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Synthesis and Structure of Metallocene Cyclophosphazene Derivatives[1a,b]

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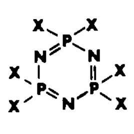
Abstract: Significant mechanistic differences exist between the reactions of mono- and dilithioferrocene or ruthenocene with P–F or P–Cl bonds in cyclophosphazenes. The fluorophosphazenes $(NPF_2)_3$ and $(NPF_2)_4$ react by a nucleophilic-type substitution pathway to yield mono and bis nongeminal metallocenyl derivatives (**6–9**) or transannular bridged metallocenylphosphazenes (**10–13**). By contrast, the chlorophosphazene $(NPCl_2)_3$ reacts initially by a metal–halogen exchange pathway to generate an unusual series of metallocenyl cyclophosphazenes and -bi(cyclophosphazenes) (**18–20**), including examples in which chloro metallocene units are linked to phosphorus (**21**,**22**) and one in which a ferrocene unit bridges the P–P linkage site connecting two cyclophosphazene rings (**23**). Cleavage of the phosphazene skeleton occurs with $(NPCl_2)_4$. The molecular structures of four ferrocenyl- and ruthenocenylcyclophosphazenes prepared by these routes have been determined by X-ray diffraction techniques. Confirmation of a covalent linkage between a cyclopentadienyl group and the phosphazene ring was obtained for the prototype, $N_3P_3F_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ (**6a**). The effect of transannular bridging of the phosphazene ring by metallocene units was studied in $N_3P_3F_4(\eta\text{-}C_5H_4)_2Ru$ (**10b**) and $N_4P_4F_6(\eta\text{-}C_5H_4)_2Ru$ (**12b**). The structure of species $N_6P_6Cl_8(\eta\text{-}C_5H_4)_2Fe$ (**23**), with two phosphazene rings linked by a P–P bond and a ferrocenyl bridging site, was also examined. The structural peculiarities are a consequence of the low deformability of the metallocenyl units and the relatively high flexibility of the phosphazene rings. Crystal data: Crystals of **6a** are monoclinic with the space group $C2/c$, $a = 19.946$ (9) Å, $b = 6.922$ (2) Å, $c = 22.340$ (9) Å, $\beta = 111.19$ (5)°, and $V = 2876$ (4) Å^3 and $Z = 8$. Crystals of **10b** are triclinic with the space group $P\bar{1}$ and with $a = 8.029$ (2) Å, $b = 8.286$ (4) Å, $c = 11.555$ (7) Å, and $\alpha = 87.16$ (4)°, $\beta = 87.91$ (3)°, $\gamma = 61.83$ (3)°, and $V = 676.7$ (7) Å^3 and $Z = 2$. Crystals of **12b** are orthorhombic with the space group $Pbca$ and with $a = 15.534$ (3) Å, $b = 14.610$ (3) Å, $c = 14.430$ (2) Å, and $V = 3275$ (2) Å^3 and $Z = 8$. Crystals of **23** are monoclinic with the space group $P2_1/n$ and with $a = 11.064$ (2) Å, $b = 13.019$ (4) Å, $c = 18.196$ (3) Å, $\beta = 102.55$ (3)°, and $V = 2558$ (2) Å^3 and $Z = 4$.

The reactions of organometallic reagents with halophosphazenes **1**–**3** (X = halogen) are of considerable importance[1-12] because



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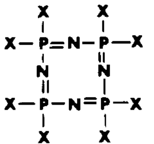

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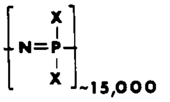

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they provide a key to the synthesis of a wide range of phosphazene high polymers that are not accessible by any other route. Such high polymers are expected to possess unique physical properties not found in conventional organic macromolecules. Specific high polymeric phosphazenes with transition-metal organometallic side groups are of interest as prospective catalytic or electroactive materials. Among these, polyphosphazenes with metallocenyl[13] side groups are of special interest. Here we describe the reactions of lithiometallocenes[14] with **1** and **2** and discuss the molecular structures of four products. These cyclophosphazene species function as small molecule reaction and structural models for **3**.[2]

Results and Discussion

In the following sections the reactions of mono- or dilithioferrocene or mono- or dilithioruthenocene with the fluorophosphazenes $(NPF_2)_3$ and $(NPF_2)_4$ will be described first, and these will then be constrasted with the reactions of the same reagents with the chlorophosphazenes $(NPCl_2)_3$ and $(NPCl_2)_4$.

Reactions of Mono- and Dilithiometallocenes with $(NPF_2)_3$ and $(NPF_2)_4$. Scheme I contains a summary of the products isolated from these reactions. The ferrocenyl and ruthenocenyl anions behaved similarly.

Fluorophosphazenes **4** and **5** reacted with the monolithiometallocenes by a high-yield, nucleophilic, halogen replacement pathway, with first one (**6** or **8**) and then two metallocene units (**7** or **9**) becoming linked to the phosphazene ring. The substitution pattern was nongeminal for both the phosphazene trimer and tetramer, presumably for steric reasons, and with a predominantly trans configuration found for **7**. A nongeminal pathway has also been reported for the reaction of phenyllithium or *tert*-butyllithium with $(NPF_2)_3$.[15a,b] Species **6** and **8** were converted to the trifluoroethoxy derivatives (**14** and **15**) without detectable cleavage

$$\underset{\mathbf{6}}{N_3P_3F_5(C_5H_4MC_5H_5)} \xrightarrow[\text{-NaF}]{\substack{NaOCH_2CF_3\\ THF}} \underset{\mathbf{14}}{N_3P_3(OCH_2CF_3)_5(C_5H_4MC_5H_5)}$$

$$\underset{\mathbf{8}}{N_4P_4F_7(C_5H_4MC_5H_5)} \xrightarrow[\text{-NaF}]{\substack{NaOCH_2CF_3\\ THF}} \underset{\mathbf{15}}{N_4P_4(OCH_2CF_3)_7(C_5H_4MC_5H_5)}$$

of the skeleton or reaction of the metallocene unit. This is an important result from the viewpoint of eventual polymer synthesis.

Dilithioferrocene and dilithioruthenocene reacted with an excess of $(NPF_2)_3$ in diethyl ether at −78 °C to yield the transannular,

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(1) (a) For a previous paper in this series, see: Allcock, H. R.; Wagner, L. J.; Levin, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 1321. (b) For a preliminary communication on a part of this work, see: Suszko, P. R.; Whittle, R. R.; Allcock, H. R. *J. Chem. Soc., Chem. Commun.* **1982**, 960.

(2) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.

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

(4) Allcock, H. R.; Chu, C. T.-W. *Macromolecules* **1979**, *12*, 551.

(5) Allcock, H. R.; Evans, T. L.; Patterson, D. B. *Macromolecules* **1980**, *13*, 201.

(6) Evans, T. L.; Patterson, D. B.; Suszko, P. R.; Allcock, H. R. *Macromolecules* **1981**, *14*, 218.

(7) Harris, P. J.; Allcock, H. R. *J. Am. Chem. Soc.* **1978**, *100*, 6512.

(8) Allcock, H. R.; Harris, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 6221.

(9) Allcock, H. R.; Harris, P. J.; Connolly, M. S. *Inorg. Chem.* **1981**, *20*, 11.

(10) Allcock, H. R.; Scopelianos, A. G.; O'Brien, J. P.; Bernheim, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 350.

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

(12) Allcock, H. R.; Greigger, P. P.; Wagner, L. J.; Bernheim, M. Y. *Inorg. Chem.* **1981**, *20*, 716.

(13) Wilkinson, G.; Cotton, F. A. *Prog. Inorg. Chem.* **1959**, *1*, 1; "Advanced Inorganic Chemistry", 4th Ed.; Wiley: New York, 1980; pp 99-106, 1161-1174.

(14) Blake, A. J.; Mayers, F. R.; Osborne, A. G.; Rosseinsky, D. R. *J. Chem. Soc., Dalton Trans.* **1982**, 2379.

(15) (a) Allen, C. W.; Moeller, T. *Inorg. Chem.* **1968**, *7*, 2177. (b) Ramachandran, K.; Allen, C. W. *J. Am. Chem. Soc.* **1982**, *104*, 2396.

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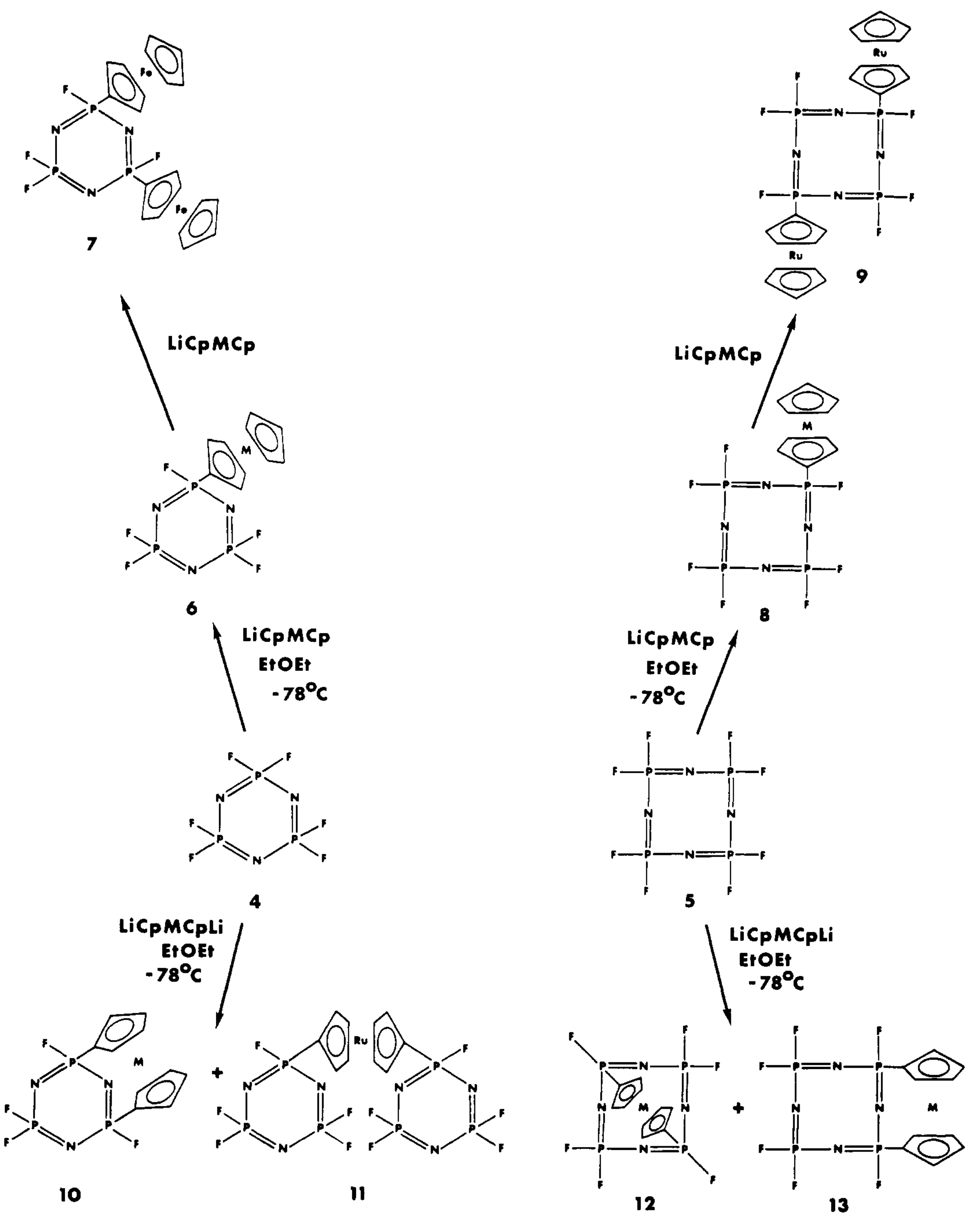
Scheme I



Cp = cyclopentadienyl. a, M = Fe; b, M = Ru.

intramolecular coupled products **10**, again presumably by a nucleophilic substitution process. In addition, the reaction with dilithioruthenocene yielded a small amount (5.0%) of an *inter*molecular coupled product (**11**).

