of tetracarbonyldicyclopentadienyldiiron (0.36 g, 1.02 mmol) in tetrahydrofuran (100 mL), and the mixture was stirred at room temperature for 4.5 h. A color change from dark red to bright red was observed. The anion solution was transferred to an addition funnel and was added dropwise to a solution of **8** (1.0 g, 1.50 mmol) in tetrahydrofuran (50 mL). The mixture was stirred at room temperature for 3 days, after which time the ^{31}P NMR spectrum of the reaction solution was consistent with a mixture of starting material **8** and product **16**. Longer reaction times did not bring about complete conversion to **16**. A solution of sodium trifluoroethoxide (prepared from sodium (0.052 g, 2.3 mmol) and trifluoroethanol (0.2 mL, 2.7 mmol) in tetrahydrofuran (25 mL)) was added to the reaction mixture. The mixture was stirred for 6 h after which time ^{31}P NMR spectrum of the reaction mixture indicated the presence of $[NP(OCH_2CF_3)_2]_3$ and product **16** (60% conversion).

Generation of the iron anion by cleavage of tetracarbonyldicyclopentadienyldiiron by potassium triethylborohydride gave similar results.[25]

Synthesis of $N_3P_3Cl_5N(CH_3)_2$ (6). Compound **6** was prepared by the method of Goldschmidt and Weiss,[17] with the use of 100 g of $(NPCl_2)_3$. Product **6** was isolated by careful fractional distillation. Gas chromatographic analysis of the product showed only one peak. Species **6** was obtained as a clear, viscous oil (54.8 g, 55% yield).

Synthesis of $N_3P_3(OCH_2CF_3)_5N(CH_3)_2$ (7). Compound **6** (60.5 g, 0.17 mol) was dissolved in dry THF (700 mL). Sodium trifluoroethoxide, prepared by the reaction of trifluoroethanol (110 g, 1.1 mol) with sodium (23 g, 1.0 mol) in dry THF (700 mL), was added dropwise to the solution of **6** at a rate sufficient to control the exothermic reaction. The reaction mixture was then heated to reflux overnight. The mixture was allowed to cool, and the solvents were removed by rotary evaporation. The residue was redissolved in dichloromethane and was filtered through Fuller's earth. The solvents were removed by rotary evaporation. The product was purified by vacuum distillation (0.1 Torr, 105 °C). Species **7** was obtained as a clear, viscous oil (108 g, 94% yield). The ^{31}P NMR spectrum of **7** consisted of an AB_2 pattern (ν_A = 24.4 ppm, $P(OCH_2CF_3)(N(CH_3)_2)$; ν_B = 17.2 ppm, $P(OCH_2CF_3)_2$; J_{PNP} = 75.2 Hz). ^1H NMR: δ 4.25 (m, $P(OCH_2CF_3)_2$, 4.10 (p, $P(OCH_2CF_3)N(CH_3)_2$), 2.67 (d, J_{PNCH} = 12.1 Hz, $N(CH_3)_2$). Mass spectrum: calcd *m/z* 654, found *m/z* 654.

Synthesis of $N_3P_3(OCH_2CF_3)_5Cl$ (8). A heavy-walled glass tube, 25 mm × 400 mm, equipped with a Teflon Fischer-Porter valve, was charged with **7** (20.0 g, 35 mmol). Hydrogen chloride gas (4.2 L, 0.17 mol) was condensed into the tube at −196 °C. The tube was sealed and was allowed to warm to room temperature. It was then placed in an oil bath behind a safety shield at 110 °C for 96 h (CAUTION). The tube was removed from the bath, the pressure was released slowly, and the contents were extracted with a mixture of diethyl ether and water (1:1). The ethereal layer was removed and dried over magnesium sulfate, which was then separated by filtration. The solvent was removed by rotary evaporation to give product **8** as a slightly cloudy oil. It was then purified by vacuum distillation (0.5 Torr, 96 °C) to give **8** as a clear, colorless oil (17.9 g, 77% yield).

Synthesis of $N_3P_3(OCH_2CF_3)_4(N(CH_3)_2)_2$ (10). Compound **9** (56.5 g, 0.155 mol) was dissolved in THF (250 mL). Sodium trifluoroethoxide, prepared by the reaction of trifluoroethanol (89 g, 0.89 mol) with sodium (17.1 g, 0.74 mol) in THF, was added slowly to the solution of **9** at a rate sufficient to control the exothermic reaction. The mixture was heated to reflux overnight. The solvent was removed by rotary evaporation, and the residue was dissolved in dichloromethane. The insoluble salts were removed by filtration through Fuller's earth. Removal of the solvent gave **10** as a pale-yellow oil, which was purified further by vacuum distillation (0.3 Torr, 107 °C). Species **10** (89.3 g, 93% yield) was obtained as a clear oil which later crystallized partially. ^{31}P NMR: AB_2; ν_A = 18.15 ppm, $P(OCH_2CF_3)_2$; ν_B = 23.83 ppm, $P(OCH_2CF_3)N(CH_3)_2$; J_{PNP} = 46.88 Hz. ^1H NMR: δ 4.10 (m, OCH_2CF_3), 2.64 (d, $N(CH_3)_2$, J_{PNCH} = 12.5 Hz). Mass spectrum: calcd *m/z* 619, found *m/z* 619.

