the important interligand steric interactions take place 2–3 bonds distant from the central atom.

Acknowledgment. This research was supported by the National Science Foundation (Grant CHE-8116355), U.C. Davis NMR Facility, and a generous loan of rhodium chloride by Johnson Matthey, Inc. B.D.M. thanks U.C. Davis for a generous graduate research award. J.H. is on leave from the University of Oslo, Norway.

Registry No. 1, 89178-74-5; 2, 89178-75-6; 3, 89178-76-7; 4, 14694-95-2; 5, 89196-39-4; 6, 81177-96-0; 7, 87451-18-1; 8, 87451-19-2; $PCl\{CH(SiMe_3)_2\}_2$, 63429-87-8; $\{RhCl(COD)\}_2$, 12092-47-6; $\{RhCl(COE)_2\}_2$, 12279-09-3; $\{RhCl(CO)_2\}_2$, 14523-22-9; $\{IrCl(COD)\}_2$, 12112-67-3; $PMe\{CH(SiMe_3)_2\}_2$, 70360-01-9; $IrCl(COD)(PH\{CH(SiMe_3)_2\}_2)$, 89178-77-8; $IrCl(COD)(PMe\{CH(SiMe_3)_2\}_2)$, 89178-78-9; $IrCl(COD)(PCl\{CH(SiMe_3)_2\}_2)$, 89178-79-0; $RhCl(COE)_2(PH\{CH(SiMe_3)_2\}_2)$, 89178-80-3; *trans*-$RhCl(COE)(PH\{CH(SiMe_3)_2\}_2)_2$, 89178-81-4.

Supplementary Material Available: Tables of bond distances and angles, structure factors, and calculated hydrogen positional and thermal parameters (90 pages). Ordering information is given on any current masthead page.

Reaction of Mono- and Dilithioferrocene with Octachlorocyclotetraphosphazene. The Crystal and Molecular Structures of $N_4P_4Cl_6[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]_2$ and $N_3P_3Cl_4[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]N_4P_4Cl_7$

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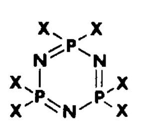
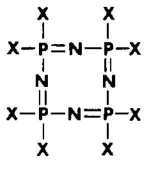
Received August 30, 1983

New and unusual derivatives of cyclophosphazenes bearing ferrocene substituents have been synthesized by the reactions of mono- and dilithioferrocene with octachlorocyclotetraphosphazene, $(NPCl_2)_4$, and with equimolar mixtures of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, and $(NPCl_2)_4$. The reactions of monolithioferrocene with $(NPCl_2)_4$ gave $N_4P_4Cl_6[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]_2$ (4) in which the tetrameric ring has contracted to give a cyclic trimer with a phosphorus–nitrogen–phosphorus pendent chain. The two ferrocene units were found to be attached to the terminal phosphorus atom of this chain. The structure of 4 was examined by X-ray diffraction techniques. Crystals of 4 are monoclinic of space group $P2_1/c$ with a = 11.199 (3) Å, b = 22.774 (7) Å, c = 11.504 (7) Å, β = 104.81 (3)°, V = 2837 (4) Å^3, and Z = 4. The structure was refined to discrepancy indices R = 0.055 and R_w = 0.063. The most striking feature of the molecule is the structure of the pendent chain. Here, the bond angle at nitrogen is unusually wide, being 142.7 (3)°. Also, the single bond between this nitrogen atom and the ring phosphorus (1.54 Å) is significantly shorter than the supposed double bond to the terminal phosphorus atom of the chain (1.57 Å). These observations are compatible with appreciable delocalization within the phosphorus–nitrogen skeleton. The reactions of lithioferrocene with a 1:1 molar mixture of $(NPCl_2)_3$ and $(NPCl_2)_4$ gave the bi(cyclophosphazenes), $N_3P_3Cl_4[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_4X)]N_4P_4Cl_7$ (**5a**, X = H; **5b**, X = Cl). The structure of **5a** was also examined by X-ray diffraction techniques. Crystals of **5a** were triclinic of space group $P\bar{1}$ with a = 12.899 (5) Å, b = 14.206 (3) Å, c = 10.003 (4) Å, α = 99.77 (3)°, β = 105.76 (3)°, γ = 112.99 (2)°, V = 1543 (2) Å^3, and Z = 2. The structure was refined to discrepancy indices R = 0.053 and R_w = 0.061. The most striking feature of this molecule is the linkage of the cyclic trimeric and tetrameric rings by a P–P bond. This is the first example of a trimer–tetramer bi(cyclophosphazene). Possible mechanisms leading to the formation of these ferrocenylphosphazenes are also discussed.

This investigation is part of an exploration of the reactions of a variety of organometallic reagents with halogenophosphazenes 1–3 (X = halogen).



1



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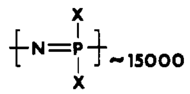

3

Increasing interest exists in the preparation of new cyclic and high polymeric phosphazenes linked to transition-metal organometallic units, partly because such species are prospective catalyst systems or electroactive species. Recently, six methods have been developed to link transition metals to phosphazenes. They are (a) coordination of metals to skeletal nitrogen atoms,[1] (b) coordination of organometallic units to phosphine donors linked to the phosphazene skeleton through aryloxy-spacer groups,[2] (c) attachment of the metal via π-complexing through pendent acetylenic units,[3] (d) metal coordination to phosphazenes that bear *nido*-carborane units,[4] (e) the formation of phosphazenes with direct skeletal phosphorus–transition-metal bonds,[5-7] and (f) linkage of metallocene units to the

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(1) Allcock, H. R.; Allen, R. W.; O'Brien, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 3984.

(2) Allcock, H. R.; Lavin, K. D.; Tollefson, N. M.; Evans, T. L. *Organometallics* **1983**, *2*, 267.

(3) Allcock, H. R.; Harris, P. J.; Nissan, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 2256 and unpublished results.

(4) Allcock, H. R.; Scopelianos, A. G.; Whittle, R. R.; Tollefson, N. M. *J. Am. Chem. Soc.* **1983**, *105*, 1316.

(5) Allcock, H. R.; Greigger, P. P.; Wagner, L. J.; Bernheim, M. Y. *Inorg. Chem.* **1981**, *20*, 717.

(6) Allcock, H. R.; Wagner, L. J.; Levin, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 1321.

(7) Suszko, P. R.; Whittle, R. R.; Allcock, H. R. *J. Chem. Soc., Chem. Commun.* **1982**, 649.

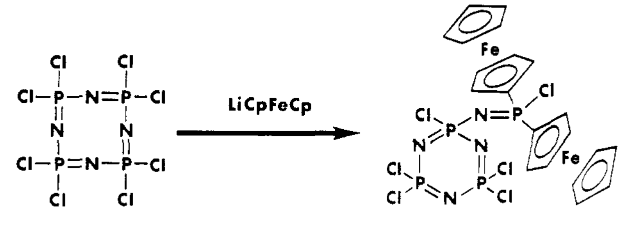
skeletal phosphorus atoms through carbon–phosphorus bonds.[8] The present work is connected with the last topic.

