Anal. Calcd (based on $C_{11}H_{13}F_{15}N_3O_5P_3$): C, 20.48; H, 2.04; N, 6.83. Found: C, 20.90; H, 1.93; N, 7.01. Other characterization data are listed in Table I.

Synthesis of $N_3P_3(OCH_2CF_3)_5CH_2Ph$ (8). This compound was prepared from **6** and $PhCH_2Br$ by a procedure similar to that used for **7**. Purification was achieved by column chromatography using hexane/CH_2Cl_2 (5:1). Mass spectral data: m/z = 721, identified fragments included loss of F, CH_2PH, and OCH_2CF_3 groups. Anal. Calcd (based on $C_{17}H_{17}F_{15}N_3O_5P_3$): C, 28.31; H, 2.38; N, 5.83. Found: C, 29.04; H, 2.40; N, 5.90. Other characterization data are listed in Table I.

Synthesis of $N_3P_3(OCH_2CF_3)_5H$ (9). This compound was prepared in a manner similar to that described previously. After the formation of the anion **6** was confirmed by ^{31}P NMR spectroscopy, dry trifluoroethanol (12 mmol) was added to the reaction mixture. Following 6–8 h of reaction, a ^{31}P NMR spectrum showed that the anion had reacted completely. To this solution was added excess $NaOCH_2CF_3$, and the solution was refluxed for 6 h. The product was isolated and purified by column chromatography using hexane/methylene chloride as the eluting solvent. Mass spectral data: m/z = 631, identified fragments included loss of F, H, and OCH_2CF_3 groups. Anal. Calcd (based on $C_{10}H_{11}F_{15}N_3O_5P_3$): C, 19.03; H, 1.76; N, 6.67. Found: C, 18.83; H, 2.19; N, 6.85. Other characterization data are listed in Table I.

Synthesis of $N_3P_3(OCH_2CF_3)_5[CpFe(CO)_2]$ (10). This compound was prepared from **6** and $CpFe(CO)_2I$ by a procedure similar to that used for **7**. The compound was isolated by column chromatography using hexane/methylene chloride as the eluting solvent. Species **10** was recrystallized from ethanol/Et_2O (5:1). Mass spectral data: m/z = 807, identified fragments included loss of F, $CpFe(CO)_2$, CO, and OCH_2CF_3 groups. Anal. Calcd (based on $C_{17}H_{15}F_{15}FeN_3O_7P_3$): C, 25.30; H, 1.88; N, 5.21. Found: C, 25.50; H, 2.12; N, 4.90. Other characterization data are listed in Table I.

Reaction of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ with $Li[BEt_3H]$. To a cooled (5 °C) solution of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (1.40 g, 3.54 mmol) in THF (20 mL) was added a 1.0 M solution of $Li[BEt_3H]$ in the same solvent (11.0 mL, 11.0 mmol). Hydrogen evolved, and the solution was allowed to warm to room temperature and was stirred overnight. Analysis of the reaction mixture by ^{31}P NMR spectroscopy revealed the presence of species **15** (ca. 75%) together with small quantities of compounds **17** and **18**. Concentration of the reaction solution to ca. 5 mL and dilution with diethyl ether (30 mL) followed by cooling to −20 °C for 14 days in the absence of light afforded yellow-orange crystals, which become opaque on exposure to light or on warming to room temperature.

Protonation of $[N_3P_3F_2H(BEt_3)(\eta\text{-}C_5H_4)_2Fe]^-$ (15) with ^iPrOH. To a solution of **15** (5 mmol), generated as above in THF (20 mL), was added excess ^iPrOH (2 mL). Analysis of the reaction mixture by ^{31}P NMR spectroscopy showed that **15** had been converted to **17**. Solutions of **17** decomposed at room temperature during 24 h to yield metallic iron and a complex uncharacterized mixture.

Acknowledgment. The support of the U.S. Army Research Office and the Air Force Office of Scientific Research is greatly appreciated. We also acknowledge the suggestions of M. N. Mang.

Supplementary Material Available: Table S-I, giving general displacement parameter expressions for **15** (2 pages); Table S-II, listing structure factors (23 pages). Ordering information is given on any current masthead page.

Synthesis of Strained Ferrocenylorganocyclophosphazenes: X-ray Crystal Structures of $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$, $N_3P_3(OPh)_4(\eta\text{-}C_5H_4)_2Fe$, and $N_3P_3Ph_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$

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A series of transannular ferrocenylcyclotriphosphazenes were synthesized for studies of the relationship between molecular structure and polymerization behavior. Species $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$ and $N_3P_3(OPh)_4(\eta\text{-}C_5H_4)_2Fe$ were synthesized by the reaction of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ with $NaOCH_2CF_3$ and NaOPh, respectively. Cyclic trimers $N_3P_3R(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ [R = OPh, R = Me, R = Ph (*gem* to Cp) and R = Ph (non-*gem* to Cp)] were prepared by reactions of the appropriate fluoroferrocenylphosphazene precursors [$N_3P_3(OPh)F_3(\eta\text{-}C_5H_4)_2Fe$, $N_3P_3MeF_3(\eta\text{-}C_5H_4)_2Fe$, $N_3P_3PhF_3(\eta\text{-}C_5H_4)_2Fe$, and $N_3P_3PhF_3(\eta\text{-}C_5H_4)_2Fe$] with $NaOCH_2CF_3$. The synthesis of $N_3P_3Ph_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$, (Ph groups non-*gem* to Cp) was achieved via the reaction of *gem*-$N_3P_3F_4Ph_2$ with dilithioferrocene to give $N_3P_3Ph_2F_2(\eta\text{-}C_5H_4)_2Fe$, followed by treatment with $NaOCH_2CF_3$. Treatment of $N_3P_3Ph_2F_2(\eta\text{-}C_5H_4)_2Fe$ with $NaOCH_2CF_3$ yielded $N_3P_3Ph_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ (Ph groups *gem* to Cp). A 1-equiv amount of NaOPh reacts with $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ to form a mixture of *cis*- and *trans*-$N_3P_3(OPh)F_3(\eta\text{-}C_5H_4)_2Fe$. The molecular structures of $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$, $N_3P_3(OPh)_4(\eta\text{-}C_5H_4)_2Fe$, and $N_3P_3Ph_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ were determined by single-crystal X-ray diffraction. All were found to possess nonplanar, strained cyclotriphosphazene rings. Crystals of $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$ are monoclinic with space group $P2_1/c$, with a = 9.529 (5) Å, b = 14.515 (2) Å, c = 19.012 Å, β = 97.94 (2)°, V = 2605.8 Å^3, and Z = 4. Crystals of $N_3P_3(OPh)_4(\eta\text{-}C_5H_4)_2Fe$ are orthorhombic of space group $P2_12_12_1$ with a = 9.890 (2) Å, b = 15.962 (3) Å, c = 19.629(3) Å, V = 3098.8 Å^3, and Z = 4. The diphenyl species, $N_3P_3Ph_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$, crystallizes in the trigonal space group $R3$ (hexagonal axes) with a = 23.954 (8)Å, b = 23.94 (1) Å, c = 13.17 (1) Å, V = 6544 Å^3, and Z = 9.

One of the main routes for the synthesis of stable high-polymeric phosphazenes is via the ring-opening polymerization of cyclic chloro- or fluorophosphazenes such as $[NPCl_2]_3$ or $[NPF_2]_3$, followed by replacement of the halogen atoms in the polymer by organic side groups.[1-3] However, until recently, all attempts to prepare poly(organophosphazenes) by the polymerization of cyclic phos-

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(1) Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic Press: New York, 1972.