Similarly, the cyclic tetramer $(NPF_2)_4$ reacted with the dilithiometallocenes to give the two isomeric transannular substitution products of types **12** and **13**. Both isomers were formed in approximately equal amounts from dilithioferrocene, but the 1,5-isomer (**12b**) predominated when dilithioruthenocene was employed. All these reactions follow logically from the known behavior of lithiometallocenes with other electrophiles. The transannular bridged derivatives can be compared with the wide range of related bridged metallocenes (metallocenophanes) reported during recent years from several laboratories.[16-18]

Reactions of Mono- and Dilithiometallocene with $(NPCl_2)_3$ and $(NPCl_2)_4$. The behavior of the chlorophosphazenes in the presence of the same organometallic reagents was quite different, as shown in Scheme II. The monolithiometallocenes reacted with hexachlorocyclotriphosphazene (**16**) in a complex manner to yield the monometallocenyl derivative **18** and a bi(cyclophosphazene), **19**. In general, the ferrocenyl and ruthenocenyl derivatives behaved in a similar manner, except that the latter reagent also brought

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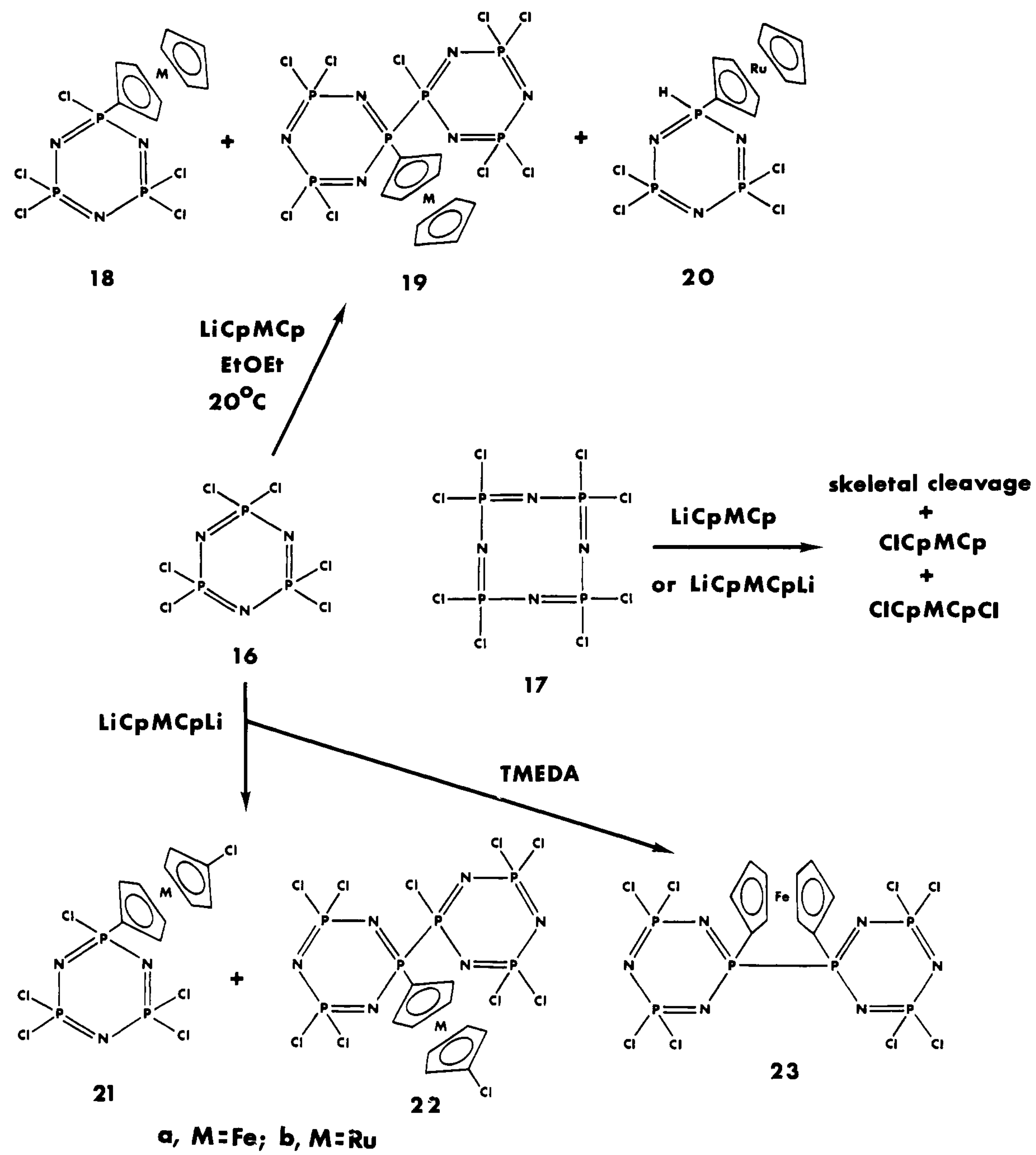
(16) Osborne, A. G.; Whitely, R. H. *J. Organomet. Chem.* **1975**, *101*, C27. Osborne, A. G.; Whitely, R. H.; Meads, R. E. *Ibid.* **1980**, *193*, 345.

(17) Fischer, A. B.; Kinney, J. B.; Staley, R. H.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 6501.

(18) Seyferth, D.; Withers, H. P. *Organometallics* **1982**, *1*, 1275.

Scheme II



about the formation of a trace of the hydridophosphazene **20**.

The reactions of the dilithiometallocenes with $(NPCl_2)_3$ were similarly complex. First, no transannular analogues of **10**, **12**, or **13** were detected. Instead, $(NPCl_2)_3$ reacted with dilithioferrocene or dilithioruthenocene to give species **21** and **22** as the main products. The presence of a chlorine atom attached to a cyclopentadienyl group in both of these products provides a clue to the reaction mechanism, and this will be discussed later.

Second, it is well-known that the reactivity of organolithium reagents may be enhanced in the presence of an electron-rich chelating amine, such as tetramethylethylenediamine (TMEDA).[19] Dilithioferrocene–TMEDA reacted with an excess of $(NPCl_2)_3$ to give **21a**, as before, in good yield, together with a smaller amount of **18a**. However, species **23**, in which the metallocene unit spans the P–P linkage site between the two phosphazene rings, was also obtained.

The cyclic tetramer $(NPCl_2)_4$ reacted with the mono- and dilithiometallocenes with apparent decomposition of the phosphorus–nitrogen skeleton and formation of chlorometallocene.

Reaction Mechanisms. The reactions between both mono- and dilithiometallocenes and *fluoro*phosphazenes appear to proceed via direct nucleophilic substitution by the organometallic reagent on the phosphazene.

The reactions of the chlorophosphazenes are clearly more complex. Consider first the interaction of monolithiometallocenes with $(NPCl_2)_3$. Both substitution and metal–halogen exchange reactions are possible. Scheme III illustrates two alternative pathways that could be followed. If the first step involves nucleophilic substitution to yield **18**, a metal–halogen exchange process at the geminal chlorine atom could then lead to the key intermediate, **26**. Species **26** could readily react with $(NPCl_2)_3$ to yield the bi(cyclophosphazene) **19**. This is the least complex explanation for the formation of the products.

Alternatively, the first step could involve a metal–halogen exchange process between $(NPCl_2)_3$ and the lithiometallocene to yield ionic intermediate **27**. Subsequent substitution at the

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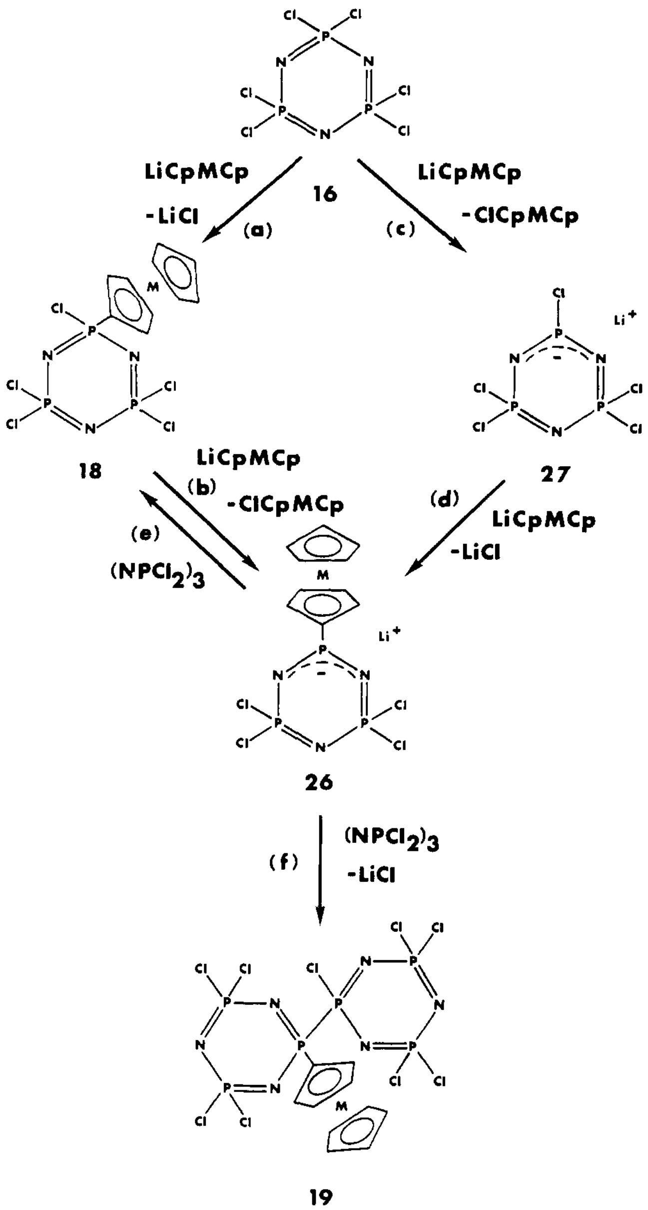
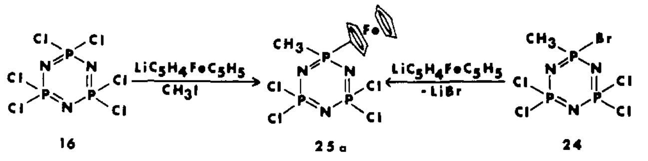
[19] Rausch, M. D.; Ciappenelli, D. J. *J. Organometal. Chem.* **1967**, *10*, 127.