In this paper we discuss some unexpected nuances of the reactions of lithiometallocenes with chlorocyclophosphazenes. These reactions provide an insight into the mechanisms of reaction of a range of organometallic anions with cyclophosphazenes. They may also serve as models for the reactions of organometallic reagents with halogenophosphazene high polymers.

Results and Discussion

Overview of the Reactions. We describe here the reactions of lithiated ferrocenes with octachlorocyclotetraphosphazene, $(NPCl_2)_4$ (2, X = Cl), and with equimolar mixtures of $(NPCl_2)_4$ and $(NPCl_2)_3$ (1, X = Cl).

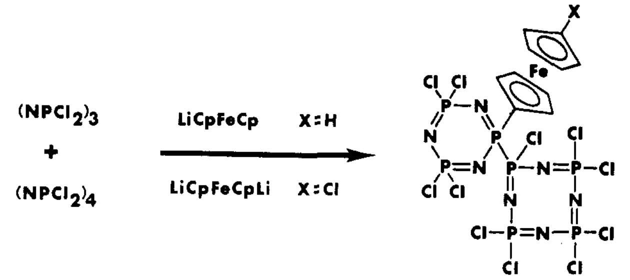
In earlier work we showed that monolithioferrocene reacts with $(NPCl_2)_3$ to give a monoferrocenylcyclophosphazene without disruption of the six-membered phosphazene ring. By contrast, the reactions of $(NPCl_2)_4$ with monolithioferrocene leads to the formation of species 4, in which cleavage of the tetrameric ring has occurred followed by recyclization to form a cyclic trimer with a pendent chain. The terminal phosphorus atom of the chain bears two ferrocene residues.



4

Similar products have been isolated from the reactions of $(NPCl_2)_4$ with diphenylmagnesium in 1,4-dioxane and with phenylmagnesium bromide.[9-11]

Monolithioferrocene reacts with a 1:1 mixture of $(NPCl_2)_3$ and $(NPCl_2)_4$ to yield a bi(cyclophosphazene) (**5a**) in which a trimeric and tetrameric ring are linked through a P–P bond. The bridging phosphorus atom of the trimeric ring was found to bear a ferrocene residue. (The normal reaction products expected for the interaction of $(NPCl_2)_3$ with monolithioferrocene[8] were also formed in low yield.)

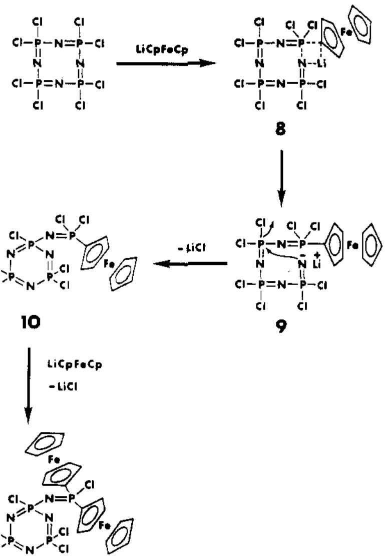


5

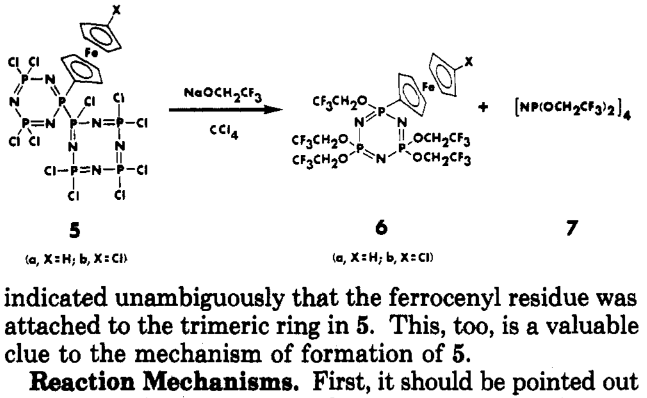
(a, X:H; b, X:Cl)

When *di*lithioferrocene reacted with a 1:1 mixture of $(NPCl_2)_3$ and $(NPCl_2)_4$, product **5b** was formed, in which a chlorine atom has been attached to the "free" cyclopentadienyl ring. These products provide clues to the reaction mechanism, as will be discussed later.

Scheme I



The trimer–tetramer bi(cyclophosphazenes) **5a** and **5b** were treated with a slight excess of sodium trifluoroethoxide and carbon tetrachloride. This is a method developed earlier for the P–P bond cleavage of trimer–trimer bi(cyclophosphazenes).[12] Species **6** and $[NP(OCH_2CF_3)_2]_4$ were isolated as products. The isolation of these products indicated unambiguously that the ferrocenyl residue was attached to the trimeric ring in **5**. This, too, is a valuable clue to the mechanism of formation of **5**.



5 6 7

(a, X=H; b, X=Cl) (a, X=H; b, X=Cl)

Reaction Mechanisms. First, it should be pointed out that the yields of species 4 and 5 were low (11–18%). This can be ascribed partly to the low efficiency of formation of both monolithio- and dilithioferrocene by the methods employed. Moreover, substantial quantities of ferrocene itself, along with unreacted $(NPCl_2)_4$ and $(NPCl_2)_3$, were recovered from the reaction mixtures. Thus, we believe that the reaction pathways discussed below constitute an important part of the overall mechanism.

The reactions of lithioferrocene with $(NPCl_2)_4$ are clearly different from those of the same reagent with $(NPCl_2)_3$.[8] A plausible pathway for the reaction of monolithioferrocene with $(NPCl_2)_4$ is illustrated in Scheme I.

The initial interaction of the organometallic reagent with the phosphazene probably involves coordination of the lithium atom to a skeletal nitrogen atom and cleavage of the ring via the four center transition state (**8**). This would generate a lithiated phosphazene chain, substituted on the terminal phosphorus with a ferrocene unit (**9**). Internal substitution at the PCl_2 unit adjacent to the terminal group would then lead to **10**. A second lithioferrocene unit could then react with a P–Cl unit at the exposed, terminal

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[8] Allcock, H. R.; Lavin, K. D.; Riding, G. H.; Suszko, P. R.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 0000.