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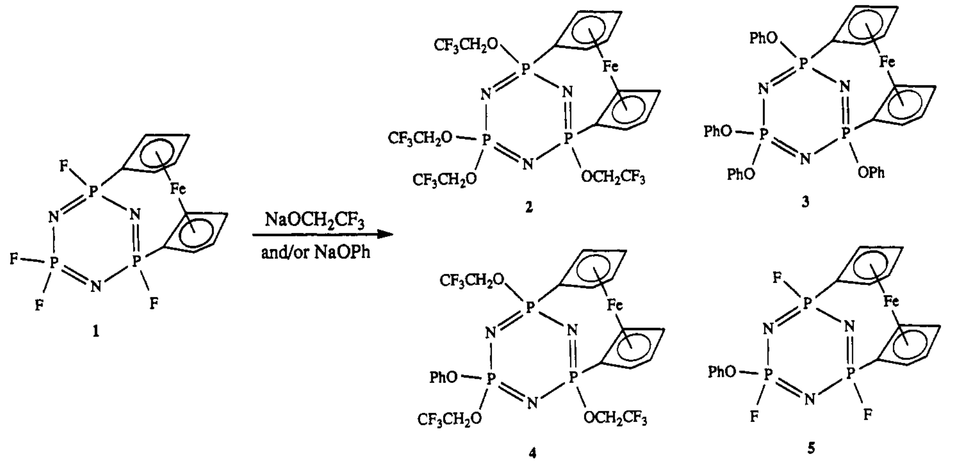
Scheme I



1 2 3 4 5

phazenes that bear organic side groups only were unsuccessful.[4] We have found that the ferrocenylphosphazene $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$ (2) undergoes ring-opening polymerization at 250 °C in the presence of a catalytic amount (1 mol %) of $[NPCl_2]_3$ to yield a high polymer.[5] This result is significant because it had been assumed previously that phosphorus–halogen bonds were necessary for access to the phosphazene ring-opening polymerization mechanism. The polymerization of 2 appears to be due to the presence of the transannular ferrocenyl group, which imparts significant strain to the phosphazene ring.[6] Thus, a systematic study of methodology for the synthesis of related ferrocenylphosphazenes was undertaken as a prelude to an examination of their polymerization behavior. Studies of the polymerization of these compounds are reported elsewhere.[7]

The synthetic and structural work reported here was designed to answer two questions. (1) What limits exist to the synthesis of ferrocenylphosphazenes that lack phosphorus–halogen bonds and what methods are available to direct cosubstituent groups to specific sites around the phosphazene ring with predetermined configurational control? (2) In what ways do the side-group dispositions affect the overall molecular structure and ring strain in a manner that might be relevant to the interpretation of polymerization behavior?

Results and Discussion

Synthesis of $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$ (2) and $N_3P_3(OPh)_4(\eta\text{-}C_5H_4)_2Fe$ (3). Synthetic routes to fluorophosphazenes with transannular ferrocenyl groups were developed in our research program several years ago.[8-11] The present work utilizes the transannular ferrocenylphosphazene $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (1) as a precursor for the preparation of cyclic trimers with four identical side groups in addition to the ferrocenyl unit.

The fluoroalkoxy derivative, $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$ (2), was prepared by the reaction of 1 with excess sodium trifluoroethoxide (refluxing THF, 66 °C) (Scheme I). The product was isolated by column chromatography followed by recrystallization to give an orange, crystalline solid. The ^{31}P NMR spectrum of 2 was characteristic of an A_2X spin system, with a doublet resonance at 41.9 ppm (assigned to the phosphorus atoms that bear the ferrocenyl unit) and a triplet at 21.2 ppm (from the remaining phosphorus atom). The ^1H NMR spectrum consisted of a complex series of peaks between 4.35 and 4.86 ppm that result from coincident resonances of the Cp and methylene protons. The electron-impact mass spectrum of 2 clearly indicated the presence of the expected molecular ion at m/e 715.

The tetraphenoxy derivative (3) was synthesized via the reaction of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ with sodium phenoxide (Scheme I). Forcing reaction conditions (reflux in diglyme, 162 °C, for 4 weeks, or heating in a high-pressure reaction vessel at 200 °C[5]) were necessary to achieve complete fluorine replacement. This is consistent with both the steric crowding in product 3 and the relatively low nucleophilicity of the phenoxide anion. The product was isolated by column chromatography and recrystallization. The ^{31}P NMR spectrum of 3 was indicative of an A_2X spin system. The ^1H NMR spectrum contained resonances in the expected ratio for the phenoxy and cyclopentadienyl protons. The mass spectrum of 3 contained an intense peak at m/e 691, which corresponded to the molecular ion.

Synthesis of $N_3P_3R(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ (7, R = Me; 9, R = Ph) and $N_3P_3R_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ (13, R = Ph) (R Groups *gem* to Cp). Ferrocenylphosphazenes with alkyl or aryl substituents geminal to one or both of the ferrocenyl Cp rings are accessible via the reaction of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ with organolithium reagents. The product stereochemistry is believed to result from the preferential coordination of the lithium reagent to the skeletal nitrogen atom that lies between the two cyclopentadienyl rings.[10] Thus, the alkyl derivative $N_3P_3MeF_3(\eta\text{-}C_5H_4)_2Fe$ (6) was prepared by the reaction of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ with MeLi.[10] Compound 7, $N_3P_3Me(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$, was then obtained by treatment of 6 with sodium trifluoroethoxide (Scheme II). The ^{31}P NMR spectrum of 7 was characteristic of an AMX spin system, and this can be attributed to the presence of three different phosphorus atom environments. Specifically, resonances at 40.2, 35.3, and 16.9 ppm were detected, which were assigned to the phosphorus atoms bonded to methyl

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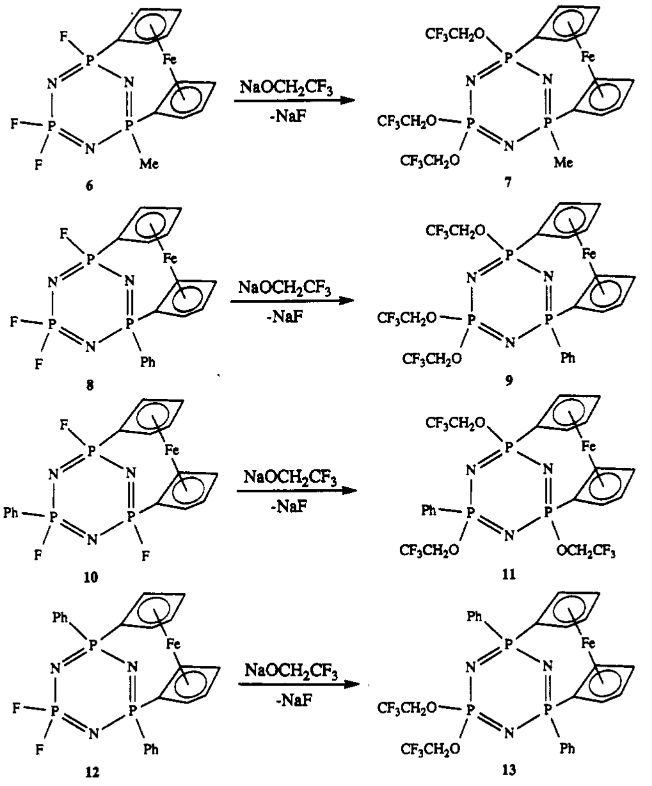
(11) Riding, G. H.; Parvez, M.; Allcock, H. R. *Organometallics* **1986**, *5*, 2153.