Scheme III

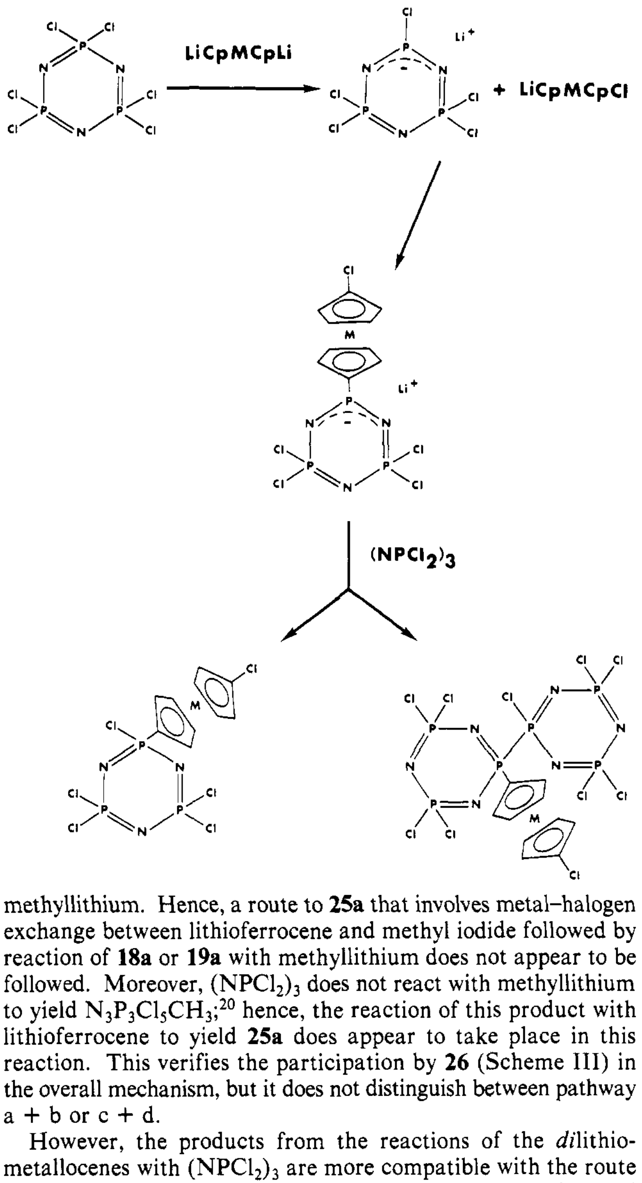


tricoordinate phosphorus atom would give **26**. The formation of **18** would require a metal–halogen exchange reaction between **26** and $(NPCl_2)_3$, while product **19** would be formed as before by a substitutive interaction between **26** and $(NPCl_2)_3$. If this is the case, the ratio of **18** to **19** in the product mixture would reflect the ease of metal–halogen exchange vs. substitution when **26** reacts with $(NPCl_2)_3$.

Several observations are pertinent to the mechanism. First, evidence was obtained for the existence of intermediate **26** from the reaction of lithioferrocene with $(NPCl_2)_3$ in the presence of an equimolar amount of methyl iodide as a "trap" for species **26**. A ^{31}P NMR spectrum of the resultant mixture was compatible with the presence of **25a** and **18a** as the principal products, together with a small quantity of **19a**. Species $N_3P_3Cl_5CH_3$ was not detected. Compound **25a** was synthesized independently by the reaction of **24** with monolithioferrocene. However, species **18a** or **19a** does not yield **25a** or methylferrocene in the presence of methyllithium. Hence, a route to **25a** that involves metal–halogen exchange between lithioferrocene and methyl iodide followed by reaction of **18a** or **19a** with methyllithium does not appear to be followed. Moreover, $(NPCl_2)_3$ does not react with methyllithium to yield $N_3P_3Cl_5CH_3$;[20] hence, the reaction of this product with lithioferrocene to yield **25a** does appear to take place in this reaction. This verifies the participation by **26** (Scheme III) in the overall mechanism, but it does not distinguish between pathway a + b or c + d.



Scheme IV



However, the products from the reactions of the *di*lithiometallocenes with $(NPCl_2)_3$ are more compatible with the route that initially involves steps c and d. If steps a and b were followed initially, it would be expected that at least small amounts of transannular substitution products would be formed in the same way as found for $(NPF_2)_3$. In fact, no products of this type were isolated or detected. On the other hand (Scheme IV), if metal–halogen exchange was the initial reaction followed by a substitution by the remaining organolithium unit on the metallocene, then all the metallocenylphosphazene products would bear a chlorine substituent on the unbound cyclopentadienyl ring, as was observed.

The key point in this proposition is that metal–halogen exchange between the dilithiometallocenes and $(NPCl_2)_3$ results mainly in the replacement of only one lithio unit by chlorine, not two. This is a reasonable supposition. If the dichlorometallocene were formed, it would be unlikely to react with **27** to yield **21**, because of its preferred tendency to undergo metal–hydrogen exchange with organolithium reagents.[14] An attempt to react dichloroferrocene with **27** did not yield **21**.

Finally, the role played by species **26** is compatible with evidence obtained for other systems that chlorophosphazenes are extremely prone to metal–halogen exchange. This is illustrated in the following section.

Relationship to Other Organometallic Reactions. The results obtained in this work show some similarities to the reactions of

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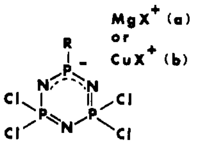
(20) Harris, P. J.; Fadeley, C. L. *Inorg. Chem.* **1983**, *22*, 561.

Grignard,[3] organolithium,[4,5,10,11,15] organocopper,[7-9] and transition-metal anion[7-9] reagents with $(NPCl_2)_3$ and $(NPF_2)_3$ and some important differences.

First, the pattern of virtually exclusive substitution with $(NPF_2)_3$ and metal–halogen exchange plus substitution with $(NPCl_2)_3$ is found when the organometallic reagent is RMgX.[3] The available evidence suggests that this is also at least partly true for KFe$(CO)_2$Cp[1a] or organolithium reagents.[5,15]

For the reactions of $(NPCl_2)_3$, it has been shown that metal–halogen exchanged intermediates similar to **26** are formed when Grignard or organocopper reagents are employed.[3,7-9] These intermediates are depicted in **31**. Of these, the copper intermediate **31b** is more stable in solution at 25 °C than are **31a** or **26**, but all three react with methyl iodide to yield the geminal disubstituted derivatives **32**. Similarly, all three species, **26**, **31a**, and **31b**, yield hydridophosphazenes when treated with alcohols,[3,7-9] although this tendency is least obvious with the metallocenyl systems **26**.



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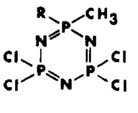

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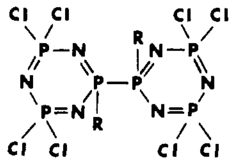
Phosphazene anions derived from both Grignard and lithiometallocene reagents react with $(NPCl_2)_3$ or $N_3P_3Cl_5R$ to generate P–P linked bi(cyclophosphazene) dimers, but no evidence has yet been obtained that the copper intermediate, **31b**, behaves in the same way. This may be a consequence of the generally lower reactivity of the copper intermediate. Although Grignard reagents yield exclusively symmetrically substituted dimers of type **33**, the lithiometallocenes yielded only asymmetrically substituted dimers **34**. Presumably, this reflects a greater steric hindrance in the reaction of **26** with **18** than with $(NPCl_2)_3$.

It has been shown in earlier work[21,22] that the P–P bonds in Grignard-derived **33** can be cleaved by trifluoroethoxide or by LiEt$_3$BH. As shown in Scheme V, species **23** undergoes similar cleavage reactions.



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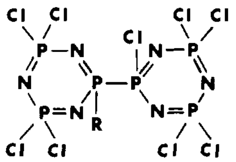

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Finally, a correlation exists between the liberation of methyl chloride during metal–halogen exchange between $(NPCl_2)_3$ and methylmagnesium halides[3] and the formation of products, such as **21**, from the dilithiometallocene reactions. In the latter case, the generation of $LiC_5H_4MC_5H_4Cl$ is probably followed by immediate attack on $N_3P_3Cl_5^-$ to generate an analogue of **26** within the confines of a solvent cage.

Structure Proof for Reaction Products. The structures of compounds **6–25** were determined unambiguously by a combination of ^{31}P, ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy, mass spectrometry, and, in selected cases, elemental microanalysis. These results are described in the Experimental Section and in the supplementary material. In addition, four of the new compounds, **6a**, **10b**, **12b**, and **23**, were studied by single-crystal X-ray diffraction methods.

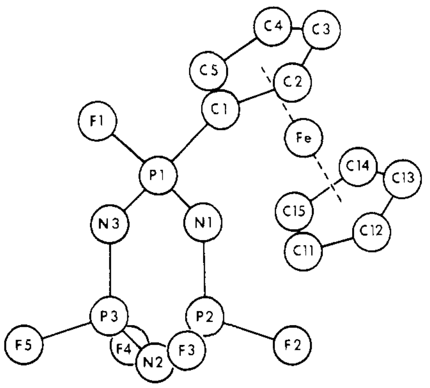

Figure 1. Atom designations and molecular structure for $N_3P_3F_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ (**6a**).

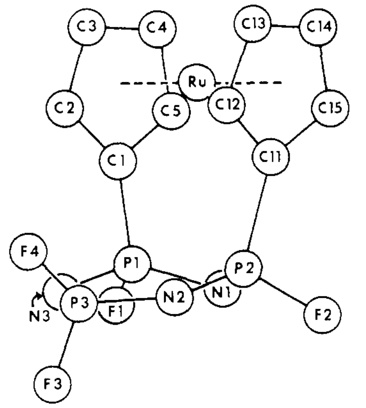

Figure 2. Atom designations and molecular structure for $N_3P_3F_4(\eta\text{-}C_5H_4)_2Ru$ (**10b**).

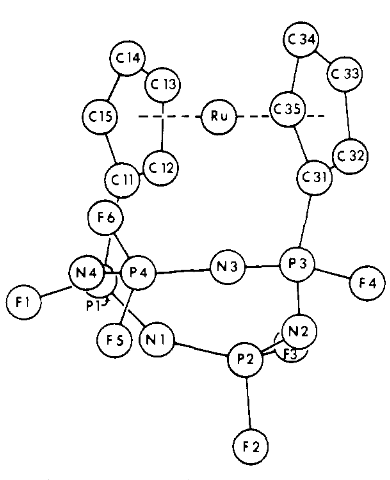

Figure 3. Atom designations and molecular structure for $N_4P_4F_6(\eta\text{-}C_5H_4)_2Ru$ (**12b**).

X-ray Structural Examination of 6a, 10b, 12b, and 23: General Aspects. The structures of species **6a**, **10b**, **12b**, and **23** are of special interest for the following reasons. Compound **6a** is the simplest (cyclophosphazenyl)metallocene synthesized so far, and it serves as a starting point for comparisons with the more complex systems. Species **10b** is the simplest available transannular bridged (cyclophosphazenyl)ruthenocene derivative. It is a key compound for an assessment of the relative flexibilities of the cyclotriphosphazene and ruthenocene units. Compound **12b** is important because its 1,5-transannular structure permits the phosphazene ring to undergo its maximum distortion. Species **6a**, **10b**, and **12b** are of interest also because they are *fluoro*phosphazenes, compounds in which the π-system within the phosphazene rings is expected to attain its highest degree of influence.[23] The bi(cyclophosphazene) **23** is an unusual structure that offers opportunities for the assessment of the effects of phosphazene–phosphazene ring bonding coupled with the influence of the

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(21) Allcock, H. R.; Connolly, M. S.; Harris, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 2482.

(22) Allcock, H. R.; Connolly, M. S.; Whittle, R. R. *Organometallics* **1983**, *2*, 1514.

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

Table I. Summary of Crystal Data and Intensity Collection Parameters

	compound			
	6a	10b	12b	23
f_W, amu	415.0	440.2	523.2	737.5
space group	$C2/c$	$P\bar{1}$	$Pbca$	$P2_1/n$
a, Å	19.946 (9)	8.029 (2)	15.534 (3)	11.064 (2)
b, Å	6.922 (2)	8.286 (4)	14.610 (3)	13.019 (4)
c, Å	22.340 (9)	11.555 (7)	14.430 (2)	18.196 (3)
α, deg		87.16 (4)		
β, deg	111.19 (5)	87.91 (3)		102.55 (3)
γ, deg		61.83 (3)		
V, Å^3	2876 (4)	676.7 (7)	3275 (2)	2558 (2)
Z	8	2	8	4
d(calcd), g/cm^3	1.917	2.160	2.122	1.915
2θ limits	3.0-51.0	3.0-48.0	3.0-47.5	3.0-43.7
scan width (A + 0.347 tan θ), deg	0.80	1.50	0.70	0.70
scan rate, deg min^{-1}	1.0-4.0	1.0-7.0	1.0-5.0	1.0-5.0
unique obsd data[a,b]	1938	1958	2005	2590
μ, cm^{-1}	14.65	15.31	13.97	18.19
R/R_W	0.052/0.047	0.065/0.076	0.041/0.045	0.036/0.039
esd	3.015	2.373	3.226	2.212
data/parameter	8.57	10.31	8.87	8.52
drift correction	0.925-1.109	0.998-1.120	0.962-1.044	0.958-1.050
largest residual peak, e Å^{-3}	0.27	0.92	0.25	0.26
max shift/error	0.03	0.00	0.00	0.08

[a] $I > 2\sigma(I)$. [b] The total numbers of reflections obtained were 2982, 2125, 2835, and 3421 for the four structures.