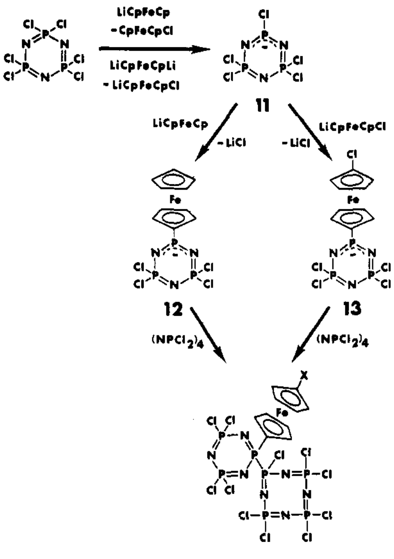
[9] Shaw, R. A.; Biddlestone, M. *J. Chem. Soc. A* **1970**, 1750.

[10] Shaw, R. A.; Biddlestone, M. *J. Chem. Soc. A* **1969**, 178.

[11] Shaw, R. A.; Biddlestone, M. *J. Chem. Soc. A* **1971**, 2715.

[12] Allcock, H. R.; Connolly, M. S.; Harris, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 2482.

Scheme II



5

(a, X:H; b, X:Cl)

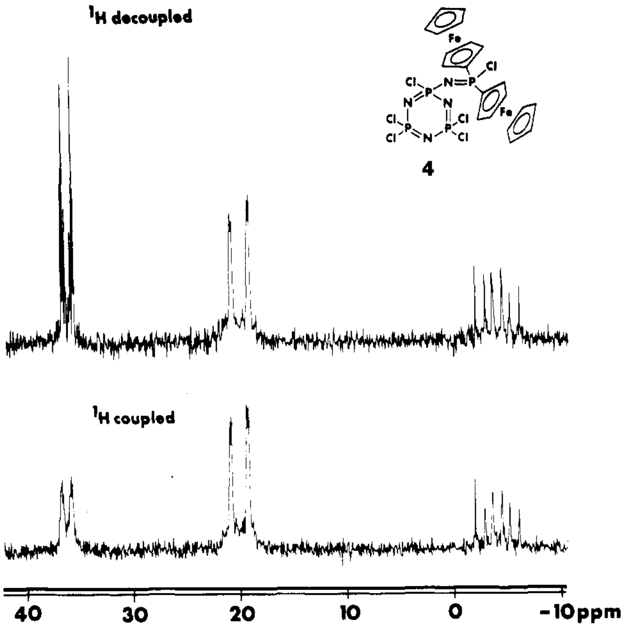


Figure 1. ^{31}P NMR spectrum of compound 4.

phosphorus atom to yield the final product (4). This mechanism is similar to the one proposed by Shaw for the reactions of phenylmagnesium bromide with $(NPCl_2)_4$.[9-11]

A possible pathway for the formation of **5a** and **5b** is illustrated in Scheme II. The key features of this mechanism are (a) that $(NPCl_2)_3$ reacts more readily with organometallic reagents than does $(NPCl_2)_4$[12,13] and (b) that the initial reaction between $(NPCl_2)_3$ and the lithiometallocene is a metal–halogen exchange process rather than a substitution.[8]

Thus, an initial metal–halogen exchange reaction between $(NPCl_2)_3$ and the lithiometallocene would yield a metallophosphazene-type intermediate with a three-coordinate phosphorus atom (**11**). This would then undergo rapid substitution with lithioferrocene to generate **12**. Species **12** could then react with $(NPCl_2)_4$ to give **5a**. Alternatively, if dilithioferrocene is present, an initial metal–halogen exchange with $(NPCl_2)_3$ could then generate **11** and monolithiomonochloroferrocene. Subsequent substitution between these two species would yield **13**. Compound **13** would then react with $(NPCl_2)_4$ to yield **5b**.

We believe that the formation of product **5** reflects the greater ease of metal–halogen exchange with $(NPCl_2)_3$ than with $(NPCl_2)_4$. Although this behavior contrasts with the generally greater ease of substitution of $(NPCl_2)_4$ compared with $(NPCl_2)_3$, it is compatible with other observations, both from our laboratory and elsewhere,[9-11,13] $(NPCl_2)_3$ is much more reactive in metal–halogen exchange reactions. Moreover, the results described confirm that $(NPCl_2)_4$ is more sensitive to substitution than $(NPCl_2)_3$. Otherwise, the main product would be the bicyclotriphosphazene rather than species **5**.

Structure Proof for 4, 5a, and 5b. The structures of **4**, **5a**, and **5b** were determined from a combination of ^{31}P, ^{1}H NMR, and IR spectroscopy and by mass spectrometry.

The ^{1}H-decoupled ^{31}P NMR spectrum of **4** (Figure 1) was interpreted as an AM_2X spin system with peaks at 36.9 (P_{ClM_2} as a doublet of triplets with $J_{P(A)NP(X)} = 28$ Hz and $J_{P(A)NP(X)NP(M)} = 4$ Hz), 20.0 (P_{Cl_2} as a doublet of doublets with $J_{P(M)NP(X)} = 52$ Hz and $J_{P(M)NP(X)NP(A)} = 4$ Hz), and −2.7 ppm (P_{ClNP} as a doublet of triplets with $J_{P(X)NP(M)} = 52$ Hz and $J_{P(X)NP(A)} = 28$ Hz). The ^{1}H-coupled ^{31}P NMR spectrum of **4** (Figure 1) again consisted of three sets of resonances with identical peak positions and assignments. However, the resonance at +36.9 ppm, which corresponded to the phosphorus atom bearing the two metallocene units, was broadened considerably by coupling to the cyclopentadienyl ring hydrogens and was reduced in intensity by the loss of the nuclear Overhauser effect. The 360-MHz ^{1}H NMR spectrum of **4** consisted of four unresolved multiplets at 4.813 (2 H), 4.761 (2 H), 4.574 (2 H), and 4.535 (2 H) ppm, attributed to four sets of inequivalent protons on the phosphazene-substituted cyclopentadienyl rings, and a sharp singlet at 4.383 (10 H), assigned to the two freely rotating, unbound cyclopentadienyl rings. The unexpected presence of four signals for the hydrogen atoms attached to the two equivalent, bound cyclopentadienyl rings is probably a consequence of restricted rotation around the two P–C bonds. Such restriction would be imposed by the presence of two adjacent ferrocene units, a chlorine atom, and the phosphazene skeleton.

The infrared spectrum of **4** contains two different P–N stretching peaks at 1220 and 1180 cm^{-1}. These two vibrations are attributed to the two environments of the P–N units in the ring and chain.

The electron-impact mass spectrum of **4** revealed the expected molecular ion at *m/e* 760, with a Cl_6 isotope pattern.