Scheme II



and Cp, trifluoroethoxy and Cp, and two trifluoroethoxy substituents, respectively.

Similarly, reaction of 1 or 2 equiv of phenyllithium with $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ gave $N_3P_3PhF_3(\eta\text{-}C_5H_4)_2Fe$ (8) and $N_3P_3Ph_2F_2(\eta\text{-}C_5H_4)_2Fe$ (12), respectively, with the phenyl substituents located geminal to the cyclopentadienyl rings.[10] Subsequent treatment of 8 and 12 with sodium trifluoroethoxide yielded the aryl derivatives $N_3P_3Ph(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ (9) and $N_3P_3Ph_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ (13), respectively (Scheme II). Products 7, 9, and 13 were isolated and characterized in a manner similar to that for 2 and 3 described above.

Synthesis of $N_3P_3R(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ (4, R = OPh; 11, R = Ph) and $N_3P_3R_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ (16, R = Ph) (R Groups Non-*gem* to Cp). Compound 4, which contains a phenoxy substituent non-*gem* to the Cp rings, together with three trifluoroethoxy side groups, was synthesized by using $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (1) as an intermediate. The reaction of 1 with 1 equiv of sodium phenoxide gave an inseparable mixture of two compounds with the molecular formula $N_3P_3(OPh)F_3(\eta\text{-}C_5H_4)_2Fe$ (5) (Scheme I). These are two isomers with the phenoxy substituents presumed to be in cis and trans configurations with respect to the transannular ferrocenyl unit. The phenoxide anion preferentially attacks the phosphorus atom distal to the ferrocenyl bridge, presumably because this reaction site is less sterically hindered. Subsequent reaction of 5 with sodium trifluoroethoxide yielded $N_3P_3(OPh)(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ (4, cis and trans) (Scheme I). The ^{31}P NMR spectrum of 4 consisted of resonances from two different A_2X spin systems, because the phosphorus atoms of each isomer are located in slightly different environments. The phosphorus atoms that bear the cis or trans phenoxy groups showed the largest chemical shift difference (δ_a = 19.7 ppm, δ_b = 21.1 ppm). By contrast, the chemical shifts of the phosphorus atoms bonded to the Cp rings differed only slightly (δ_a = 41.3 ppm, δ_b = 41.1 ppm) because their environments are similar.

Ferrocenylphosphazenes with aryl substituents non-*gem* to the Cp rings were prepared by an alternative route. The reaction of dilithioferrocene with $N_3P_3F_5Ph$ gave the transannular ferrocenylphosphazene $N_3P_3PhF_3(\eta\text{-}C_5H_4)_2Fe$ (10) with the phenyl group distal to the ferrocenyl unit.[10] Subsequent treatment of 10 with sodium trifluoroethoxide yielded $N_3P_3Ph(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ (11) (Scheme II). The ^{31}P NMR spectrum of 11 was characteristic of an A_2X spin system. The phenyl group is non-*gem* to the cyclopentadienyl rings, thus generating two different phosphorus atom environments.

A similar route was used for the synthesis of the diphenyl trimer $N_3P_3Ph_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ (16) (Scheme III). The *gem*-diphenyl species $N_3P_3F_4Ph_2$ (14) was first treated with dilithioferrocene to give $N_3P_3Ph_2F_2(\eta\text{-}C_5H_4)_2Fe$ (15) with the phenyl groups bonded to the phosphorus atom distal to the transannular ferrocenyl unit. Reaction of 15 with sodium trifluoroethoxide then gave the geminally substituted ferrocenylphosphazene $N_3P_3Ph_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ (16). This compound also yielded a ^{31}P NMR spectrum characteristic of an A_2X spin system. Products 4, 5, 11, 15, and 16 were isolated and characterized in a manner similar to that for 2 and 3 described above.

Crystal and Molecular Structures of 2, 3, and 16. The X-ray crystal structures of compounds 2, 3, and 16 were determined in order to obtain information needed to assess structural factors such as ring strain and side-group crowding. These three compounds were chosen, in part, because of their contrasting thermal behavior. When heated at 250 °C in the presence of 1% $[NPCl_2]_3$, 2 undergoes ring-opening polymerization to give a high polymer, while 3 yields a cyclic hexamer under the same conditions.[5] However, diphenyl species 16 polymerizes thermally in the *absence* of any added polymerization initiator.[7] The main structural features of these compounds are summarized in Tables I–VII, and their molecular structures are shown in Figures 1–3.

Compound 2 contains the ferrocenyl unit attached in a transannular manner to the phosphazene ring through covalent P–C bonds (Figure 1). The average P–C bond lengths are 1.78 Å. The cyclopentadienyl rings are planar and nearly parallel to each other, with a dihedral angle of only 3.2°. As has been found for transannular ferrocenylphosphazenes studied earlier,[8-11] the phosphazene ring is markedly distorted to accommodate the strain imposed by the ferrocenyl unit. This is clearly evident from the

Scheme III

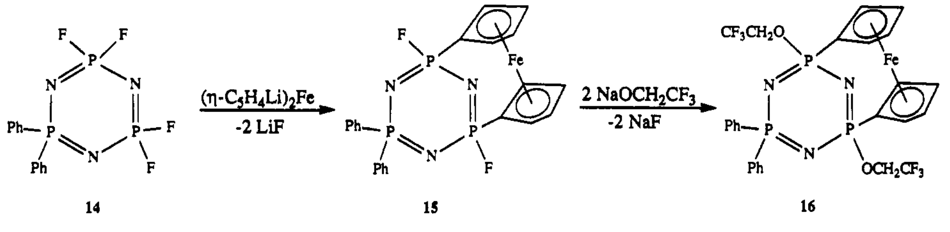


Table I. Summary of Crystal Data and Intensity Collection Parameters

	2	3	16
formula	$C_{18}H_{16}N_3F_{12}FeO_4P_3$	$C_{34}H_{28}N_3FeO_4P_3$	$C_{26}H_{22}N_3F_6FeO_2P_3$
fw	715	691	671
space group	$P2_1/c$	$P2_12_12_1$	$R3$
cryst system	monoclinic	orthorhombic	trigonal (hexagonal axes)
a, Å	9.529 (5)	9.890 (2)	23.954 (8)
b, Å	14.515 (2)	15.962 (3)	23.945 (12)
c, Å	19.012 (2)	19.629 (3)	13.175 (14)
α, deg			
β, deg	97.94 (2)		
γ, deg			
V, Å^3	2605.8	3098.8	6544.8
Z	4	4	9
d(calcd), g/cm^3	1.823	1.482	1.533
F(000)	1436	1472	3060
μ, cm^{-1}	8.739	57.706	40.49
abs corr, cm^{-1}			
min transm	0.9449	0.6842	
max transm	0.9995	0.9989	
θ_{max}, deg	25	70	25
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
radiation type	Mo	Cu	Mo
ω scan width (A + 0.35 tan θ), deg	(0.80 + 0.35 tan θ)	(0.75 + 0.14 tan θ)	(1.00 + 0.35 tan θ)
no. of unique data measd	4576	3323	4339
no. of data used ($I > 3\sigma(I)$)	3795	2463	2606
R, $R_w = (\sum\omega\Delta^2/\sum F_o^2)^{1/2}$	0.0699, 0.124	0.0602, 0.0806	0.0876, 0.0876