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) (esd) for $N_3P_3F_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ (**6a**)

Fe-Cp$_1$[a]	1.651 (4)	F(1)-P(1)-C(1)	103.0 (1)
Fe-Cp$_2$[a]	1.669 (4)	N(1)-P(1)-N(3)	116.7 (1)
P(1)-C(1)	1.761 (3)	F(2)-P(2)-F(3)	98.4 (1)
P(1)-F(1)	1.543 (2)	N(1)-P(2)-N(2)	120.2 (1)
P(1)-N(1)	1.592 (3)	F(4)-P(3)-F(5)	97.1 (1)
P(1)-N(3)	1.580 (3)	N(2)-P(3)-N(3)	120.4 (1)
P(2)-F(2)	1.525 (2)	P(1)-N(1)-P(2)	121.6 (2)
P(2)-F(3)	1.525 (2)	P(2)-N(2)-P(3)	119.6 (2)
P(2)-N(1)	1.543 (3)	P(1)-N(3)-P(3)	121.2 (2)
P(2)-N(2)	1.557 (3)	C(2)-C(1)-C(5)	109.3 (3)
P(3)-F(4)	1.526 (2)		
P(3)-F(5)	1.529 (2)		
P(3)-N(2)	1.554 (3)		
P(3)-N(3)	1.558 (3)		

[a] Distance between atom and ring plane.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) (esd) for $N_3P_3F_4(\eta\text{-}C_5H_4)_2Ru$ (**10b**)

Ru-Cp$_1$[a]	1.81	C(1)-P(1)-F(1)	105.8 (3)
Ru-Cp$_2$[a]	1.81	N(1)-P(1)-N(3)	115.2 (3)
P(1)-C(1)	1.791 (7)	C(11)-P(2)-F(2)	105.0 (3)
P(1)-F(1)	1.536 (5)	N(1)-P(2)-N(2)	116.2 (4)
P(1)-N(1)	1.586 (6)	F(3)-P(3)-F(4)	98.4 (3)
P(1)-N(3)	1.596 (6)	N(2)-P(3)-N(3)	121.3 (3)
P(2)-C(11)	1.757 (8)	P(1)-N(1)-P(2)	113.1 (4)
P(2)-F(2)	1.544 (5)	P(2)-N(2)-P(3)	117.4 (4)
P(2)-N(1)	1.588 (7)	P(1)-N(3)-P(3)	118.9 (4)
P(2)-N(2)	1.605 (7)	C(2)-C(1)-C(5)	108.9 (6)
P(2)-F(3)	1.549 (5)	C(12)-C(11)-C(15)	105.6 (7)
P(3)-F(4)	1.520 (5)		
P(3)-N(2)	1.565 (7)		
P(3)-N(3)	1.549 (7)		

[a] Distance between atom and ring plane.

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) (esd) for $N_4P_4F_6(\eta\text{-}C_5H_4)_2Ru$ (**12b**)

Ru-Cp$_1$[a]	1.820 (5)	C(11)-P(1)-F(1)	103.0 (2)
Ru-Cp$_2$[a]	1.816 (5)	N(1)-P(1)-N(4)	120.1 (2)
P(1)-C(11)	1.755 (4)	N(1)-P(2)-N(2)	124.5 (2)
P(1)-F(1)	1.556 (3)	F(2)-P(2)-F(3)	98.9 (3)
P(1)-N(1)	1.569 (4)	C(31)-P(3)-F(4)	103.2 (2)
P(1)-N(4)	1.566 (4)	N(2)-P(3)-N(3)	118.8 (2)
P(2)-F(2)	1.526 (3)	F(5)-P(4)-F(6)	94.9 (3)
P(2)-F(3)	1.542 (4)	N(3)-P(4)-N(4)	124.2 (2)
P(2)-N(1)	1.529 (4)	P(1)-N(1)-P(2)	136.6 (3)
P(2)-N(2)	1.541 (4)	P(2)-N(2)-P(3)	136.2 (3)
P(3)-C(31)	1.722 (5)	P(3)-N(3)-P(4)	138.2 (3)
P(3)-F(4)	1.539 (3)	P(1)-N(4)-P(4)	136.5 (3)
P(3)-N(2)	1.531 (4)	C(12)-C(11)-C(15)	108.1 (4)
P(3)-N(3)	1.540 (4)	C(32)-C(31)-C(35)	105.8 (5)
P(4)-F(5)	1.522 (4)		
P(4)-F(6)	1.527 (4)		
P(4)-N(3)	1.525 (4)		
P(4)-N(4)	1.510 (4)		

[a] Distance between atom and ring plane.

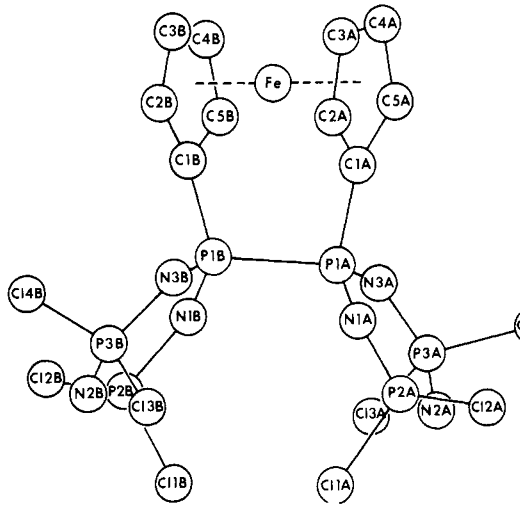

Figure 4. Atom designations and molecular structure for $N_6P_6Cl_8(\eta\text{-}C_5H_4)_2Fe$ (**23**).

bridging metallocene unit. The main structural parameters for these four compounds are summarized in Tables I–V and in Figures 1–4.

For compound **6a**, the ferrocenyl group is oriented over one face of the phosphazene ring (Figure 1) with a dihedral angle of 46.8° between the inorganic and organic rings. This, perhaps coupled with crystal packing forces, causes a slight deviation from planarity of the phosphazene ring.

Compound **10b** contains the ruthenocenyl unit linked in a nongeminal, transannular manner to the cyclotriphosphazene ring through two covalent C–P bonds (Figure 2) with an average C–P distance of 1.77 (1) Å. The angles between the cyclopentadienyl rings and a plane through the phosphazene ring were found to be nearly 90°. The most unusual feature of this structure is the

Scheme V

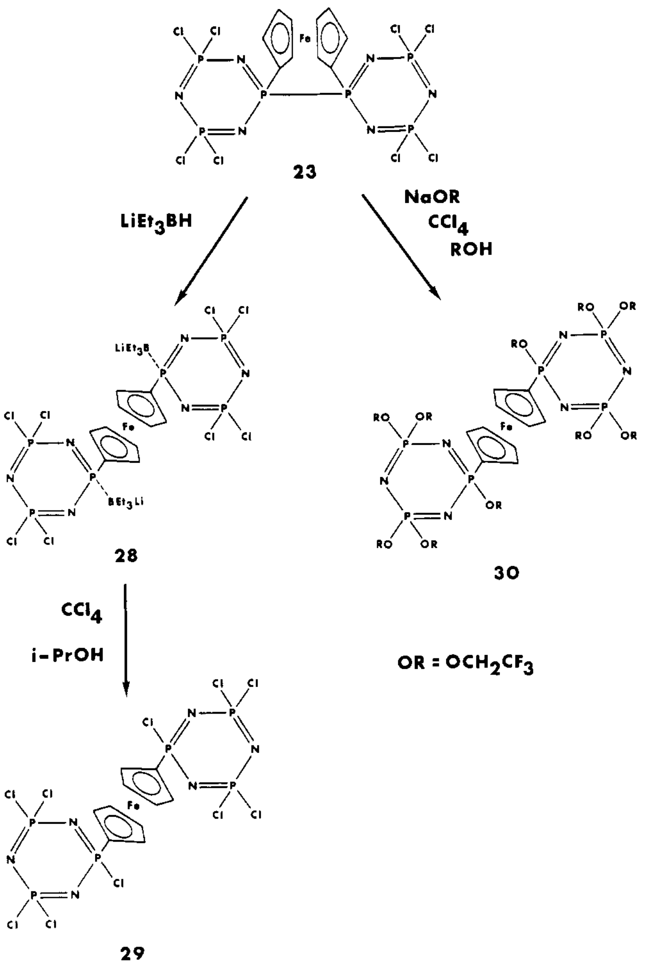

Table V. Selected Bond Lengths (Å) and Bond Angles (deg) (esd) for $N_6P_6Cl_8(\eta\text{-}C_5H_4)_2Fe$ (**23**)

Fe-Cp$_1$[a]	1.641 (4)	C(1A)-P(1A)-P(1B)	102.7 (1)
Fe-Cp$_2$[a]	1.639 (4)	N(1A)-P(1A)-N(3A)	116.9 (2)
P(1A)-C(1A)	1.756 (4)	Cl(1A)-P(2A)-Cl(2A)	100.6 (1)
P(1A)-N(1A)	1.593 (3)	N(1A)-P(2A)-N(2A)	119.6 (2)
P(1A)-N(3A)	1.608 (3)	Cl(3A)-P(3A)-Cl(4A)	100.7 (1)
P(1A)-P(1B)	2.219 (1)	N(2A)-P(3A)-N(3A)	119.7 (2)
P(2A)-Cl(1A)	2.003 (2)	P(1A)-N(1A)-P(2A)	121.6 (2)
P(2A)-Cl(2A)	1.974 (2)	P(2A)-N(2A)-P(3A)	120.4 (2)
P(2A)-N(1A)	1.553 (3)	P(1A)-N(3A)-P(3A)	121.0 (2)
P(2A)-N(2A)	1.570 (4)	C(1B)-P(1B)-P(1A)	103.4 (1)
P(3A)-Cl(3A)	1.997 (2)	N(1B)-P(1B)-N(3B)	116.6 (2)
P(3A)-Cl(4A)	1.984 (2)	Cl(1B)-P(2B)-Cl(2B)	101.1 (1)
P(3A)-N(2A)	1.579 (4)	N(1B)-P(2B)-N(2B)	119.9 (2)
P(3A)-N(3A)	1.556 (3)	Cl(3B)-P(3B)-Cl(4B)	100.8 (1)
P(1B)-C(1B)	1.768 (4)	N(2B)-P(3B)-N(3B)	119.6 (2)
P(1B)-N(1B)	1.604 (3)	P(1B)-N(1B)-P(2B)	121.5 (2)
P(1B)-N(3B)	1.603 (3)	P(2B)-N(2B)-P(3B)	120.3 (2)
P(2B)-Cl(1B)	1.998 (2)	P(1B)-N(3B)-P(3B)	121.6 (2)
P(2B)-Cl(2B)	1.978 (2)	C(2A)-C(1A)-C(5A)	106.5 (4)
P(2B)-N(1B)	1.554 (3)	C(2B)-C(1B)-C(5B)	107.5 (4)
P(2B)-N(2B)	1.574 (3)		
P(3B)-Cl(3B)	1.990 (2)		
P(3B)-Cl(4B)	1.988 (2)		
P(3B)-N(2B)	1.578 (4)		
P(3B)-N(3B)	1.558 (3)		

[a] Distance between atom and ring plane.

marked distortion of the phosphazene ring to accommodate the constraints imposed by the metallocene unit.

Species **12b** contains a ruthenocenyl unit linked through C–P bonds in a transannular manner to the 1,5-phosphorus atoms of the cyclotetraphosphazene ring. The average C–P bond distance is 1.738 (6) Å. The cyclotetraphosphazene ring is distorted into a boat conformation to accommodate to the steric requirements of the metallocenyl unit.