The ^{31}P NMR spectrum of **5a** and **5b** consisted of three complex sets of resonances with peaks at 22.0 (m), −1.07 (m), and −6.94 ppm (m). These resonances were too complex to be assigned in detail. They result from overlapping peaks from the different types of phosphorus environments and complex couplings. The 360-MHz ^{1}H NMR spectrum of **5a** consisted of two unresolved multiplets at 4.718 (2 H) and 4.669 (2 H), ppm, assigned to the two inequivalent sets of protons on the phosphazene-bound cyclopentadienyl ring, and a sharp singlet at 4.435 (5 H) ppm, which was assigned to the equivalent protons of the freely rotating, unbound cyclopentadienyl ring. The 360-MHz ^{1}H NMR spectrum of **5b** consisted of four unresolved multiplets at 4.718 (2 H), 4.680 (2 H), 4.660 (2 H), and 4.388 (2 H) ppm, which correspond to the four inequivalent sets of protons in a compound with a phosphazene-bound cyclopentadienyl ring and a second cyclopentadienyl ring bearing a chlorine substituent.

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(13) Allcock, H. R.; Desorcie, J. L.; Harris, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 2814.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) (esd) for $N_4P_4Cl_6[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]_2$ (4)

	Bond Lengths		
Fe–Cp_1[a]	1.638 (1)	P(3)–Cl(5)	2.038 (2)
Fe–Cp_2[a]	1.643 (1)	P(3)–N(1)	1.603 (4)
P(1)–Cl(1)	1.997 (2)	P(3)–N(3)	1.610 (4)
P(1)–Cl(2)	1.993 (2)	P(3)–N(4)	1.537 (4)
P(1)–N(1)	1.552 (4)	P(4)–C(1)	1.772 (5)
P(1)–N(2)	1.590 (5)	P(4)–C(11)	1.744 (5)
P(2)–Cl(3)	1.995 (2)	P(4)–Cl(6)	2.033 (2)
P(2)–Cl(4)	1.981 (2)	P(4)–N(4)	1.566 (4)
P(2)–N(2)	1.578 (5)	C(1)–C(2)	1.411 (7)
P(2)–N(3)	1.543 (5)	C(6)–C(7)	1.412 (10)
	Bond Angles		
N(1)–P(1)–N(2)	120.1 (2)	P(1)–N(1)–P(3)	123.2 (2)
N(2)–P(2)–N(3)	121.1 (2)	P(1)–N(2)–P(2)	117.7 (3)
N(1)–P(3)–N(3)	114.2 (2)	P(2)–N(3)–P(3)	121.8 (3)
N(1)–P(3)–N(4)	116.3 (2)	P(3)–N(4)–P(4)	142.7 (3)
N(3)–P(3)–N(4)	110.2 (3)	C(2)–C(1)–C(5)	108.1 (4)
C(1)–P(4)–C(11)	109.4 (2)	C(7)–C(6)–C(10)	109.3 (7)

[a] Distance between atom and ring plane.

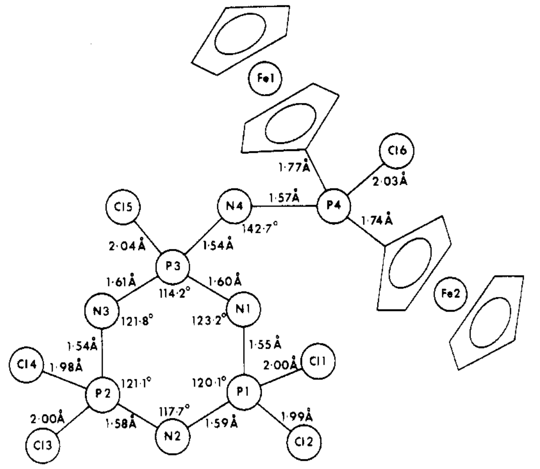

Figure 2. Molecular structural features of compound 4 (derived from X-ray diffraction data).

The infrared spectra of **5a** and **5b** contained evidence for the presence of two different P–N stretching frequencies at 1300 and 1180 cm^{-1}. These result from the tetramer and trimer rings, respectively.

The electron-impact mass spectra of **5a** and **5b** contained peaks for the expected molecular ions at m/e 885 and 920, with Cl_{11} and Cl_{12} isotope patterns, respectively.

Crystal and Molecular Structure of 4. An X-ray single-crystal analysis confirmed that 4 consists of two ferrocene units linked via two P–C covalent bonds to a pendent phosphorus atom acyclic to the cyclotriphosphazene ring. All features of the molecule were identified, including the hydrogen atoms attached to the cyclopentadienyl rings. The main structural features of 4 are summarized in Table I and are illustrated in Figures 2 and 3. Positional parameters are listed in Table II.

The cyclopentadienyl rings are planar and coplanar as in ferrocene. The dihedral angle between the rings is ~2.6°. They are equally separated from the iron atoms by a distance of 1.64 Å. This is close to the separation of 1.66 Å found in ferrocene.[14] The average C–C bond distance around the rings (1.44 Å) is also close to the value of 1.40 Å found for ferrocene.[14] The two ferrocenyl units are bonded in a geminal manner to the pendent phosphorus atom acyclic to the phosphazene ring, with an average carbon–phosphorus distance of 1.76 Å. This is close to the C–P distance of 1.77 Å detected in other metallocenylphosphazenes.[8,9]

An unusual feature of the structure is the distortion of the angle at N(4) (see Figure 2). The P–N–P angle at N(4) was found to be ~143°. This wide angle at nitrogen is probably due to the steric distortions imposed by the two adjacent ferrocene units. Also of interest is the length of the "double bond" from N(4) to P(4). This was significantly longer than the "single bond" between P(3) to N(4). This suggests extensive delocalization of electron density