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) for $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$ (2)

	Bond Lengths		
Fe–Cp(1)	1.655	P(2)–O(2)	1.585 (4)
Fe–Cp(2)	1.651	P(2)–N(1)	1.585 (4)
P(1)–C(1)	1.779 (6)	P(2)–N(2)	1.596 (4)
P(1)–O(1)	1.593 (3)	P(3)–O(3)	1.588 (4)
P(1)–N(1)	1.591 (4)	P(3)–O(4)	1.573 (4)
P(1)–N(3)	1.599 (4)	P(3)–N(2)	1.571 (4)
P(2)–C(6)	1.785 (5)	P(3)–N(3)	1.572 (4)
	Bond Angles		
C(1)–P(1)–O(1)	107.1 (3)	P(1)–N(1)–P(2)	112.2 (2)
N(1)–P(1)–N(3)	116.2 (3)	P(2)–N(2)–P(3)	119.9 (2)
C(6)–P(2)–O(2)	103.6 (3)	P(1)–N(3)–P(3)	117.8 (2)
N(1)–P(2)–N(2)	115.2 (2)	C(2)–C(1)–C(5)	108.8 (5)
O(3)–P(3)–O(4)	100.5 (3)	C(7)–C(6)–C(10)	109.1 (5)
N(2)–P(3)–N(3)	119.3 (2)		

Table III. Positional Parameters and Their Estimated Standard Deviations for $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$ (2)

atom	x	y	z	B, Å^2
Fe	0.15842 (7)	0.47118 (5)	0.88635 (3)	2.71 (1)
P(1)	0.2881 (1)	0.43273 (8)	0.73977 (6)	2.47 (2)
P(2)	0.4617 (1)	0.39391 (8)	0.85593 (6)	2.69 (2)
P(3)	0.5081 (1)	0.54867 (9)	0.77971 (7)	2.84 (2)
O(1)	0.2277 (4)	0.3830 (2)	0.6673 (2)	3.43 (7)
O(2)	0.5610 (4)	0.3137 (2)	0.8904 (2)	3.50 (7)
O(3)	0.4714 (4)	0.6479 (2)	0.8073 (2)	3.81 (8)
O(4)	0.6436 (4)	0.5714 (4)	0.7440 (2)	5.4 (1)
N(1)	0.3718 (4)	0.3541 (3)	0.7864 (2)	2.66 (7)
N(2)	0.5544 (4)	0.4828 (3)	0.8442 (2)	3.08 (8)
N(3)	0.3786 (4)	0.5211 (3)	0.7234 (2)	2.87 (8)
C(1)	0.1400 (5)	0.4731 (3)	0.7787 (2)	2.65 (9)
C(2)	0.1251 (6)	0.5641 (4)	0.8055 (3)	3.5 (1)
C(3)	0.0074 (6)	0.5652 (4)	0.8426 (3)	4.2 (1)
C(4)	−0.0511 (6)	0.4762 (5)	0.8419 (3)	4.8 (1)
C(5)	0.0312 (6)	0.4159 (4)	0.8005 (3)	3.9 (1)
C(6)	0.3514 (5)	0.4193 (4)	0.9222 (2)	2.92 (9)
C(7)	0.2449 (6)	0.3594 (4)	0.9421 (3)	3.9 (1)
C(8)	0.1632 (6)	0.4140 (5)	0.9849 (3)	4.2 (1)
C(9)	0.2191 (6)	0.5021 (5)	0.9925 (3)	4.0 (1)
C(10)	0.3367 (5)	0.5068 (4)	0.9528 (3)	3.4 (1)

position of nitrogen atom N(1), located between the two phosphorus atoms that bear the metallocenyl bridge (Figure 1). Atom N(1) is displaced 0.57 Å from the plane defined by the remaining five atoms of the phosphazene ring.

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) for $N_3P_3(OPh)_4(\eta\text{-}C_5H_4)_2Fe$ (3)

	Bond Lengths		
Fe–Cp	1.652	P(2)–O(2)	1.582 (5)
Fe–Cp	1.648	P(2)–N(1)	1.584 (5)
P(1)–C(1)	1.767 (8)	P(2)–N(2)	1.601 (7)
P(1)–O(1)	1.583 (4)	P(3)–O(3)	1.588 (6)
P(1)–N(1)	1.576 (6)	P(3)–O(4)	1.586 (6)
P(1)–N(3)	1.594 (6)	P(3)–N(2)	1.576 (6)
P(2)–C(6)	1.762 (7)	P(3)–N(3)	1.565 (7)
	Bond Angles		
C(1)–P(1)–O(1)	103.4 (3)	P(1)–N(1)–P(2)	113.2 (3)
N(1)–P(1)–N(3)	115.9 (3)	P(2)–N(2)–P(3)	119.2 (5)
C(6)–P(2)–O(2)	102.8 (3)	P(1)–N(3)–P(3)	120.0 (4)
N(1)–P(2)–N(2)	114.9 (4)	C(2)–C(1)–C(5)	106.4 (7)
O(3)–P(3)–O(4)	98.0 (3)	C(7)–C(6)–C(10)	106.1 (7)
N(2)–P(3)–N(3)	118.4 (3)		

Table V. Positional Parameters and Their Estimated Standard Deviations For $N_3P_3(OPh)_4(\eta\text{-}C_5H_4)_2Fe$ (3)

atom	x	y	z	B, Å^2
Fe	0.16995 (13)	0.04252 (7)	0.35953 (5)	3.79 (2)
P(1)	0.0653 (2)	−0.0423 (1)	0.2200 (1)	3.35 (3)
P(2)	−0.1289 (2)	0.0232 (1)	0.2952 (1)	3.26 (3)
P(3)	−0.1072 (2)	−0.1477 (1)	0.2873 (1)	3.46 (3)
O(1)	0.1203 (5)	−0.0435 (3)	0.1443 (2)	3.7 (1)
O(2)	−0.2488 (5)	0.0886 (3)	0.2912 (3)	4.1 (1)
O(3)	−0.2107 (6)	−0.2143 (3)	0.2573 (2)	4.2 (1)
O(4)	−0.0525 (6)	−0.2020 (3)	0.3491 (2)	4.0 (1)
N(1)	−0.0452 (6)	0.0284 (3)	0.2265 (3)	3.1 (1)
N(2)	−0.1859 (7)	−0.0680 (4)	0.3132 (3)	3.7 (1)
N(3)	0.0174 (7)	−0.1346 (4)	0.2393 (3)	3.8 (1)
C(1)	0.2090 (8)	−0.0142 (5)	0.2684 (4)	3.9 (2)
C(2)	0.2723 (8)	0.0670 (6)	0.2710 (4)	4.6 (2)
C(3)	0.3618 (9)	0.0698 (6)	0.3269 (4)	5.5 (2)
C(4)	0.3607 (9)	−0.0098 (7)	0.3589 (4)	5.8 (2)
C(5)	0.2674 (9)	−0.0629 (6)	0.3242 (4)	4.9 (2)
C(6)	−0.0339 (8)	0.0596 (4)	0.3651 (4)	3.8 (1)
C(7)	0.0373 (9)	0.1383 (4)	0.3684 (4)	4.5 (2)
C(8)	0.1215 (10)	0.1370 (5)	0.4270 (4)	5.4 (2)
C(9)	0.1070 (10)	0.0578 (6)	0.4591 (4)	5.0 (2)
C(10)	0.0141 (9)	0.0103 (5)	0.4228 (4)	4.1 (2)