Finally, the structure of **23** was confirmed by an X-ray analysis. The two phosphazene rings are joined by a P–P bond (2.219 (1) Å), with each phosphorus at the linkage site being connected symmetrically to a cyclopentadienyl unit through C–P bonds (av 1.762 (6) Å). The two phosphazene rings are noncoplanar. The angles between the cyclopentadienyl rings and a plane through the phosphazene rings were slightly less than 90°, probably due to a distortion induced by the constraints at the linkage site.

Influence of the Phosphazene Rings on the Metallocenyl Units. In compound **6a** the two cyclopentadienyl rings are virtually coplanar ($\chi^2 = 2.5$ av), with a dihedral angle of only 1.4°. The two cyclopentadienyl rings appear to be nearly eclipsed, although the unsubstituted ring shows longer thermal elipsoids than the substituted ring. This suggests a "free spinning" arrangement for the unsubstituted ring, and this was confirmed by NMR analysis. The average C–C bond distance of 1.396 (8) Å is similar to the value of 1.40 Å reported elsewhere for ferrocene compounds.[24,25] The iron atom is positioned almost equidistant between the planes of the two cyclopentadienyl rings at an average distance of 1.66 (1) Å from them. This is comparable to the value found in ferrocene. Thus, the ferrocenyl structure in **6a** is normal, and apart from the immobilization of one cyclopentadienyl ring, no influence by the phosphazene unit can be discerned.

In compound **10b**, in spite of the bridging connection to the cyclotriphosphazene ring, the cyclopentadienyl rings are planar and almost coplanar (the dihedral angle is $\simeq 5°$). The rings are also eclisped as in free ruthenocene. Both rings are separated from the ruthenium atom by a distance of 1.81 (1) Å. This is very close to the value of 1.84 Å found in ruthenocene.[26] The average C–C distance around the rings of 1.416 (9) Å is similar to the value of 1.43 Å reported for ruthenocene.[26] Thus, in this structure also, the metallocenyl unit is essentially unperturbed by its 2-fold linkage to the phosphazene ring. The structural accommodation is by the inorganic ring, as will be discussed later.

As in the previous two cases, the cyclopentadienyl rings in **12b** are planar and virtually coplanar, with a dihedral angle of only $\simeq 4°$. The separation from the ruthenium atom is 1.82 (1) Å, and the average C–C bond distance is 1.416 (9) Å. Once again the cyclophosphazene unit appears to have little or no influence on the metallocene structure.

Perhaps even more surprisingly, the same situation exists in compound **23**. Again, the cyclopentadienyl rings are virtually coplanar, as in free ferrocene, with a dihedral angle of $\simeq 5°$. They are equally separated from the iron atom by a distance of 1.64 (1) Å. The average C–C bond distance around the rings is 1.421 (5) Å, which is close to the 1.40-Å value found for ferrocene.

Influence of the Metallocene Unit on the Phosphazene Rings. As mentioned earlier, the ferrocenyl group in **6a** brings about a modest distortion of the phosphazene ring from planarity. Moreover, the presence of the metallocene unit induced changes in the bond lengths and angles around the ring. In the unsubstituted trimer $(NPF_2)_3$ the ring is planar and all bond lengths are equal (1.57 Å) as are all the N–P–N angles (119.4°) and P–N–P angles (120.4°).[27] In compound **6a**, the two longest P–N bonds (av 1.586 (4) Å) are those closest to the linkage site of the metallocene unit. The four remaining P–N bond lengths are all approximately equal (av 1.553 (3) Å). The N–P–N ring angle at the metallocene linkage site is abnormally narrow (116.7 (1)°), while the F–P–C exocyclic angle is wider than expected (103.0 (1)°) (in most fluorophosphazenes the F–P–F angle is near 97.8 (1)°). These distortions probably reflect a steric influence by the metallocene group, since similar effects have been detected when carboranyl,[10] methylenecarboranyl,[11] or phenyl[28] occupy the same site in chlorocyclophosphazenes, although a weak electronic influence cannot be ruled out.

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The influence by the metallocene on the phosphazene ring is more marked in compound **10b**. The phosphazene ring is distorted appreciably, and the bond lengths and angles vary considerably from those in $(NPF_2)_3$. For example, the four P–N bonds near the metallocene linkage sites are longer than expected (av 1.594 (4) Å), and atom N(1) between the bridging sites (Figure 2) is displaced by 0.56 Å from the plane defined by the five remaining atoms of the phosphazene ring. Also, the ring angle at N(1) (113.1 (4)°) is significantly narrower than those of 117.4 (4)° and 118.9 (4)° at the other nitrogen atoms. The angles at P(1) and P(2) (at the bridging sites) of 115.2 (3)° and 116.2 (4)° are also narrower than the angle at P(3) of 121.3 (3)°. These distortions can be understood in terms of an attempt by the phosphazene ring to relieve the ring strain imposed by the metallocenyl bridge.

Although the ring distortion in the cyclotriphosphazene **10b** is quite marked, the effect becomes more pronounced in the cyclotetraphosphazene **12b**. Here the eight-membered ring adopts a boat conformation in contrast to the near-planar ring found in $(NPF_2)_4$.[29] Once again, the P–N bonds flanking one of the metallocene linkage sites [at P(1)] are longer than the others (1.568 (6) Å). However, surprisingly, those flanking the other linkage site [at P(3)] are not especially long (1.536 (6) Å). By comparison, the P–N bond lengths in $(NPF_2)_4$ average 1.51 Å.[29]

The phosphazene ring bond angles in **12b** at the bridgehead sites [P(1) and P(3)] are narrower (120.1 (2)° and 118.8 (3)°), respectively, than the values of 124.5 (2)° and 124.2 (2)° at P(2) and P(4). Moreover, the ring angles at N(1), N(2), N(3), and N(4) are significantly wider than those at phosphorus, with an angle of 136.9 (3)° being typical. These distortions of the cyclotetraphosphazene ring in **12b** can be understood best in terms of the strain imposed by the metallocene bridge.

Surprisingly, in compound **23** the metallocene unit generates virtually no distortion in the bi(cyclophosphazene) component. The P–P bond length in **23** is identical with that found in both $(N_3P_3Cl_4Me)_2$[30] and $(N_3P_3Cl_4Ph)_2$.[28] Both cyclotriphosphazene rings in **23** are almost planar, closer to planarity in fact than the analogous rings in $(N_3P_3Cl_4Ph)_2$.[28] The phosphazene bond lengths (1.578 (6) Å) and angles (N–P–N = 118.6 (6)°) in **23** are similar to those found for $(N_3P_3Cl_4Ph)_2$.

Experimental Section

Materials. Hexachlorocyclotriphosphazene $[(NPCl_2)_3]$ and octachlorocyclotetraphosphazene $[(NPCl_2)_4]$ (Ethyl Corp.) were purified by recrystallization and by sublimation. $(NPF_2)_3$, $(NPF_2)_4$, and $N_3P_3Cl_4(CH_3)Br$ were prepared by literature procedures.[31,32] Ferrocene (Aldrich), $Ru^{III}Cl_3 \cdot 3H_2O$ (Strem), zinc dust (Aldrich), *n*-butyllithium (Aldrich) (1.5 M solution in hexane), and *tert*-butyllithium (Aldrich) (2.6 M solution in pentane) were used as received. Chloromercuriferrocene, bromoferrocene, ruthenocene, and bromoruthenocene were all prepared by literature procedures.[33-35] Tetrahydrofuran (THF) (Fisher) was distilled under nitrogen from sodium benzophenone ketyl. Diethyl ether (Fisher) and hexane (Fisher) were dried and distilled over sodium benzophenone ketyl. Tetramethylethylenediamine (TMEDA) was dried over CaH_2 and then over BaO and was finally purified by fractional distillation with fractions boiling at 120–122 °C only being used. Column chromatography was performed using silica gel (230–400 mesh) (VWR) as packing material. All reactions were performed under an atomosphere of dry nitrogen using standard airless ware (Kontes).

Equipment. ^1H, ^{31}P, ^{13}C, and ^{19}F NMR spectra were recorded on Varian EM 360 and CFT-20 NMR, JEOL PFT-100 FT 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 NMR and ^{13}C NMR shifts were referenced to internal $CHCl_3$ or acetone. The ^{19}F NMR shifts were referenced to external C_6H_5F in a chloroform solution. Infrared (KBr disk) spectra were recorded on a Perkin-Elmer 580 or 283B grating spectrometer. Electron impact mass spectral results were obtained by using an AEI MS 950 spectrometer and were tabulated by a linked computer. Mass spectral isotope patterns were also calculated and tabulated.

General Comments on the Preparation of Lithiometallocenes. Monolithioferrocene was prepared by the following three procedures: (a) Ferrocene was lithiated directly by the method of Slocum and co-workers.[36] Ferrocene (5 g, 26.9 mmol) was stirred together with *n*-butyllithium (107.5 mL, 6 eq.) in diethyl ether (100 mL) at room temperature for 6 h. This route is reported to yield only 25% lithioferrocene, the remaining material being unreacted starting materials. (b) Monolithioferrocene was also prepared by using a published method[37] by a metal–halogen exchange reaction between bromoferrocene (1.0 g, 3.7 mmol) and *n*-butyllithium (2.7 mL, 1.2 eq.) in diethyl ether (100 mL). This procedure is reported to give lithioferrocene in almost quantitative yield. (c) Monolithioferrocene was prepared, as described previously,[38] via a transmetalation reaction between chloromercuriferrocene (2.0 g, 4.8 mmol) and *n*-butyllithium (3.8 mL, 1.2 equiv) in diethyl ether (100 mL) at room temperature. A yield of 50% is reported for this method. Ruthenocene was lithiated by the following procedures: (d) Ruthenocene (1 g, 4.3 mmol) was dissolved in diethyl ether (75 mL), and *n*-butyllithium (7.6 mL, 3 equiv) was added.[39] The reaction was allowed to proceed for 24 h at 25 °C. This resulted in a 3:1 mixture of di- to monolithioruthenocene. (e) Monolithioruthenocene (uncontaminated with the dilithio derivative) was prepared by a metal–halogen exchange reaction between bromoruthenocene and *n*-butyllithium in diethyl ether.

Synthesis of $N_3P_3F_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ (6a). A solution of lithioferrocene was prepared as described (method b) from *n*-butyllithium (1.83 mL, 2.8 mmol) and bromoferrocene (0.75 g, 2.83 mmol) in diethyl ether (75 mL). The mixture was allowed to warm to room temperature and was stirred for 45 min. This mixture was then recooled to –78 °C and a solution of $(NPF_2)_3$ (0.7 g, 2.8 mmol) in diethyl ether (25 mL) was added dropwise. The mixture was then stirred for 6 h at room temperature. The solvent was removed and the residue was chromatographed. Elution with hexane gave ferrocene, identified by ^1H NMR. Further elution with dichloromethane–hexane (1:5) gave a yellow band, which yielded orange crystals of **6a** (0.9 g, 77%, mp 65–66 °C). Further elution with dichloromethane–hexane (1:1) gave a yellow band, which yielded a small amount of **7a**.

For **6a**: IR 1200–1350 cm^{-1} (br, P–N); ^1H NMR δ 4.32 (s), 4.56 and 4.64 (both m); ^{13}C NMR δ 70.0 (s), 71.3 (d, $J_{CP} = 18.6$ Hz), 72.5 (d, $J_{CP} = 16.4$ Hz); ^{31}P NMR δ 44.3 (dtm, $J_{PF} = 965$, $J_{PNP} \sim 80$ Hz), 8.9 (tm, $J_{PF} \sim 933$ Hz). ^{19}F NMR ~66 (dm, $J_{FP} \sim 963$ Hz), ~44 (dm, $J_{FP} \sim 930$ Hz) ppm; MS, *m/e* calcd 414.92785, found 414.9285. Anal. Calcd for $C_{10}H_9N_3F_5FeP_3$: C, 28.93; H, 2.17; Fe, 13.46. Found: C, 29.02; H, 2.13; Fe, 13.66.