Table II. Positional Parameters for 4

atom	*x*	*y*	*z*
Fe(1)	0.1975 (1)	0.36707 (6)	0.5288 (1)
Fe(2)	0.3759 (1)	0.40022 (6)	1.0520 (1)
Cl(1)	−0.4144 (3)	0.4256 (2)	0.5670 (3)
Cl(2)	−0.2457 (3)	0.3946 (1)	0.4039 (2)
Cl(3)	−0.3345 (3)	0.2539 (2)	0.7899 (3)
Cl(4)	−0.1742 (4)	0.2003 (1)	0.6366 (4)
Cl(5)	−0.1218 (3)	0.4077 (1)	0.9196 (2)
Cl(6)	0.1507 (3)	0.5093 (1)	0.8382 (2)
P(1)	−0.2615 (2)	0.3798 (1)	0.5700 (2)
P(2)	−0.2168 (3)	0.2775 (1)	0.6942 (3)
P(3)	−0.0692 (2)	0.3733 (1)	0.7768 (2)
P(4)	0.1724 (2)	0.4258 (1)	0.7844 (2)
N(1)	−0.1497 (7)	0.4077 (3)	0.6617 (7)
N(2)	−0.2944 (8)	0.3125 (4)	0.5817 (8)
N(3)	−0.0992 (7)	0.3042 (3)	0.7778 (7)
N(4)	0.0712 (7)	0.3832 (3)	0.8075 (7)
C(1)	0.1797 (8)	0.4350 (4)	0.6334 (7)
C(2)	0.0800 (8)	0.4352 (4)	0.5295 (8)
C(3)	0.130 (1)	0.4399 (4)	0.4279 (8)
C(4)	0.2600 (9)	0.4434 (4)	0.4705 (8)
C(5)	0.2921 (8)	0.4395 (4)	0.5961 (8)
C(6)	0.183 (1)	0.2896 (4)	0.612 (1)
C(7)	0.098 (1)	0.2906 (5)	0.498 (1)
C(8)	0.172 (2)	0.2976 (5)	0.416 (1)
C(9)	0.294 (1)	0.3017 (5)	0.480 (1)
C(10)	0.301 (1)	0.2971 (5)	0.599 (1)
C(11)	0.3170 (8)	0.4043 (4)	0.8719 (7)
C(12)	0.3491 (9)	0.3450 (4)	0.9099 (9)
C(13)	0.474 (1)	0.3444 (5)	0.9737 (9)
C(14)	0.5228 (8)	0.4017 (5)	0.9757 (8)
C(15)	0.4265 (8)	0.4380 (4)	0.9126 (8)
C(16)	0.2335 (9)	0.4262 (5)	1.1225 (8)
C(17)	0.275 (1)	0.3683 (6)	1.161 (1)
C(18)	0.397 (1)	0.3709 (6)	1.220 (1)
C(19)	0.436 (1)	0.4291 (6)	1.2254 (9)
C(20)	0.337 (1)	0.4623 (5)	1.1655 (8)

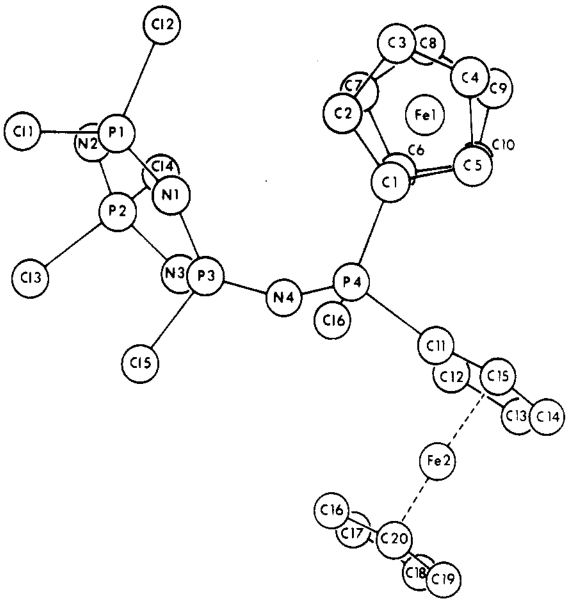

Figure 3. Structure of 4 showing details of the pendent group.

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(14) Dunitz, J. D.; Orgel, L. E.; Rich, A. *Acta Crystallogr.* **1956**, *9*, 373.

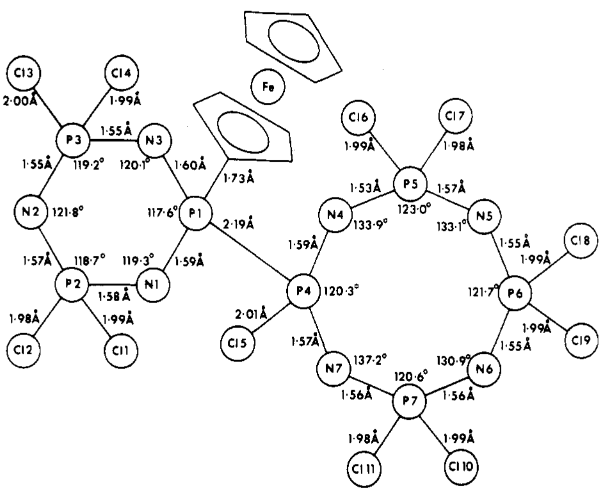

Figure 4. Molecular structural features of compound **5a** (derived from X-ray diffraction data).

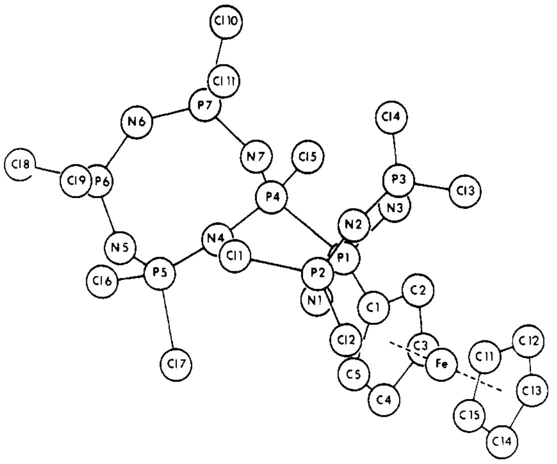

Figure 5. Structure of compound **5a** showing orientation of the ferrocenyl group.

throughout the P–N–P chain. This unusual feature is even more remarkable when this structure is compared to that of $N_4P_4Cl_4Ph_4$.[15] The exocyclic P–N bond lengths and bond angles of the phosphazene ring are similar to those found in other metallocenylphosphazenes studied previously.[8] In 4, the P–N bond lengths near the bridgehead phosphorus P(3) are longer than those at P(1) and P(2) (1.607 vs. 1.566 Å) and the bond angle at P(3) is constricted (114 vs. 121°) due to the presence of the NPCl(CpFeCp)$_2$ unit.

Crystal and Molecular Structure of 5a. An X-ray single-crystal analysis confirmed that the molecule consists of a ferrocene unit linked via a P–C covalent bond to a cyclotriphosphazene ring, which is itself linked geminally to a cyclotetraphosphazene ring via a P–P covalent bond. All features of the molecule were identified, including hydrogen atoms attached to the cyclopentadienyl rings. The main structural features of **5a** are summarized in Table III and are illustrated in Figures 4 and 5. Positional parameters are listed in Table IV.