Compound 3 also has the ferrocenyl unit bonded to the phosphazene ring in a transannular fashion through covalent P–C bonds (Figure 2). The cyclopentadienyl rings are planar and nearly parallel, with a dihedral angle of 4.1°. Again, ring strain is apparent from the nonplanarity of the

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for $N_3P_3Ph_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ (16)

Bond Lengths			
Fe–Cp(1)	1.707	P(2)–O(2)	1.595 (12)
Fe–Cp(2)	1.636	P(2)–N(1)	1.605 (13)
P(1)–C(1)	1.761 (17)	P(2)–N(2)	1.580 (15)
P(1)–O(1)	1.586 (10)	P(3)–C(11)	1.809 (10)
P(1)–N(1)	1.625 (14)	P(3)–C(17)	1.805 (10)
P(1)–N(3)	1.593 (12)	P(3)–N(2)	1.620 (15)
P(2)–C(6)	1.772 (17)	P(3)–N(3)	1.632 (12)
Bond Angles			
C(1)–P(1)–O(1)	99.7 (7)	P(1)–N(1)–P(2)	110.4 (8)
N(1)–P(1)–N(3)	116.2 (7)	P(2)–N(2)–P(3)	119.9 (8)
C(6)–P(2)–O(2)	101.1 (8)	P(1)–N(3)–P(3)	117.8 (8)
N(1)–P(2)–N(2)	116.0 (7)	N(2)–C(1)–C(5)	109.3 (15)
C(11)–P(3)–C(17)	105.2 (5)	C(7)–C(6)–C(10)	109.6 (19)
N(2)–P(3)–N(3)	117.4 (7)		

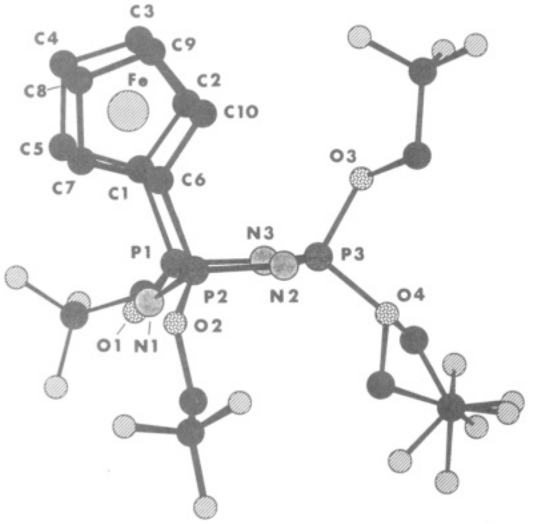


Figure 1. Perspective view of the molecular structure of $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$ (**2**).

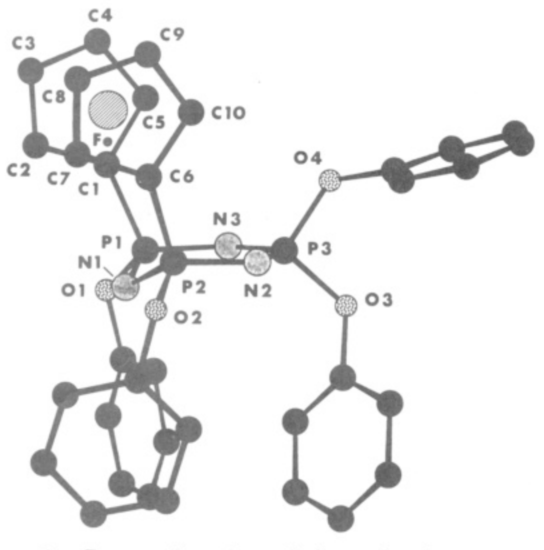


Figure 2. Perspective view of the molecular structure of $N_3P_3(OPh)_4(\eta\text{-}C_5H_4)_2Fe$ (**3**).

phosphazene ring. The nitrogen atom between the bridging sites (N(1)) is displaced 0.56 Å from the plane defined by the remaining five ring atoms. Overall, the structure of compound **2** is similar to that of **3**. The main structural differences are the narrower P–N–P bond angles in **2** (P(1)–N(1)–P(2) = 112.2 (2)°, P(1)–N(3)–P(3) = 117.8 (2)°) compared to those of **3** (P(1)–N(1)–P(2) = 113.2 (3)°, P(1)–N(3)–P(3) = 120.0 (4)°).

Table VII. Positional Parameters and Their Estimated Standard Deviations for $N_3P_3Ph_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ (16)

atom	*x*	*y*	*z*	*U*, Å^2
Fe	0.5887 (1)	0.0515 (1)	0.0000 (0)	0.0379
P(1)	0.4387 (2)	0.0105 (2)	–0.0400 (4)	0.0386
P(2)	0.4896 (2)	–0.0360 (2)	–0.1706 (4)	0.0528
P(3)	0.3922 (2)	–0.1208 (2)	–0.0426 (4)	0.0458
O(1)	0.4068 (5)	0.0545 (5)	–0.0322 (10)	0.0428
O(2)	0.5000 (6)	–0.0399 (6)	–0.2894 (9)	0.0747
N(1)	0.4612 (6)	0.0117 (6)	–0.1568 (11)	0.0433
N(2)	0.4465 (7)	–0.1066 (7)	–0.1278 (13)	0.0649
N(3)	0.3910 (7)	–0.0588 (6)	0.0064 (12)	0.0567
C(1)	0.5055 (8)	0.0537 (7)	0.0405 (14)	0.0472
C(2)	0.5226 (8)	0.0246 (9)	0.1244 (15)	0.0404
C(3)	0.5870 (11)	0.0731 (10)	0.1571 (17)	0.0874
C(4)	0.6076 (10)	0.1278 (10)	0.0959 (16)	0.0561
C(5)	0.5569 (8)	0.1164 (8)	0.0224 (15)	0.0488
C(6)	0.5694 (7)	–0.0033 (8)	–0.1249 (16)	0.0348
C(7)	0.5917 (10)	–0.0294 (11)	–0.0471 (16)	0.0739
C(8)	0.6539 (11)	0.0173 (13)	–0.0123 (23)	0.0614
C(9)	0.6732 (10)	0.0721 (13)	–0.0738 (24)	0.0554
C(10)	0.6191 (12)	0.0642 (13)	–0.1451 (19)	0.0890
C(11)	0.3140 (4)	–0.1767 (5)	–0.0950 (9)	0.0523
C(17)	0.4030 (5)	–0.1632 (4)	0.0619 (8)	0.0418

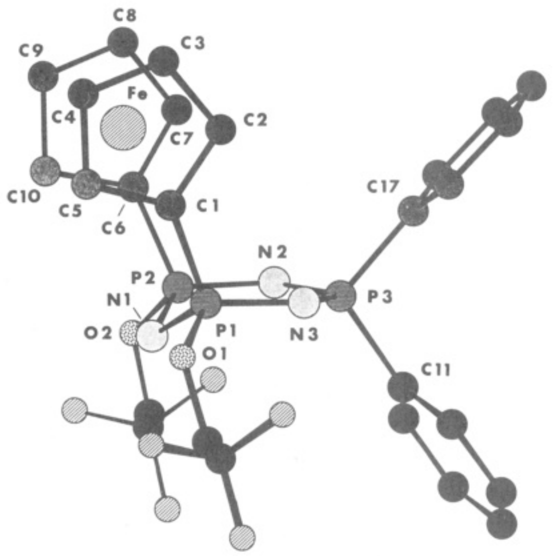


Figure 3. Perspective view of the molecular structure of $N_3P_3Ph_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ (**16**).