Synthesis of $N_3P_3(OCH_2CF_3)_4Cl_2$ (11). Compound **10** (9.0 g, 14.5 mmol) was placed in the heavy-walled glass tube described above. Hydrogen chloride (4.2 L, 0.17 mol) was condensed into the tube at −196 °C. The tube was allowed to warm to room temperature and was placed in an oil bath behind a safety shield at 110 °C for 100 h (CAUTION). After careful release of the pressure, the contents of the tube were extracted with a diethyl ether: water mixture (1:1). The ethereal layer was removed and was dried over magnesium sulfate, which was removed by filtration. Removal of solvent gave **11** as a brown oil which was purified by vacuum distillation (0.1 Torr, 106 °C). Compound **11** was obtained as a clear, colorless oil (6.29 g, 72% yield).

Reaction of 11 with $LiBEt_3H$. Compound **11** (2.00 g, 3.3 mol) was dissolved in tetrahydrofuran (25 mL). Lithium triethylborohydride (26 mL of a 1.0 M tetrahydrofuran solution) was added via syringe, and the mixture was stirred overnight. A ^{31}P NMR spectrum of the reaction mixture showed only **12**. The reaction mixture was then heated to reflux for 10 days. A ^{31}P NMR spectrum of the reaction mixture was consistent with the presence of **13** and a small amount of **12**. The phosphazene anions **12** and **13** were not isolated from the reaction mixture.

Reaction of 12 with $LiBEt_3H$ and $FeCp(CO)_2I$. A solution of **12** was prepared as above and was placed in a Parr bomb reactor with dicarbonylcyclopentadienyliodoiron (1.09 g, 3.6 mmol). The reactor was charged with carbon monoxide (500 psi), sealed, and placed in an oil bath at 65 °C for 24 h (CAUTION). The reactor was then cooled to 25 °C and vented in a hood. Solvents were removed by rotary evaporation. The residue was dissolved in dichloromethane and filtered through a short alumina column. Removal of solvents gave **14** as a red oil. Compound **14** was dissolved in tetrahydrofuran (25 mL). Lithium triethylborohydride (6.0 mL of a 1.0 M tetrahydrofuran solution) was added via syringe, and the mixture was stirred at room temperature overnight. A ^{31}P NMR spectrum of the reaction mixture showed that no reaction had occurred. The reaction mixture was then heated to reflux for 24 h. A ^{31}P spectrum of the reaction mixture was not compatible with any of the expected products. The peak at 118.0 ppm for $P(OCH_2CF_3)(FeCp(CO)_2)$ had also disappeared.

A solution of **13** was prepared as above from **11** (1.70 g 2.8 mmol), and dicarbonylcyclopentadienyliodoiron (6.80 g, 22.4 mmol, 8 equiv) was added as a solution in THF (15 mL). This mixture was stirred at room temperature for 24 h. The ^{31}P NMR spectrum of the reaction mixture indicated that a complex mixture of products was present which resisted separation.

X-ray Crystal Structure Determination Technique. Single crystals of **16** suitable for X-ray crystallographic studies were grown from a mixture of dichloromethane and hexane. A crystal of **16** used for data collection was cemented to a glass fiber in air and was mounted on an Enraf-Nonius CAD4 diffractometer. Accurate cell dimensions and crystal orientation matrix were determined by least-squares treatment of the setting angles of 25 reflections within the range 10–15°. Intensity data were collected by the $\omega/2\theta$ scan method using monochromatic Mo K_α radiation. The intensities of three reflections, chosen as standards, were monitored at regular intervals and decreased by 1.8% during data collection. This decay was corrected for by appropriate scaling. The final crystal parameters are given in Table II together with details of the data collection procedure.

The structure was solved by the heavy-atom method.[26] Fourier synthesis allowed the location of all non-hydrogen atoms. Refinement of the structure was by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic thermal parameters for the non-hydrogen atoms. At an intermediate stage in the refinement, a difference map showed peaks for H atoms in positions close to those expected. The H atoms were included in the refinement with an overall B_{iso} 4.0 Å^2 but were not refined.

A gross disorder was observed in the CF_3 groups as depicted in the large thermal parameters of the F atoms. Refinement converged with $R = 0.063$ and $R_w = (\sum \Delta^2/\sum_w F_o^2)^{1/2} = 0.098$. In the refinement cycles, weights were derived from the counting statistics. Scattering factors were those of Cromer and Mann[27] and Stewart et al.,[28] and allowance was made for anomalous dispersion.[29]

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Registry No. **6**, 1078-85-9; **7**, 109088-36-0; **8**, 55975-53-6; **9**, 2203-74-9; **10**, 109088-37-1; **11**, 75267-51-5; **12**, 109122-70-5; **13**, 109122-68-1; **14**, 109122-71-6; **16**, 109122-69-2; $FeCp(CO)_2Na$, 12152-20-4; $FeCp(CO)_2I$, 12078-28-3.

Supplementary Material Available: Table VI listing least-squares planes for **16** (1 page); Table IV listing calculated and observed structure factors (37 pages). Ordering information is given on any current masthead page.

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