As in the other metallocenylphosphazenes,[8] the metallocene portion of the molecule appears to be unaffected by the presence of the phosphazene rings. The average C–C bond distance around the rings of 1.41 Å is close to the value found in ferrocene. The ferrocene unit is bound to the same phosphorus atom as the P–P bond. The C–P distance is 1.70 Å. This is close to the C–P distance of 1.77 Å found in other metallocenylphosphazenes studied previously.[1]

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) (esd) for $N_7P_7C_{11}(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ (5a)

Bond Lengths

P(1)-C(1)	1.732 (6)	P(5)-Cl(6)	1.992 (2)
P(1)-N(1)	1.590 (5)	P(5)-Cl(7)	1.984 (2)
P(1)-N(3)	1.597 (5)	P(5)-N(4)	1.534 (6)
P(1)-P(4)	2.187 (2)	P(5)-N(5)	1.574 (5)
P(2)-Cl(1)	1.990 (3)	P(6)-Cl(8)	1.988 (3)
P(2)-Cl(2)	1.979 (3)	P(6)-Cl(9)	1.991 (5)
P(2)-N(1)	1.582 (5)	P(6)-N(5)	1.551 (5)
P(2)-N(2)	1.568 (6)	P(6)-N(6)	1.545 (6)
P(3)-Cl(3)	1.999 (3)	P(7)-Cl(10)	1.990 (3)
P(3)-Cl(4)	1.987 (3)	P(7)-Cl(11)	1.976 (2)
P(3)-N(2)	1.549 (6)	P(7)-N(6)	1.564 (6)
P(3)-N(3)	1.554 (5)	P(7)-N(7)	1.561 (5)
P(4)-Cl(5)	2.010 (2)	C(1)-C(2)	1.434 (9)
P(4)-N(4)	1.590 (6)	C(11)-C(12)	1.31 (2)
P(4)-N(7)	1.572 (5)		

Bond Angles

N(1)-P(1)-N(3)	117.6 (3)	N(5)-P(6)-N(6)	121.7 (3)
P(4)-P(1)-C(1)	107.1 (2)	N(6)-P(7)-N(7)	120.6 (3)
P(4)-P(1)-N(1)	103.2 (2)	P(1)-N(1)-P(2)	119.3 (3)
P(4)-P(1)-N(3)	105.2 (2)	P(2)-N(2)-P(3)	121.8 (4)
N(1)-P(2)-N(2)	118.7 (3)	P(1)-N(3)-P(3)	120.1 (3)
N(2)-P(3)-N(3)	119.2 (3)	P(4)-N(4)-P(5)	133.9 (4)
P(1)-P(4)-N(4)	112.8 (2)	P(5)-N(5)-P(6)	133.1 (4)
P(1)-P(4)-N(7)	102.0 (2)	P(6)-N(6)-P(7)	130.9 (4)
N(4)-P(4)-N(7)	120.3 (3)	P(4)-N(7)-P(7)	137.2 (4)
N(4)-P(5)-N(5)	123.0 (2)	C(2)-C(1)-C(5)	107.7 (6)
		C(12)-C(11)-C(15)	109 (1)

Table IV. Positional Parameters for 5a

atom	x	y	z
Fe	0.2833 (1)	0.1968 (1)	0.5193 (1)
Cl(1)	−0.0038 (2)	0.4776 (2)	0.2696 (4)
Cl(2)	0.2626 (3)	0.5883 (2)	0.4649 (4)
Cl(3)	0.3448 (3)	0.3768 (3)	0.1008 (4)
Cl(4)	0.0858 (3)	0.2788 (3)	−0.1223 (3)
Cl(5)	−0.1399 (2)	−0.0127 (2)	0.0323 (3)
Cl(6)	−0.3963 (2)	0.0507 (2)	0.3273 (3)
Cl(7)	−0.1468 (3)	0.2471 (2)	0.5156 (3)
Cl(8)	−0.5502 (3)	0.1542 (3)	0.0547 (4)
Cl(9)	−0.3525 (3)	0.3831 (2)	0.1025 (4)
Cl(10)	−0.3042 (3)	0.0851 (3)	−0.2709 (3)
Cl(11)	−0.1783 (3)	0.3329 (2)	−0.1316 (3)
P(1)	0.0775 (2)	0.2230 (2)	0.2682 (3)
P(2)	0.1270 (2)	0.4331 (2)	0.3020 (3)
P(3)	0.1746 (3)	0.3264 (2)	0.0925 (3)
P(4)	−0.1172 (2)	0.1313 (2)	0.1396 (3)
P(5)	−0.2550 (2)	0.1649 (2)	0.3086 (3)
P(6)	−0.3748 (2)	0.2346 (2)	0.0906 (3)
P(7)	−0.2451 (2)	0.1984 (2)	−0.0822 (3)
N(1)	0.0907 (7)	0.3327 (6)	0.3602 (8)
N(2)	0.1614 (8)	0.4248 (6)	0.163 (1)
N(3)	0.1410 (7)	0.2283 (6)	0.1511 (8)
N(4)	−0.1964 (7)	0.1059 (6)	0.2383 (9)
N(5)	−0.2950 (7)	0.2446 (6)	0.2447 (9)
N(6)	−0.3610 (7)	0.1847 (6)	−0.0491 (9)
N(7)	−0.1361 (7)	0.1977 (6)	0.0327 (8)
C(1)	0.1136 (8)	0.1530 (7)	0.384 (1)
C(2)	0.1441 (9)	0.0670 (7)	0.354 (1)
C(3)	0.168 (1)	0.0383 (8)	0.483 (1)
C(4)	0.157 (1)	0.1048 (9)	0.592 (1)
C(5)	0.1234 (9)	0.1767 (8)	0.534 (1)
C(11)	0.403 (1)	0.332 (1)	0.504 (2)
C(12)	0.430 (1)	0.255 (2)	0.462 (2)
C(13)	0.450 (1)	0.221 (1)	0.585 (3)
C(14)	0.445 (2)	0.278 (2)	0.684 (2)
C(15)	0.441 (2)	0.344 (2)	0.634 (2)

The most unusual feature of the structure is the linkage of a cyclic trimeric and a cyclic tetrameric ring by a P–P

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[15] Biddlestone, M.; Bullen, G. J.; Dann, P. E.; Shaw, R. A. *J. Chem. Soc., Chem. Commun.* **1974**, 56.

covalent bond. This is the first example of a compound of this type. The P–P bond length was found to be 2.187 (2) Å. This is similar to the P–P distance in $N_6P_6Cl_8(\eta\text{-}C_5H_4)_2Fe$ studied previously[8] (2.219 (1) Å) and in both $(N_3P_3Cl_4Me)_2$[16] and $(N_3P_3Cl_4Ph)_2$.[17]

The P–N bond lengths and bond angles of the trimeric ring are similar to those in other metallocenylphosphazenes.[8] The P–N bond lengths near the bridgehead phosporus P(1) are longer (1.60 vs. 1.56 Å) and the bond angle at P(1) is constricted (117.6 vs. 119.8°) due to the presence of the attached tetramer unit. There appears to be little influence by the rest of the molecule on the cyclic tetrameric ring. The cyclic tetrameric ring adopts a "boat-like" conformation similar to the metastable K form of $(NPCl_2)_4$.[18] The P–N bond lengths and bond angles of the cyclic tetrameric ring are similar to those found in octachlorocyclotetraphosphazene: average 1.56 vs. 1.57 (1) Å for $(NPCl_2)_4$, N–P–N average 121.4 vs. 121.2(5)° for $(NPCl_2)_4$, and P–N–P average 133.7 vs. 131.3 (6)° for $(NPCl_2)_4$.