The distortions imposed on the phosphazene ring by the transannular ferrocenyl unit in **3** are particularly evident when its structure is compared with that of its closest structural counterpart, the cyclic trimer $[NP(OPh)_2]_3$.[12,13] The phosphazene ring in $[NP(OPh)_2]_3$ is nearly planar, and the P–N bonds are equal in length (1.58 Å). In addition, the P–N–P bond angles are all similar (121.9°). The N–P–N bond angles are also approximately equal (117.3°). Appreciable deviations from these values occur in compound **3**. The P–N–P bond angle at the nitrogen atom between bridging sites is narrow (P(1)–N(1)–P(2) = 113.2 (3)°) compared to the situation in $[NP(OPh)_2]_3$ (121.9°). The bond angles at the remaining nitrogen atoms (P(2)–N(2)–P(3) = 119.2 (5)°, P(1)–N(3)–P(3) = 120.0 (4)°) are wider than the P–N–P angle at N(1) but are still significantly narrower than those in $[NP(OPh)_2]_3$. In addition, the N–P–N bond angles at the bridging sites P(1) and

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

(13) The best structural comparison of compound **2** would be with the cyclic trimer $[NP(OCH_2CF_3)_2]_3$. However, to our knowledge, X-ray structure studies on this compound have not been reported.

P(2) (115.9 (3) and 114.9 (4)°) are narrower than those found in $[NP(OPh)_2]_3$ (117.3°). The bond angle at the remaining phosphorus atom, P(3), is significantly wider (118.4 (3)°) than at the other two N–P–N bond angles in **3**. Fewer differences exist between **3** and $[NP(OPh)_2]_3$ in their respective P–N bond lengths. The four P–N bonds that involve the phosphorus atoms bound to the ferrocenyl unit are all slightly longer in **3** (average 1.59 Å) than in $[NP(OPh)_2]_3$ (1.58 Å). The remaining P–N bonds (P(3)–N(2), P(3)–N(3)) are slightly shorter (average 1.57 Å). All the structural deviations found in **3** can be understood in terms of the phosphazene ring being markedly puckered in order to accommodate the structural requirements of the rigid transannular ferrocenyl group. However, this puckering and (by implication) the resultant ring strain is itself not sufficient to induce polymerization to a high polymer. Steric interactions by the four phenoxy cosubstituent groups may be so serious that conversion to the cyclic hexamer provides the maximum degree of side-group crowding that this system can tolerate. Linear structures almost always bring the side groups closer to each other than in small molecule cyclic oligomers.

The diphenyl species, **16**, is structurally similar to **2** and **3**, but there are significant differences, which may explain its unusual polymerization behavior. The P(1)–N(1)–P(2) bond angle in **16** (Figure 3) is quite narrow at 110.4 (8)°. This compares well with the P(1)–N(1)–P(2) bond angle of 111.0 (2)° found previously for $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$[10] (a species that also polymerizes thermally in the absence of an added initiator[6]) but is significantly narrower than the angle at N(1) found in both **2** and **3** (neither of which polymerize thermally in the absence of an initiator[5]). Another notable feature is the narrow N–P–N bond angle at P(3) (117.4 (7)°). This is narrower than the analogous angles found in **2**, **3**, and $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (119.3 (2), 118.4 (3), and 120.5 (1)°, respectively). In addition, atom N(1) of **16** is displaced further from the plane of the ring (0.67 Å) than in **2** and **3**. The cyclopentadienyl rings are planar and nearly coplanar, with a dihedral angle of 3.59°.

In all three structures, the distance that atom N(1) is displaced from the plane of the phosphazene ring appears to be an indicator of phosphazene ring strain, and this, in turn, may reflect the ability of the compound to undergo ring-opening polymerization. Thus, cyclic trimer **16**, in which atom N(1) is displaced most (0.67 Å), polymerizes readily when heated. Species **1** also polymerizes readily:[6] it has an out-of-plane displacement at N(1) of 0.62 Å.[10] Compound **2** has a smaller ring distortion at N(1) (0.57 Å) and, in fact, only polymerizes when heated in the presence of an initiator. However, atom N(1) in **3** is displaced the least (0.56 Å), but this compound does not polymerize under any conditions. Thus, it appears that side-group steric hindrance can counteract the effect of ring strain and inhibit polymerization.

A similar trend was found with respect to the P(1)–N(1)–P(2) bond angles, with a narrower angle at N(1) favoring polymerization. Compound **16** contains one of the narrowest P–N–P bond angles yet found in a phosphazene (P(1)–N(1)–P(2) = 110.4 (8)°).[1] The bond angles at N(1) for **2** and **3** are increasingly wider (112.2 (2) and 113.2 (3)°, respectively) and this trend apparently underlies their decreasing ability to polymerize.

Summary

A range of transannular ferrocenylcyclophosphazenes with different substituent groups and substitution patterns has been synthesized. Synthetic methodology is now available to tailor the cosubstituent patterns in a predictable manner in order to prepare "monomers" for comparative polymerization experiments. In addition, the X-ray crystallographic studies revealed the presence of a nonplanar, and therefore strained, phosphorus–nitrogen ring in several of these species. This structural feature is believed to be a driving force for the ring-opening polymerization of these compounds.[5] However, steric crowding by bulky aryloxy cosubstituent groups can counteract this effect. Thus, the prediction of polymerization behavior depends on a balancing of ring strain and side-group steric hindrance in ways that will be discussed elsewhere.[7]

Experimental Section

Materials. Tetrahydrofuran (THF) (EM Science), diglyme (Aldrich), hexanes, and diethyl ether (both Fisher) were distilled under nitrogen from sodium benzophenone ketyl before use. Trifluoroethanol (Halocarbon Products Corp.) was purified by distillation from BaO under argon. Phenol (Aldrich) was purified by sublimation. Compounds $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (**1**),[6] $N_3P_3MeF_3(\eta\text{-}C_5H_4)_2Fe$ (**6**),[10] $N_3P_3PhF_3(\eta\text{-}C_5H_4)_2Fe$ (**8**),[10] $N_3P_3PhF_3(\eta\text{-}C_5H_4)_2Fe$ (**10**),[10] $N_3P_3Ph_2F_2(\eta\text{-}C_5H_4)_2Fe$ (**12**),[10] 1,1′-dilithioferrocene–TMEDA[14] and $N_3P_3Ph_2F_4$ (**14**)[15] were prepared as reported elsewhere. Column chromatography was conducted by using silica gel (60–200 mesh, VWR) as packing material. All reactions were carried out by using an atmosphere of dry argon with standard airless glassware (Kontes) and Schlenk techniques.

Equipment. ^{31}P and ^1H NMR spectra were recorded for $CDCl_3$ solutions by using a Bruker WM-360 NMR spectrometer. Positive ^{31}P NMR shifts are downfield from external 85% H_3PO_4. The ^1H NMR shifts were referenced to internal $CHCl_3$. Electron-impact mass spectra were obtained with the use of a Kratos MS-9/50 spectrometer. Elemental microanalyses were obtained by Galbraith Laboratories, Knoxville, TN.