Synthesis of $N_3P_3F_4[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]_2$ (7a). Lithioferrocene was generated by method b with the use of *n*-butyllithium (0.7 mL, 1.1 mmol). Compound 6a was added to this solution (–78 °C), and the mixture was allowed to warm to room temperature. The mixture was then boiled at reflux for 12 h. The solvent was removed and the residue chromatographed. Elution with hexane gave ferrocene, identified by ^1H NMR. Further elution with dichloromethane–hexane (1:5) gave a yellow band, which yielded orange crystals of **6a**. Further elution with dichloromethane–hexane gave an orange band, which gave orange crystals of a mixture of products (~10% yield) that appeared to consist of $N_3P_3F_4(OCH_2CH_3)(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ and $N_3P_3F_3(OCH_2CH_3)_2(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ (MS, *m/e* calcd 441, found 441; calcd 467, found 469, respectively). Finally, elution with dichloromethane–hexane (1:1) gave a yellow band, which yielded **7a** as an orange-colored oil (0.16 g, 25%).

For **7a**: ^{31}P NMR 41.2 (ddm, J_{PF} 938 Hz), 5.9 (tdt, $J_{PF} = 902$, $J_{PNP} = 70$, $J_{PPF} \sim 9$ Hz) ppm; ^{19}F NMR 69 (d, $J_{FP} = 927$ Hz), 46 (d, $J_{FP} = 896$ Hz) ppm; MS, *m/e* calcd for $C_{20}H_{18}N_3F_4Fe_2P_3$ 581, found 581.

Synthesis of $N_4P_4F_7(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ (8a). $(NPF_2)_4$ (0.63 g, 1.9 mmol), in diethyl ether (~15 mL), was added to a cooled (–78 °C) solution of lithioferrocene (prepared by method b). The resultant mixture was allowed to warm slowly to room temperature. After 4 h at room temperature, the solvent was removed and the residue chromatographed. Elution with hexane gave a broad orange-colored band (N_2 pressure applied). After removal of the solvent, the residue was placed in a sublimator, and ferrocene (identified by ^1H NMR) was sublimed from this mixture during an 18 h period (30 °C/0.5 torr). The residue was chromatographed on fine silica gel. Elution with hexane gave an orange-colored band, which yielded **8a** (0.54 g, 57%) as an orange oil. A second band was also observed, which proved to contain a small quantity

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of a second (unidentified) orange-colored oil (≤5%).

For **8a**: IR 1300–1500 cm^{-1} (br, P–N); ^{1}H NMR δ 4.33 (s), 4.55, 4.62 (both m); ^{31}P NMR 21.4 (br, dm, J_{PF} = 929 Hz), ~−16 (br, tm, J_{PF} = 850 Hz) ppm; ^{19}F NMR 65 (d, J_{FP} = 925 Hz), 44 (d, J_{FP} = 857 Hz) ppm; MS, *m/e* calcd for $C_{10}H_9N_4F_7FeP_4$ 497.9015, found 497.9027, a parent peak at *m/e* 664 indicated the presence of **9a**.

Synthesis of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (10a). A solution of dilithioferrocene was prepared by the addition of *tert*-butyllithium (35.5 mmol) to a solution of ferrocene (3 g, 16.1 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 $(NPF_2)_3$ (8 g, 32.1 mmol) in diethyl ether (75 mL) at −78 °C, and the mixture was allowed to warm to room temperature. The reaction was then stirred for 17 h. The solvent was removed and the residue chromatographed. Elution with hexane gave ferrocene, identified by ^{1}H NMR. Further elution with dichloromethane–hexane (1:9) gave a yellow band, which yielded orange crystals of **10a** (2.55 g, 40%, mp 175 °C).

For **10a**: IR 3080 (w, CH), 1230 (vs, PN) cm^{-1}; ^{1}H NMR δ 5.023, 5.006, 4.738, 4.374 (all m, 2 H); ^{13}C NMR δ 78.9 (d, $J_{PC(1)}$ = 20 Hz), 76.8 (d, $J_{PC(2)}$ = 15 Hz), 73.5 (d, $J_{PC(3)}$ = 17 Hz), 72.2 (d, $J_{PC(4)}$ = 14 Hz); ^{31}P NMR 46.6 (dd, $J_{PF(1)}$ = 930, J_{PNP} 60 Hz), 15.4 (tt, $J_{PF(2)}$ = 890, J_{PNP} 60 Hz) ppm; ^{19}F NMR 38.7 (d, $J_{PF(1)}$ = 980 Hz), 41.7 (d, $J_{PF(2)}$ = 950 Hz), 45.1 (d, $J_{PF(3)}$ = 910 Hz) ppm. MS, *m/e* calcd for $C_{10}H_8N_3F_4FeP_3$ 394.9216, found 394.9243 (deviation 6.8 ppm). Anal. Calcd: C, 30.41; H, 2.04; F, 19.24; P, 23.53. Found: C, 30.37; H, 2.18; F, 19.09; P, 23.81.

Synthesis of 1,5- and 1,3-$N_4P_4F_6(\eta\text{-}C_5H_4)_2Fe$ (12a and 13a). A solution of dilithioferrocene was prepared as described above with *tert*-butyllithium (35.5 mmol) and ferrocene (3 g, 16.1 mmol) and was added to a solution of $(NPF_2)_4$ (11 g, 33.1 mmol) in diethyl ether (75 mL) at −78 °C. The mixture was allowed to warm to room temperature and was stirred for 17 h. The solvent was removed and the residue chromatographed. Elution with hexane gave ferrocene, identified by ^{1}H NMR. Further elution with dichloromethane–hexane (1:9) gave a yellow band from which an equal mixture of 1,5-$N_4P_4F_6(\eta\text{-}C_5H_4)_2Fe$ (**12a**) and 1,3-$N_4P_4F_6(\eta\text{-}C_5H_4)_2Fe$ (**13a**) (3.08 g, 40%, mp 128 °C) crystallized. Species **12a** and **13a** were separated by preparative liquid chromatography.

For **12a**: IR 3100 (w, CH), 1360 (vs, PN) cm^{-1}; ^{1}H NMR δ 4.779, 4.717 (both m. 4 H); ^{31}P NMR 23.3 (dd, $J_{PF(1)}$ = 850, J_{PNP} 80 Hz), 15.0 (tt, $J_{PF(2)}$ = 870, J_{PNP} 80 Hz), ppm; ^{19}F NMR 57.3 (dm, $J_{PF(1)}$ = 880 Hz), 45.0 (dm, $J_{PF(2)}$ = 840 Hz), 43.5 (dm, $J_{PF(3)}$ = 830 Hz) ppm; MS, *m/e* calcd for $C_{10}H_8N_4F_6FeP_4$ 477.8953, found 477.8924 (deviation 6.1 ppm).

For **13a**: ^{1}H NMR δ 5.111, 5.030, 4.564, 4.413 (all m, 2 H); ^{31}P NMR 35.8 (dd, $J_{PF(1)}$ = 850, J_{PNP} = 80 Hz), −13.3 (tt, $J_{PF(2)}$ = 870, J_{PNP} = 80 Hz) ppm.

Synthesis of $N_3P_3F_5(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)$ (6b), $N_6P_6F_{10}(\eta\text{-}C_5H_4)_2Ru$ (11), and $N_3P_3F_4(\eta\text{-}C_5H_4)_2Ru$ (10b). A solution of $N_3P_3F_6$ (5 g, 20.1 mmol) in diethyl ether (50 mL) was added to a solution of lithioruthenocene, prepared as described (method d), at −78 °C. The reaction was allowed to warm to room temperature and was stirred for 17 h. The solvent and excess $N_3P_3F_6$ were removed under reduced pressure, and the products were carefully separated by column chromatography on silica gel. Elution with hexane gave unreacted ruthenocene identified by ^{1}H NMR. Further elution with dichloromethane–hexane (1:9) gave a colorless band, which yielded white crystals of **6b** (0.080 g, 4.04%, mp 135–136 °C). Further elution with dichloromethane–hexane (1:4) gave another colorless band, which yielded crystals of **11** (0.15 g, 5.0%, mp 100–101 °C). Finally, elution with dichloromethane–hexane (1:3) yielded a colorless band that gave white crystals of **10b** (1.13 g, 6.84%, mp 169–170 °C).

For **6b**: IR 3100 (w, CH), 1275 (vs, PN) cm^{-1}; ^{1}H NMR δ 4.986 (m, 2 H), 4.844 (m, 2 H), 4.684 (s, 5 H); ^{13}C NMR δ 74.0 (d, J_{PC} = 16 Hz), 72.8 (d, J_{PC} = 20 Hz), 72.5 (s); ^{31}P NMR 42.9 (dt, $J_{PF(1)}$ = 960, J_{PNP} = 80 Hz), 9.14 (td, $J_{PF(2)}$ = 910, J_{PNP} = 80 Hz) ppm; ^{19}F NMR 64.0 (dm, $J_{PF(1)}$ = 960 Hz), 44.8 (dm, $J_{PF(2)}$ = 885 Hz) ppm; MS, *m/e* calcd for $C_{10}H_9N_3F_5P_3Ru$ 460.8972, found 460.8966 (deviation 2.7 ppm).

For **11**: IR 3100 (w, CH), 1270 (vs, PN) cm^{-1}; ^{1}H NMR δ 5.097, 4.971 (both m, 4 H); ^{31}P NMR 38.3 (dd, $J_{PF(1)}$ = 970, J_{PNP} = 80 Hz), 8.5 (tt, $J_{PF(2)}$ = 890, J_{PNP} = 80 Hz) ppm; ^{19}F NMR 63.5 (dm, $J_{PF(1)}$ = 980 Hz), 44.2 (dm, $J.\mathrm{P}_{F(2)}$ = 900 Hz) ppm; MS, *m/e* calcd for $C_{10}H_8N_6F_{10}RuP_6$ 689.8119, found 689.8069 (deviation 7.3 ppm).

For **10b**: IR 3090 (w, CH), 1225 (vs, b, PN) cm^{-1}; ^{1}H NMR δ 5.397, 5.312, 5.079, 4.796 (all m, 2 H); ^{31}P NMR 43.6 (dd, $J_{PF(1)}$ = 920, J_{PNP} = 80 Hz), 16.7 (tt, $J_{PF(2)}$ = 920, J_{PNP} = 80 Hz) ppm; ^{19}F NMR 36.0 (d, $J_{PF(1)}$ = 920 Hz), 40.5 (d, $J_{PF(2)}$ = 900 Hz), 44.5 (d, $J_{PF(3)}$ = 890 Hz) ppm; MS, *m/e* calcd for $C_{10}H_8N_3F_4RuP_3$ 440.8910, found 440.8908 (deviation 0.5 ppm). Anal. Calcd: C, 27.29; H, 1.83; P, 21.11. Found: C, 27.95; H, 2.05; P, 20.68.

Reaction of Mono- and Dilithioruthenocene with $(NPF_2)_4$ To Yield 8b, 9b, 12b, and 13b. A solution of $(NPF_2)_4$ (10 g, 20.1 mmol) in diethyl ether (50 mL) was added to a solution of mono- and dilithioruthenocene, prepared as described (method d), at −78 °C. The mixture was allowed to warm to room temperature and was stirred for 17 h. The solvent and excess $N_4P_4F_8$ were removed under reduced pressure, and the products were carefully separated by column chromatography on silica gel. Elution with hexane gave unreacted ruthenocene, identified by ^{1}H NMR. Further elution with dichloromethane–hexane (1:9) gave a colorless band, which yielded white crystals of $N_4P_4F_7(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)$ (**8b**) (0.7 g, 30%). Continued elution with dichloromethane–hexane (1:8) yielded colorless crystals of $N_4P_4F_6[(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)]_2$ (**9b**) (0.23 g, 7.0%), mp 175 °C. Further elution with dichloromethane–hexane (1:6) yielded a colorless mixture of **12b** and **13b**. Attempts to isolate **13b** from this mixture by high-pressure liquid chromatography were unsuccessful. Further elution with the same solvents (1:5) gave another colorless band, which yielded white crystals of **12b** (0.7 g, 30%, mp 173–174 °C).