Experimental Section

Materials. Hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene (Firestone Tire and Rubber Co.) were purified by recrystallizations from hexane and by fractional sublimation. Ferrocene (Aldrich), (chloromercuri)ferrocene (Strem), *n*-butyllithium (Aldrich) (1.5 M solution in hexane), and *tert*-butyllithium (Aldrich) (2.6 M solution in pentane) were used as received. Diethyl ether (Fisher) was dried and distilled over sodium benzophenone ketyl. Column chromatography was performed using silica gel (230–400 mesh, VWR) as packing material. All reactions were run under an atmosphere of dry nitrogen in standard airless ware (Kontes).

Equipment. ^1H and ^{31}P NMR spectra were recorded on Varian EM 360 and CFT-20 NMR and Bruker WP-200 and WH-360 MHz FT NMR spectrometers. The ^{31}P shifts are relative to aqueous 85% H_3PO_4, with positive shifts downfield from this reference. The ^1H and ^{31}P shifts were referenced to internal $CHCl_3$. Infrared (KBr disks) spectra were recorded on a Perkin-Elmer 283B grating spectrometer. Electron-impact mass spectral results were obtained using an AEI MS 950 spectrometer and were tabulated by a linked computer. Mass spectral isotope patterns were also calculated and tabulated.

Reaction of Lithioferrocene with $(NPCl)_4$. Lithioferrocene was prepared from (chloromercuri)ferrocene (5.0 g, 11.9 mmol) and *n*-butyllithium (11.5 mL, 1.2 equiv) in diethyl ether (100 mL) at room temperature.[19] This solution was added to $(NPCl_2)_4$ (10.0 g, 21.7 mmol) in diethyl ether (100 mL) at 25 °C. (Addition of the lithioferrocene to a cooled (−78 °C) solution of $(NPCl_2)_4$ did not greatly increase the yield of product.) The mixture was stirred for 17 h at 20–25 °C. The solvent was removed and the residue chromatographed. Elution with hexane gave ferrocene, chloroferrocene, and $(NPCl_2)_4$, identified by ^1H NMR or ^{31}P NMR. Further elution with dichloromethane–hexane (1:1) gave a yellow band that yielded orange crystals of $N_4P_4Cl_6[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]_2$ (4) (0.99 g, 11%, mp 135 °C).

For 4: IR 2910 (w, CH), 1220, 1180 (vs, PN), 580 (vs, PCl) cm^{-1}. ^1H NMR δ 4.761, 4.613, 4.574, 4.535 (all m, 2 H), 4.383 (s, 10 H). ^{31}P NMR (^1H decoupled) 36.9 (dt, P_{ClM_2}, $J_{P(A)NP(X)} = 28$ Hz), $J_{P(A)NP(X)NP(M)} = 4$ Hz), 20.0 (dd, P_{Cl_2}, $J_{P(M)NP(X)} = 52$ Hz, $J_{P(M)NP(X)NP(A)} = 4$ Hz), −2.7 (dt, P_{ClNP}, $J_{P(X)NP(M)} = 52$ Hz, $J_{P(X)NP(A)} = 28$ Hz) ppm. The ^1H-coupled resonance at 36.9 ppm was considerably broadened due to the cyclopentadienyl ring hydrogen atoms. The other resonances were the same, with similar coupling constants. MS calcd for $C_{20}H_{18}H_4Cl_6Fe_2P_4$, 759.7311; found, 759.7316 (6.1 ppm). Anal. Calcd for 4: C, 31.50; H, 2.38; N, 7.35. Found: C, 31.66; H, 2.25; N, 7.22.

Reaction of Dilithioferrocene with $(NPCl_2)_4$. A solution of dilithioferrocene was prepared by the addition of *tert*-butyllithium (30 mL, 2.5 equiv, 30 mmol) to a solution of ferrocene (5 g, 26.9 mmol) at 0 °C, followed by stirring for 4 h at 0 °C. Evolution of butane was noted. This solution was then added to a solution of $(NPCl_2)_4$ (10 g, 21.7 mmol) in diethyl ether (75 mL) at −78 °C, and the mixture was allowed to warm to room temperature. The mixture was then stirred for 17 h. The solvent was removed and the residue chromatographed. Elution with hexane gave ferrocene, traces of dichloroferrocene, and $(NPCl_2)_4$, identified by ^1H NMR and ^{31}P NMR. The other metallophosphazene-type products could not be identified.

Reaction of Lithioferrocene with 1:1 $(NPCl_2)_4/(NPCl_2)_3$. A solution of lithioferrocene was prepared as described above from a transmetalation reaction between (chloromercuri)ferrocene (5.0 g, 11.9 mmol) and *n*-butyllithium (11.5 mL, 1.2 equiv) in diethyl ether (75 mL) at room temperature. This solution of lithioferrocene was added to 50% $(NPCl_2)_4$ (5.0 g, 10.9 mmol) and 50% $(NPCl_2)_3$ (3.8 g, 10.9 mmol) in diethyl ether (100 mL) at −78 °C. The mixture was then allowed to warm to room temperature and was stirred for 17 h. The solvent was removed, and the residue was chromatographed. Elution with hexane gave a mixture of $(NPCl_2)_3$, $(NPCl_2)_4$, ferrocene, and chloroferrocene, identified by ^{31}P NMR and ^1H NMR. Further elution with dichloromethane–hexane (1:9) gave a yellow band which yielded orange crystals of $N_3P_3Cl_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ (0.065 g, 1.1%). This compound was detected by ^{31}P NMR spectroscopy. Further elution with dichloromethane–hexane (1:4) gave another yellow band, which yielded orange crystals of $N_7P_7Cl_{11}(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ (**5a**) (0.57 g, 5.4%, mp 215 °C). Further elution with dichloromethane–hexane (2:3) gave another yellow band, from which orange crystals of $N_6P_6Cl_9(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ (0.073 g, 0.8%) were obtained. This compound was also detected by ^{31}P NMR spectroscopy. Further elution with dichloromethane–hexane (1:1) gave a final yellow band, from which orange crystals of $N_4P_4Cl_6[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]_2$ (4) (0.57 g, 6.3%) were obtained.