Preparation of $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$ (2). To a solution of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (**1**) (5.80 g, 14.7 mmol) in THF (250 mL) was added $NaOCH_2CF_3$, prepared from Na (3.0 g, 130.4 mmol) and excess trifluoroethanol (11.0 g, 150.7 mmol) in THF (20 mL). After the mixture was heated at reflux for 24 h, 2-propanol was added (10 mL) and the solvent was removed under reduced pressure. The product was isolated by column chromatography. Elution with CH_2Cl_2/hexane (2:3) gave an orange band, which yielded orange crystals of **2**. The product was recrystallized from CH_2Cl_2/hexane at −20 °C. Yield = 3.3 g, 89%.

Data for **2** are as follows. ^{31}P NMR: 40.9 (d), 21.2 ppm (t, $^2J_{PNP}$ = 59 Hz). See also ref 6.

Preparation of $N_3P_3(OPh)_4(\eta\text{-}C_5H_4)_2Fe$ (3). To a solution of **1** (5.0 g, 12.7 mmol) in diglyme (250 mL) was added NaOPh, prepared from Na (7.0 g, 304.3 mmol) and excess phenol (32.6 g, 346.8 mmol) in diglyme (100 mL). After the solution had been heated at reflux for 4 weeks, 2-propanol (20 mL) was added, and the product was purified by column chromatography. Elution with CH_2Cl_2/hexane (1:1) gave an orange band, which yielded orange crystals of **3**. The product was recrystallized from CH_2Cl_2/hexane at −20 °C. Yield = 2.7 g, 31%.

Data for **3** are as follows. ^1H NMR: δ 7.57, 7.49, 7.26, 7.10, 6.87 (all m, 20 H), 4.91 (m, 2 H), 4.87 (m, 2 H), 4.66 (m, 2 H), 4.31 (m, 2 H). ^{31}P NMR: 35.3 (d), 11.4 ppm (t, $^2J_{PNP}$ = 60 Hz). MS: calcd for $C_{34}H_{28}N_3O_4P_3Fe$, *m/e* 691; found, *m/e* 691. Anal. Calcd: C, 59.06; H, 4.09; N, 6.08. Found: C, 59.10; H, 3.90; N, 6.06.

Preparation of $N_3P_3(OPh)(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ (4). To a mixture of *cis*- and *trans*-$N_3P_3(OPh)F_3(\eta\text{-}C_5H_4)_2Fe$ (**5**) (2.0 g, 4.3 mmol) in THF (100 mL) was added a solution of $NaOCH_2CF_3$ (15.5 mmol, prepared as above) in THF (50 mL). The mixture was stirred at reflux for 24 h, and the product was subsequently isolated by column chromatography. Elution with CH_2Cl_2/hexane (3:7) gave an orange band, which yielded an inseparable mixture of *cis*- and *trans*-$N_3P_3(OPh)(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ (**4**). The product was isolated as an orange solid by recrystallization from CH_2Cl_2/hexane at −20 °C. Yield = 1.7 g, 56%.

Data for **4** are as follows. ^1H NMR: δ 7.35 (m, 5 H), 4.59–4.15 (m, 14 H). ^{31}P NMR: isomer A, 41.3 (d), 19.7 ppm (t, $^2J_{PNP}$ =

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(14) Rausch, M. D.; Ciappenelli, D. J. *J. Organomet. Chem.* **1967**, *10*, 127.

(15) Allen, C. W.; Tsang, F. Y.; Moeller, T. *Inorg. Chem.* **1968**, *7*, 2183.

58 Hz) (65% by ^{31}P NMR integration); isomer B, 41.1 (d), 21.1 ppm (t, $^2J_{PNP}$ = 58 Hz) (35%). MS: calcd for $C_{22}H_{19}N_3O_4P_3F_9Fe$, *m/e* 709; found, *m/e* 709. Anal. Calcd: C, 37.26; H, 2.68; N, 5.92. Found: C, 36.78; H, 2.91; N, 5.68.

Preparation of $N_3P_3(OPh)F_3(\eta\text{-}C_5H_4)_2Fe$ (5). To a solution of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (1) (7.0 g, 17.7 mmol) in THF (250 mL) was slowly added a solution of NaOPh, prepared from excess Na (0.49 g, 21.2 mmol) and phenol (1.66 g, 17.7 mmol) in THF (50 mL). The mixture was stirred at room temperature for 5 days, and the product was then purified by column chromatography. Elution with CH_2Cl_2/hexane (1:1) gave a yellow band, which yielded an inseparable mixture of *cis*- and *trans*-$N_3P_3(OPh)F_3(\eta\text{-}C_5H_4)_2Fe$ (5) as a yellow-orange solid. The product mixture was recrystallized from CH_2Cl_2/hexane at −20 °C. Yield = 7.0 g, 84%.

Data for 5 are as follows. ^1H NMR: δ 7.35 (m, 5 H), 5.01 (m, 4 H), 4.65 (m, 2 H), 4.35 (m, 2 H). ^{31}P NMR: 45.0 (dm, J_{PF} = 962 Hz), 15.2 ppm (dm, J_{PF} = 919 Hz). MS: calcd for $C_{16}H_{13}N_3OP_3F_3Fe$, *m/e* 469; found, *m/e* 469. Anal. Calcd: C, 40.97; H, 2.77; N, 8.95. Found: C, 40.48; H, 3.03; N, 8.80.

Preparation of $N_3P_3Me(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ (7). $NaOCH_2CF_3$ (15.5 mmol, prepared as above) in THF (50 mL) was added slowly to a solution of $N_3P_3MeF_3(\eta\text{-}C_5H_4)_2Fe$ (6) (1.7 g, 4.3 mmol) in THF (100 mL). The mixture was heated at reflux for 18 h, and the product was then isolated by column chromatography. Elution with CH_2Cl_2 gave an orange band, which yielded orange crystals of 7. Further purification was achieved by recrystallization from CH_2Cl_2/hexane at −20 °C. Yield = 1.35 g, 49%.

Data for 7 are as follows. ^1H NMR: δ 4.86 (s, 1 H), 4.77 (s, 2 H), 4.69 (s, 1 H), 4.59 (s, 1 H), 4.55 (s, 1 H), 4.48 (m, 2 H), 4.30 (m, 6 H). ^{31}P NMR: δ_a 40.2 (dd, $^2J_{ab}$ = 15 Hz), δ_b 35.3 (dd, $^2J_{bc}$ = 29 Hz), δ_c 16.9 ppm (dd, $^2J_{ca}$ = 51 Hz). MS: calcd for $C_{17}H_{17}N_3O_3P_3F_9Fe$, *m/e* 631; found, *m/e* 631. Anal. Calcd: C, 32.36; H, 2.69; N, 6.66. Found: C, 32.22; H, 2.63; N, 6.51.

Preparation of $N_3P_3Ph(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ (9). To a solution of $N_3P_3PhF_3(\eta\text{-}C_5H_4)_2Fe$ (8) (1.9 g, 4.2 mmol) in THF (100 mL) was added $NaOCH_2CF_3$ (15.1 mmol, prepared as above) in THF (50 mL). The mixture was stirred at reflux for 18 h, and the product was then isolated by column chromatography. Elution with CH_2Cl_2/hexane (1:3) gave an orange band, which yielded orange crystals of 9. Further purification was achieved by recrystallization from CH_2Cl_2/hexane at −20 °C. Yield = 1.9 g, 65%.