For **8b**: ^{1}H NMR δ 4.925, 4.806 (both m, 4 H); ^{31}P NMR 17.1 (d, $J_{PF(1)}$ = 910, J_{PNP} = 70 Hz), 10.2 (t, $J_{PF(2)}$ = 890, J_{PNP} = 80 Hz), −16.9 (t, $J_{PF(3)}$ = 870, J_{PNP} 80 Hz) ppm; MS, *m/e* calcd for $C_{10}H_9N_4F_7P_4Ru$ 543, found 543.

For **9b**: IR 2980 (w, CH), 1400 (s, PN); ^{1}H NMR δ 4.943, 4.816 (both m, 4 H), 4.743 (s, 10 H); ^{31}P NMR 13.7 (dt, $J_{PF(1)}$ = 890, J_{PNP} 90 Hz), −22.8 (tt, $J_{PF(2)}$ = 870, J_{PNP} = 90 Hz) ppm; ^{19}F NMR 61.6 (dm, $J_{PF(1)}$ = 880 Hz), 44.7 (dm, $J_{PF(2)}$ = 880 Hz) ppm; MS, *m/e* calcd for $C_{20}H_{18}N_4F_6P_4Ru$ 755.8472, found 755.8468 (deviation 0.5 ppm).

For **12b**: IR 3100 (w, CH), 1375 (vs, PN); ^{1}H NMR δ 5.054, 5.021 (both m, 4 H); ^{13}C NMR δ 78.3 (d, J_{PC} = 14 Hz), 76.7 (d, J_{PC} = 19 Hz); ^{31}P NMR 15.0 (dd, $J_{PF(1)}$ = 840, J_{PNP} = 80 Hz), −12.7 (tt, $J_{PF(2)}$ = 870, J_{PNP} = 80 Hz) ppm; ^{19}F NMR 58.0 (dm, $J_{PF(1)}$ = 850 Hz), 46.5 (dm, $J_{PF(2)}$ = 960 Hz), 43.9 (dm, $J_{PF(3)}$ = 880 Hz) ppm; MS, *m/e* calcd for $C_{10}H_8N_4F_6P_4Ru$ 523.8647, found 523.8638 (deviation 2.1 ppm). Anal. Calcd: C, 22.96; H, 1.54; F, 21.79; P, 23.68. Found: C, 23.28; H, 1.70; F, 21.50; P, 23.77.

For **13b**: ^{1}H NMR δ 5.511, 5.376, 4.816, 4.725 (all m, 2 H); MS, *m/e* calcd $C_{10}H_8N_4F_6P_4Ru$ 523.8647, found 523.8638 (deviation 2.1 ppm).

Synthesis of $N_3P_3(OCH_2CF_3)_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ (14a). Sodium trifluoroethoxide (10.8 mmol, from 0.25 g sodium spheres and 1 mL of trifluoroethanol) was prepared in THF (75 mL). Compound **6** (0.3 g, 0.7 mmol) was added as a solution in THF (20 mL), and the mixture was heated to reflux and stirred for 9 h. The solvent was removed and the residue was filtered through a column of neutral alumina. The solvent was again removed and the residue extracted with a pentane/water mixture. Evaporation of the pentane layer yielded an orange-colored semisolid material. Recrystallization from hexane gave **14a** (0.46 g, 78%, mp 44–45 °C). The compound was further purified by sublimation at 50–60 °C (0.05 torr). ^{1}H NMR δ 4.30 (s), 4.47, 4.50 (both m), 4.14, ~4.3 (both m); ^{13}C NMR δ 69.9 (s), 70.9 (d, J_{CP} = 16.6 Hz), 71.8 (d, J_{CP} = 14.8 Hz), 70.5 (dt, $J_{CP(1)}$ = 218, $J_{CP(2)}$ ~ 7 Hz), 61.0 (q, J_{CF} = 37.5 Hz), 62.7 (q, J_{CF} = 37 Hz), 122.6 (q, J_{CF} = 277.3 Hz); ^{31}P NMR δ 37.4 (t, J_{PNP} = 53 Hz), 16.0 (d); ^{19}F NMR δ ~37 (m); MS, *m/e* calcd for $C_{20}H_{19}N_3F_{15}FeO_5P_3$ 814.9647, found 814.9580. Anal. Calcd: C, 29.47; H, 2.35; Fe, 6.85. Found: C, 29.73; H, 2.27; Fe, 7.04.

Synthesis of $N_4P_4(OCH_2CF_3)_7(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ (15a). This procedure was carried out in a similar manner to the one described above. The product was isolated by removal of solvent and filtration of the residue in dichloromethane through silica gel. The solvent was removed to yield **15a** as an orange-colored solid (0.49 g, 68%, mp 55–56 °C). Further purification was effected by recrystallization from hexane. ^{31}P NMR 18.4 (m), ~−2 (m) ppm; ^{19}F NMR ~37 (m) ppm; MS, *m/e* calcd for $C_{24}H_{23}N_4F_{21}FeO$ 1058, found 1058.

Reaction of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Ru$ (10b) with Sodium Trifluoroethoxide To Give 14b. A solution of sodium trifluoroethoxide was prepared by the addition of sodium (0.3 g, 13.0 mmol) to a solution of trifluoroethanol (1.0 mL, 12.8 mmol) in THF (10 mL). Compound **10b** (0.3 g, 0.07 mmol) was added, and the solution was stirred for 48 h at 25 °C. The solvent was removed and the residue was chromatographed. Elution with dichloromethane–hexane (1:5) gave a colorless band, which yielded white crystals of $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Ru$ (**14b**) (0.015 g, 8.9%, dec at 180 °C). ^{1}H NMR δ 5.227, 5.162, 4.979, 4.740 (all m, 2 H), 4.351 (dm, 8 H); ^{31}P NMR 22.8 (t), 38.8 (d, J_{PNP} = 54 Hz) ppm; MS, *m/e* calcd for $C_{18}H_{16}N_3O_4F_{12}RuP_3$ 760.9265, found 760.9233 (deviation 3.6 ppm).

Reaction of Monolithioferrocene with $(NPCl_2)_3$ To Give 18a and 19a. Solutions of lithioferrocene prepared by methods a–c above were each added to an excess of $(NPCl_2)_3$ (15 g, 43.1 mmol) in diethyl ether (50 mL) at 20 °C and were stirred for 17 h. The solvent was removed and the residue was chromatographed. In all cases, elution with hexane gave first a mixture of $(NPCl_2)_3$, ferrocene, and chloroferrocene, identified by ^{31}P or ^{1}H NMR. Further elution with a mixture of dichloromethane–hexane (1:9) gave an orange band from which orange crystals of

$N_3P_3Cl_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ (**18a**) (0.57 g, 31% based on bromoferrocene, mp 122–123 °C) were obtained. Continued elution gave a second orange band from which bright orange crystals of $N_6P_6Cl_9(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ (**19a**) (0.57 g, 20%, mp 195 °C) were obtained.

For **18a**: IR 3110 (w, CH), 1190 (s, PN) cm^{-1}; ^{1}H NMR δ 4.681, 4.553 (both m, 2 H), 4.445 (s, 5 H); ^{13}C NMR δ 75.6 (dt, J_{PC} = 9, J_{CPNP} = 207 Hz), 72.3 (d, J_{PC} = 17 Hz), 70.7 (d, J_{PC} = 15 Hz), 70.3 (s); ^{31}P NMR 36.1 (t), 20.21 (d, J_{PNP} = 15 Hz) ppm; MS, *m/e* calcd for $C_{10}H_9N_3Cl_5FeP_3$ 494.7801, found 494.7785 (deviation 3.1 ppm). Anal. Calcd: C, 24.16; H, 1.82; Cl, 35.65; P, 18.69. Found: C, 24.03; H, 1.77; Cl, 35.80; P, 18.56.

For **19a**: IR 3090 (w, CH), 1200 (s, PN), 590 (m, PCl) cm^{-1}; ^{1}H NMR δ 4.734, 4.661 (both m, 2 H), 4.447 (s, 5 H); ^{13}C NMR δ 73.6, 72.9 (both m, 2 C), 70.1 (s, 5 C); ^{31}P NMR 25.8 (m), 21.1 (m) ppm; MS, *m/e* calcd for $C_{10}H_9N_6Cl_9FeP_6$ 769.5860, found 769.5846 (1.8 ppm). Anal. Calcd: C, 15.51; H, 1.17; Cl, 41.22. Found: C, 15.35; H, 1.28; Cl, 41.23.

Reaction of 1,1′-Dilithioferrocene with $(NPCl_2)_3$ To Give 21a and 22a. A solution of 1,1′-dilithioferrocene was prepared by stirring together a mixture of ferrocene (3 g, 16.1 mmol) and *tert*-butyllithium (35.5 mmol) in diethyl ether (75 mL) for 6 h at 20 °C. A solution containing $(NPCl_2)_3$ (15 g, 43 mmol) in diethyl ether (75 mL) was added at −78 °C, and the mixture was allowed to warm to room temperature. The reaction was then stirred for 17 h. The solvent was removed and the mixture chromatographed. Elution with hexane gave a mixture of $(NPCl_2)_3$ and ferrocene, identified by ^{31}P NMR and ^{1}H NMR, respectively. Further elution with dichloromethane–hexane (1:9) gave a yellow band from which orange crystals of $N_3P_3Cl_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_4Cl)$ (**21a**) (0.92 g, 10.8%, based on metallocene units, mp 83–84 °C) were obtained. Elution with dichloromethane–hexane (1:8) yielded another yellow band from which orange crystals of $N_6P_6Cl_9(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_4Cl)$ (**22a**) (5.20 g, 40%, mp 158 °C) were obtained.

For **21a**: IR 3100 (w, CH), 1150 (vs, PN) cm^{-1}; ^{1}H NMR δ 4.721, 4.606, 4.590, 4.310 (all m, 2 H); ^{13}C NMR δ 75.16 (d, J_{PC} = 15 Hz), 72.51 (d, J_{PC} = 19 Hz), 70.35 (s), 69.99 (s); ^{31}P NMR 35.0 (t), 20.2 (d, J_{PNP} = 17 Hz) ppm; MS, *m/e* calcd for $C_{10}H_8N_3Cl_6FeP_3$ 528.7411, found 528.7386 (4.7 ppm).

For **22a**: IR 3000 (w, CH), 1190 (vs, PN) cm^{-1}; ^{1}H NMR δ 4.788, 4.710, 4.657, 4.404 (all m, 2 H); ^{31}P NMR 21.4 (m), 25.3 (m) ppm; MS, *m/e* calcd for $C_{10}H_8N_6Cl_{10}FeP_6$ 803.5471, found 803.5448 (4.5 ppm).

Reaction of 1,1′-Dilithioferrocene–TMEDA with $(NPCl_2)_3$ To Give 18a, 21a, and 23. 1,1′-Dilithioferrocene–TMEDA was prepared by a published procedure.[19] A solution of *n*-butyllithium (50.2 mL, 2.8 equiv) was added to a solution of TMEDA (11.1 mL, 2.8 equiv) in hexane (10 mL). This mixture was stirred for 5 min and was then added to a solution of ferrocene (5 g, 26.9 mmol) in hexane (75 mL). The mixture was stirred for 5 h at room temperature. A solution of $(NPCl_2)_3$ (15 g, 43 mmol) in hexane (75 mL) was then added at −78 °C. The mixture was then stirred for 17 h. The solvent was removed and the residue chromatographed. Elution with hexane gave unreacted $(NPCl_2)_3$, identified by ^{31}P NMR, together with a trace of ferrocene, identified by ^{1}H NMR. Further elution with dichloromethane–hexane (1:9) gave a prominent orange band from which large orange crystals containing approximately a 1:5 mixture of **18a** and **21a** (5.1 g, 40%, mp 83–84 °C) were obtained. Further elution with dichloromethane–hexane (1:4) gave a yellow band from which a small quantity of yellow crystals of $N_6P_6Cl_8(\eta\text{-}C_5H_4)_2Fe$ (**23**) (0.250 g, 1.3%, mp 246 °C) were isolated.