Reaction of Dilithioferrocene with 1:1 $(NPCl_2)_4/(NPCl_2)_3$. A solution of dilithioferrocene was prepared as described above, by stirring together a mixture of ferrocene (5 g, 26.9 mmol) and *tert*-butyllithium (30 mL, 2.5 equiv, 30 mmol) in diethyl ether (75 mL) for 6 h at 25 °C. This solution was then added to a solution of $(NPCl_2)_4$ (5.0 g, 10.9 mmol) and $(NPCl_2)_3$ (3.8 g, 10.9 mmol) in diethyl ether (100 mL) at −78 °C. The mixture was then allowed to warm to room temperature and was stirred for 17 h. The solvent was removed and the residue chromatographed. Elution with hexane gave a mixture of $(NPCl_2)_4$, ferrocene, and dichloroferrocene, identified by ^{31}P NMR and ^1H NMR, respectively. Further elution with dichloromethane–hexane (1:4) gave a yellow band from which orange crystals of $N_7P_7Cl_{11}(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_4X)$ (**5a**, 10%; **5b**, 90%) (**a**, X = H, **b**, X = Cl) (4.43 g, 17.9%, mp 165 °C) were obtained.

For **5a,b**: IR 3100 (w, CH), 1300, 1180 (vs, PN) cm^{-1}. ^1H NMR δ 4.718, 4.669 (both m, 2 H), 4.435 (s, 5 H) for **5a**; 4.718, 4.680, 4.660, 4.388 (all m, 2 H) for **5b**. ^{31}P NMR 22.0 (m), −1.07 (m), −6.94 (m) ppm. MS calcd for $C_{10}H_9N_7Cl_{11}FeP_7$, 885; found, 885, calcd for $C_{10}H_8N_7Cl_{12}FeP_7$, 920; found, 920. Anal. Calcd for **5a**: C, 13.50; H, 1.02; N, 11.02. Found: C, 13.41; H, 1.09; N, 10.93. Anal. Calcd for **5b**: C, 12.99; H, 0.87; N, 10.61. Found: C, 12.89; H, 0.91; N, 10.45.

Reaction of 5a,b with Sodium Trifluoroethoxide. Compound **5a,b** (50 mg, 0.05 mmol) was dissolved in THF (0.3 mL) in an 8-mm NMR tube. A solution of sodium trifluoroethoxide was prepared by the addition of sodium (1.6 g, 0.070 mmol) to a solution of trifluoroethanol (9.0 mL, 0.116 mmol) in THF (100 mL). A 0.7-mL portion of this solution was added to the NMR tube. A precipitate of NaCl was observed. Carbon tetrachloride (200 μL, 2.07 mmol) was added, and the complete conversion to **6a,b** and **7** was followed by ^{31}P NMR spectroscopy. ^{31}P NMR (**6a,b**) 35.6 (t), 16.5 (d, $J_{PNP} = 56$ Hz) ppm; (**7**) −1.1 (s) ppm.

X-ray Data Collection for 4 and 5a. Crystals of 4 were obtained from diethyl ether and of **5a** from a hexane/methylene chloride medium. Crystals of 4 and **5a** were mounted along the longest axes in a random orientation on an Enraf-Nonius CAD-4 diffractometer. They were optically centered, and 25 reflections were located. Least-squares treatment indicated the lattice dimensions and space groups shown in Table V.

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Table V. Summary of Crystal Data and Intensity Collection Parameters

compd	4	5a
cryst size, mm	0.14 × 0.65 × 0.65	0.23 × 0.32 × 0.43
fw, amu	762.7	889.9
space group	$P2_1/c$	$P\bar{1}$
a, Å	11.199 (3)	12.899 (5)
b, Å	22.774 (7)	14.206 (3)
c, Å	11.504 (7)	10.003 (4)
α, deg		99.77 (3)
β, deg	104.81 (3)	105.76 (3)
γ, deg		112.99 (2)
vol, Å^3	2837 (4)	1543 (2)
Z	4	2
d(calcd), g/cm^3	1.786	1.915
2θ limits, deg	2.80–44.50	2.80–43.24
scan width (A + 0.347 tan θ), deg	0.70	1.00
scan rate, deg min^{-1}	1.0–5.0	1.0–5.0
unique obsd data	2737	2562
μ, cm^{-1}	18.37	18.29
R/R_w	0.055/0.063	0.053/0.061
esd	3.58	2.75
data/parameter	7.22	7.88
drift correctn		
empirical	1.000–1.036	0.974–1.000
anisotropic	0.948–1.124	0.911–1.027
largest residual peak, e Å^{-3}	0.74	0.53
av shift/error	0.08	0.16

Intensity data were measured for 3573 (for **4**) and 3090 (for **5a**) reflections using single-crystal, graphite monochromated Mo Kα radiation (λ = 0.71073 Å). From these, 2737 unique reflections (after averaging symmetry related reflections, mean discrepancy 2.2%) were considered observed ($I > 2\sigma(I)$) for **4** and 2562 for **5a**. Three standard reflections were measured every 2 h of X-ray exposure time and were used to place the data on a common scale. No absorption corrections were applied (μ = 18.37 cm^{-1} for **4** and 18.29 cm^{-1} for **5a**), since ψ scans indicated that the absorptions were not severe. The data were corrected for Lorentz and polarization factors before use in the structure solution.

X-ray Structure Determination for 4 and 5a. All atoms including hydrogen atoms were located from Patterson and electron density difference syntheses.[20] In the final full-matrix least-squares cycle, 379 parameters were refined for **4** and 325 for **5a**, including the positional and anisotropic thermal parameters for the non-hydrogen atoms. Positional parameters for hydrogen atoms at fixed isotropic thermal parameters (B = 5.0 Å^2) were refined for **4** and were placed at fixed positions (C–H distance = 0.97 Å) for **5a**. Complex scattering factors corrected for anomalous dispersion were used.[21]

Acknowledgment. We thank the U.S. Army Research Office for the support of this work.

Registry No. 1 (X = Cl), 940-71-6; 2 (X = Cl), 2950-45-0; **4**, 88644-54-6; **5a**, 88644-55-7; **5b**, 88644-56-8; **6a**, 84462-65-7; **6b**, 88644-57-9; **7**, 562-88-9; $N_3P_3Cl_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$, 88644-58-0; $N_6P_6Cl_9(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$, 88656-94-4; LiCpFeCp, 1271-15-4; LiCpFeCpLi, 33272-09-2; $NaOCH_2CF_3$, 420-87-1.

Supplementary Material Available: Listings of anisotropic thermal parameters for 4 and 5a, positional and isotropic thermal parameters of the hydrogen atoms for 4 and 5a, least squares planes for 4, observed and calculated structure factor amplitudes for 4 and 5a, and comprehensive lists of bond lengths and angles for 4 and 5a (Tables VI–XIV) (47 pages). Ordering information is given on any current masthead page.

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(20) All parts of the programs used in this study were part of the Enraf-Nonius Structure Determination Package (SDP Plus, Version 1.0), Enraf-Nonius, Delft, Holland, 1982, and implemented on a PDP 11/34 computer.

(21) The function minimized in the least squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/(\sigma(F_o))^2$ and $R = \sum(||F_o| - |F_c||)/\sum(|F_o|)$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.