Data for 9 are as follows. ^1H NMR: δ 7.91 (m, 2 H), 7.50 (m, 3 H), 5.05 (m, 1 H), 4.85 (m, 2 H), 4.58 (m, 6 H), 4.30 (m, 5 H). ^{31}P NMR: δ_a 40.9 (dd, $^2J_{ab}$ = 15 Hz), δ_b 28.6 (dd, $^2J_{bc}$ = 32 Hz), δ_c 17.1 ppm (dd, $^2J_{ca}$ = 47 Hz). MS: calcd for $C_{22}H_{19}N_3O_3P_3F_9Fe$, *m/e* 693; found, *m/e* 693. Anal. Calcd: C, 38.10; H, 2.74; N, 6.06. Found: C, 38.35; H, 2.94; N, 5.95.

Preparation of $N_3P_3Ph(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ (11). To a solution of $N_3P_3PhF_3(\eta\text{-}C_5H_4)_2Fe$ (10) (1.7 g, 3.8 mmol) was added $NaOCH_2CF_3$ (13.7 mmol, prepared as above) in THF (50 mL). The mixture was stirred at reflux for 18 h, and the product was then isolated by column chromatography. Elution with CH_2Cl_2/hexane (1:3) gave an orange band, which yielded orange crystals of 11. Further purification was achieved by recrystallization from CH_2Cl_2/hexane at −20 °C. Yield = 2.0 g, 77%.

Data for 11 are as follows. ^1H NMR: δ 7.95 (m, 2 H), 7.55 (m, 3 H), 4.59 (s, 2 H), 4.88 (s, 2 H), 4.62 (s, 2 H), 4.25 (m, 8 H). ^{31}P NMR: 40.2 (d), 33.9 ppm (t, $^2J_{PNP}$ = 37 Hz). MS: calcd for $C_{22}H_{19}N_3O_3P_3F_9Fe$, *m/e* 693; found, *m/e* 693. Anal. Calcd: C, 38.10; H, 2.74; N, 6.06. Found: C, 38.18; H, 3.04; N, 5.95.

Preparation of $N_3P_3Ph_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ (13). To a solution of $N_3P_3Ph_2F_2(\eta\text{-}C_5H_4)_2Fe$ (12) (5.0 g, 9.8 mmol) in THF (250 mL) was added $NaOCH_2CF_3$ (23.5 mmol, prepared as above) in THF (75 mL). After the mixture had been stirred for 18 h at reflux, the product was purified by column chromatography. Elution with CH_2Cl_2/hexane (1:3) gave an orange band, which yielded orange crystals of 13. Further purification was achieved by recrystallization from Et_2O hexane at −20 °C. Yield = 2.2 g, 33%.

Data for 13 are as follows. ^1H NMR: δ 8.05 (m, 4 H), 7.49 (m, 6 H), 5.03 (m, 2 H), 4.57 (m, 6 H), 4.38 (m, 4 H). ^{31}P NMR: 23.8 (d), −1.4 ppm (t, $^2J_{PNP}$ = 30 Hz). MS: calcd for $C_{26}H_{22}N_3O_2P_3F_6Fe$, *m/e* 671; found, *m/e* 671. Anal. Calcd: C, 46.50; H, 3.28; N, 6.26. Found: C, 47.78; H, 3.72; N, 6.02.

Preparation of *gem*-$N_3P_3Ph_2F_2(\eta\text{-}C_5H_4)_2Fe$ (15). A solution of $N_3P_3Ph_2F_4$ (14) (11.1 g, 30.4 mmol) in hexanes (75 mL) was added dropwise to a solution of 1,1-dilithioferrocene–TMEDA (11.1 g, 25.8 mmol) in hexanes (500 mL) at −78 °C. The mixture was then warmed to room temperature and was stirred for an additional 24 h. 2-Propanol (25 mL) was then added, and the mixture was stirred for an additional 30 min. The solvent was removed, and the product was isolated by column chromatography. Elution with hexane gave ferrocene, which was identified by ^1H NMR spectroscopy. Elution with CH_2Cl_2/THF (1:1) gave an orange band, which yielded orange crystals of $N_3P_3Ph_2F_2(\eta\text{-}C_5H_4)_2Fe$ (15). The product was recrystallized from CH_2Cl_2/hexane at −20 °C. Yield = 5.0 g, 32%.

Data for 15 are as follows. ^1H NMR: δ 8.18 (m, 2 H), 7.87 (m, 2 H), 7.65 (m, 3 H), 7.46 (m, 3 H), 4.98 (s, 2 H), 4.67 (s, 2 H), 4.55 (s, 2 H), 4.13 (s, 2 H). ^{31}P NMR: 42.7 (dm, J_{PF} = 917 Hz), 31.7 ppm (t, $^2J_{PNP}$ = 19 Hz). MS: calcd for $C_{22}H_{18}N_3P_3F_2Fe$, *m/e* 511; found, *m/e* 511. Anal. Calcd: C, 51.67; H, 3.52; N, 8.22. Found: C, 51.58; H, 3.61; N, 7.92.

Preparation of $N_3P_3Ph_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ (16). $NaOCH_2CF_3$ (18.7 mmol) in THF (75 mL) was added slowly to a solution of $N_3P_3Ph_2F_2(\eta\text{-}C_5H_4)_2Fe$ (15) (4.0 g, 7.8 mmol) in THF (250 mL). After the mixture was stirred at reflux for 18 h, the product was isolated by column chromatography. Elution with CH_2Cl_2/THF (3:7) gave an orange band, which yielded orange crystals of 16. The product was further purified by recrystallization from CH_2Cl_2/hexane at −20 °C. Yield = 2.0 g, 31%.

Data for 16 are as follows. ^1H NMR: δ 8.15 (m, 2 H), 7.88 (m, 2 H), 7.58 (m, 3 H), 7.49 (m, 3 H), 4.88 (s, 2 H), 4.63 (s, 2 H), 4.52 (s, 2 H), 4.33 (m, 4 H), 4.10 (s, 2 H). ^{31}P NMR: 39.8 (d), 27.7 ppm (t, $^2J_{PNP}$ = 19 Hz). MS: calcd for $C_{26}H_{22}N_3O_2P_3F_6Fe$, *m/e* 671; found *m/e* 671. Anal. Calcd: C, 46.50; H, 3.28; N, 6.26. Found: C, 46.62, H, 3.32, N, 6.31.

X-ray Structure Determination Technique. Our general technique is described elsewhere,[16] and only details related to the present work will be given here. A summary of the important crystallographic data is presented in Table I.

Crystals of 2 and 3 were obtained by cooling dichloromethane/hexane solutions to −20 °C. Crystals of 16 were obtained by cooling a toluene/hexane solution to −9 °C. All structures were solved by direct methods and were refined by full-matrix least-squares calculations on *F*'s. All non-hydrogen atom positional parameters and anisotropic temperature factors were refined. The positional parameters for the hydrogen atoms were located from difference Fourier maps and were not allowed to refine; two hydrogen atoms in 2 could not be located. One trifluoroethoxy group in 2 exists in two conformations, and both are reported. The SHELX76 program was utilized for the determination of the molecular structure of 16. The molecular structures shown in Figures 1–3 were generated from positional parameters by using Chem3D (Cambridge Scientific Computing, Inc., Cambridge, MA).

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Supplementary Material Available: For 2, 3, and 16, tables of interatomic distances, bond angles, positional parameters, least-squares planes, and anisotropic thermal parameters (Tables S1–S5, S7–S11, and S13–S17) and perspective views of the molecular structures (Figures S1–S3) (30 pages); tables of structure factors (Tables S6, S12, and S18) (79 pages). Ordering information is given on any current masthead page.

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[16] Allcock, H. R.; Mang, M. N.; Riding, G. H.; Whittle, R. R. *Organometallics* **1986**, *5*, 2244.