For **23**: IR 3000 (w, CH), 1170 (vs, PN), 550 (m, PCl) cm^{-1}; ^{1}H NMR δ 5.029, 4.839 (both m, 4 H); ^{31}P NMR 22.54 (m), 18.88 (m) ppm; MS, *m/e* calcd for $C_{10}H_8N_6Cl_8FeP_6$ 733.6093, found 733.6077 (2.2 ppm).

Reaction of Monolithioferrocene with $(NPCl_2)_3$ in the Presence of CH_3I To Give 18a, 19a, and 25a. Monolithioferrocene in diethyl ether (50 mL), prepared from bromoferrocene (1 g, 3.7 mmol) by method b above, was added to a solution of $(NPCl_2)_3$ (1.3 g, 3.7 mmol) and CH_3I (0.5 g, 3.5 mmol) in diethyl ether (75 mL) at room temperature. The mixture was stirred for 17 h and the solvent was removed. A ^{31}P NMR analysis of the residue showed approximately equal quantities of **18a** and **25a**, together with a small quantity of **19a**. ^{31}P NMR for **25a**: 29.2 (t), 20.7 (d, J_{PNP} = 23 Hz) ppm.

Reaction of Lithioferrocene with $(NPCl_2)_4$. Lithioferrocene, generated by method c, was added to a solution of $(NPCl_2)_4$ (10.0 g, 0.022 mol) in diethyl ether (~50 mL) at 25 °C, and the mixture was stirred for 17 h. After removal of the solvent and chromatography using hexane eluent, unreacted $(NPCl_2)_4$, ferrocene, and chloroferrocene were isolated. The latter product was identified by ^{31}P and ^{1}H NMR spectroscopy.

Reaction of Monolithioruthenocene with $(NPCl_2)_3$ To Give 18b, 19b, and 20. Monolithioruthenocene was prepared by the addition of *n*-butyllithium (1.6 mL, 1 equiv) to a solution of bromoruthenocene (0.8 g, 2.6 mmol) at −78 °C. This solution was allowed to warm to room temperature and added to a solution of $(NPCl_2)_3$ (5 g, 14.4 mmol). The mixture was stirred for 17 h, filtered, and the solvent removed to give a white solid. The products were carefully separated by column chromatography on silica gel. Elution with hexane gave $(NPCl_2)_3$ and chlororuthenocene, identified by ^{31}P and ^{1}H NMR, respectively. Further elution with dichloromethane–hexane (1:4) gave a colorless band, which yielded pale yellow crystals of $N_3P_3Cl_5(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)$ (**18b**) (0.20 g, 20%, mp 114–115 °C). Elution with dichloromethane–hexane (1:5) gave a colorless band, which yielded pale yellow crystals of $N_6P_6Cl_9(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)$ (**19b**) (0.3 g, 15%, mp 148–149 °C). In one reaction, a third product, $N_3P_3Cl_4(H)(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)$ (**20**) was isolated in low yield (0.04 g, 3.0%, mp 180 °C dec). Its formation was attributed to the presence of traces of water, from the synthesis of bromoruthenocene.

For **18b**: IR 3100 (w, CH), 1260 (vs, br, PN), 600 (s, PCl) cm^{-1}; ^{1}H NMR δ 4.987, 4.805 (both m, 2 H), 4.704 (s, 5 H); ^{31}P NMR 33.7 (t), 20.3 (d, J_{PNP} = 17 Hz) ppm; MS, *m/e* calcd for $C_{10}H_9N_3Cl_5P_3Ru$ 540.7495, found 540.7473 (4.0 ppm).

For **19b**: IR 3000 (w, CH), 1200 (vs, br, PN), 590 (s, PCl); ^{1}H NMR δ 5.017, 4.916 (both m, 2 H), 4.787 (s, 5 H); ^{31}P NMR 24.9 (m), 21.3 (m) ppm; MS, *m/e* calcd for $C_{10}H_9N_6Cl_9P_6Ru$ 815.5554, found 815.5552 (0.3 ppm).

For **20**: ^{1}H NMR δ 7.736 (dt, 1 H, J_{PH} = 586, J_{PNPH} = 16 Hz), 4.875 (m, 2 H), 4.799 (m, 2 H), 4.704 (s, 5 H); ^{31}P NMR 18.6 (t), 8.0 (d, J_{PNP} = 11 Hz, proton decoupled), 18.4 (dd), 9.2 (tt, J_{PNP} = 12, J_{PNPH} = 16 Hz, proton coupled) ppm; MS, *m/e* calcd for $C_{10}H_{10}N_3Cl_4P_3Ru$ 506.7885, found 506.7861 (4.6 ppm).

Reaction of Lithioruthenocene with $(NPCl_2)_3$ To Give 18b, 19b, 21b, and 22b. A solution of $(NPCl_2)_3$ (10 g, 28.7 mmol) in diethyl ether (50 mL) was added to a solution of lithioruthenocene, prepared as described above, at −78 °C. The reaction was allowed to warm to room temperature and was stirred for 17 h. The solvent was removed to give a white solid. The excess $(NPCl_2)_3$ was removed by sublimation. The products were separated carefully by column chromatography on silica gel. Elution with hexane gave unreacted ruthenocene, identified by ^{1}H NMR. Further elution with dichloromethane–hexane (1:9) gave a colorless band, which gave pale yellow crystals of $N_3P_3Cl_5(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)$ (**18b**) and $N_3P_3Cl_5(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_4Cl)$ (**21b**) (0.5 g, 20%, mp 115–116 °C). Attempts to separate these two products by column chromatography were unsuccessful. Further elution with dichloromethane–hexane (1:5) gave another band from which was obtained pale yellow crystals of $N_6P_6Cl_9(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)$ (**19b**) and $N_6P_6Cl_9(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_4Cl)$ (0.5 g, 15%, mp 164 °C). Attempts to separate these two products by chromatography were also unsuccessful.

For **21b**: IR 3000 (w, CH), 1200 (vs, br, PN), 590 (s, PCl) cm^{-1}; ^{1}H NMR δ 5.042, 4.994, 4.867, 4.627 (all m, 2 H); ^{31}P NMR 32.5 (t), 20.1 (d, J_{PNP} = 18 Hz), ppm; MS, *m/e* calcd for $C_{10}H_8N_3Cl_6P_3Ru$ 574.7105, found 574.7091 (2.4 ppm).

For **22b**: IR 3000 (w, CH), 1150 (vs, br, PN) cm^{-1}; ^{1}H NMR δ 5.087, 5.077, 5.023, 4.766 (all m, 2 H); ^{31}P NMR 24.6 (m), 21.2 (m); MS, *m/e* calcd for $C_{10}H_8N_6Cl_{10}P_6Ru$ 849.5165, found 849.5099 (7.7 ppm).

Reaction of Monolithioferrocene with $N_3P_3Cl_4(CH_3)Br$ To Yield 25a. A solution of $N_3P_3Cl_4(CH_3)Br$ (5 g, 13.4 mmol) in diethyl ether (50 mL) was added to a solution of lithioferrocene, prepared from bromoferrocene (1 g, 3.8 mmol) (as in method b described earlier) at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 17 h. The solvent was removed and the residue chromatographed. Elution with dichloromethane–hexane (1:5) yielded a single yellow band from which yellow crystals of **25a** (0.6 g, 30%) were obtained, identified by ^{31}P NMR spectroscopy: ^{31}P NMR 29.2 (t), 20.7 (d, J_{PNP} = 23 Hz) ppm.

Reaction of Lithioruthenocene with $N_3P_3Cl_4(CH_3)Br$ To Give 25b. A solution of $N_3P_3Cl_4(CH_3)Br$ (5 g, 13.4 mmol) in diethyl ether (50 mL) was added to a solution of lithioruthenocene, prepared as described above, at −78 °C. The reaction was allowed to warm to room temperature and was stirred for 17 h. The solvent was removed to give a white solid. The product was purified by column chromatography on silica gel. Elution with dichloromethane–hexane (1:2) yielded a single yellow band, which appeared to contain **25b** (0.7 g, 30%): ^{31}P NMR 28.8 (t), 21.0 (d, J_{PNP} = 22 Hz) ppm.

Preparation of $[N_6P_6Cl_8(LiEt_3B)_2(\eta\text{-}C_5H_4)_2Fe]^{2-}$ (28), $[N_6P_6Cl_{10}(\eta\text{-}C_5H_4)_2Fe]$ (29), and $[N_6P_6(OCH_2CF_3)_{10}(\eta\text{-}C_5H_4)_2Fe]$ (30). Compound **23** (40 mg, 0.055 mmol) was dissolved in THF (0.75 mL) in an 8-mm NMR tube. A 1 M solution of $LiEt_3BH$ (170 μL, 0.17 mmol, 3 equiv) in THF was added via syringe, and immediate hydrogen evolution was observed. After 30 min complete P–P bond cleavage was detected by ^{31}P NMR spectroscopy. Isopropyl alcohol (100 μL, 1.3 mmol) and carbon tetrachloride (300 μL, 3.1 mmol) were added, and complete conversion to **29** took place. Product **29** was isolated by column chromatography with the use of dichloromethane–hexane (1:3) eluent. Orange crystals of **29** were obtained (35 mg, 79.9%, mp 143 °C).

Compound **23** (30 mg, 0.041 mmol) was dissolved in THF (0.75 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 1.0-mL portion of this solution was added to the NMR tube and P–P bond cleavage was followed by ^{31}P NMR spectroscopy. A precipitate of NaCl was observed. Carbon tetrachloride (200 μL, 207 mmol) was added, and the complete conversion to **30** was monitored by ^{31}P NMR spectroscopy. Product **30** was isolated by column chromatography with elution by dichloromethane–hexane (1:3). An orange oil (10 mg, 22.8%) was obtained.

For **29**: IR 2980 (w, CH), 1250 (vs, br, PN), 600 (s, PCl) cm^{-1}; ^1H NMR δ 4.843, 4.803 (both m, 4 H); ^{31}P NMR 35.0 (t), 21.1 (d, J_{PNP} = 17.4 Hz) ppm; MS, *m/e* calcd for $C_{10}H_8N_6Cl_{10}FeP_6$ 803.5471, found 803.5496 (3.2 ppm).

For **30**: IR 2980 (w, CH), 1250 (vs, br, PN) cm^{-1}; ^1H NMR δ 4.620, 4.597 (both m, 4 H), 4.296 (dm, 8 H); ^{31}P NMR; 35.6 (t), 16.4 (d, J_{PNP} = 56.2 Hz), ppm; ^{19}F NMR 37 (m) ppm; MS, *m/e* calcd for $C_{30}H_{28}N_6Fe_{30}FeO_{10}P_6$ 1444, found 1444.

X-ray Structure Determination. Our general X-ray structure technique has been described in earlier papers,[1a,11] and only the details related to the present work will be given here. A crystal of **6a**, with dimensions 0.31 × 0.25 × 0.30 mm, obtained from a saturated solution in hexane, was mounted along the longest axis. A summary of the important crystallographic data is presented in Table I. The drift correction shown in the table was used to allow for slight crystal motion or temperature changes during data collection. A crystal of **10b**, with dimensions 0.29 × 0.31 × 0.62 mm, was obtained from a solution in dichloromethane–hexane and was cut for analysis and mounted along the longest axis. Crystals of **12b** were obtained by temperature-gradient vacuum sublimation at 25–50 °C (10^{-3} torr). A single, well-formed crystal of dimensions 0.30 × 0.32 × 0.60 mm was chosen and mounted along the longest axis. A crystal of **23**, with dimensions 0.15 × 0.27 × 0.40 mm, was obtained from dichloromethane–hexane solution and was mounted along the longest axis.

The structures were solved by Patterson heavy-metal techniques. Subsequent cycles of least-squares refinement and difference Fourier syntheses yielded the remaining non-hydrogen atoms. In the final cycles of full-matrix least-squares refinement, all non-hydrogen atom positional parameters and anisotropic thermal parameters were refined. The positional and thermal parameters (B = 5.0 Å^2) for the hydrogen atoms of **10b** and **12b** were fixed in calculated positions (C–H, 0.97 Å) during the later cycles of refinement. For structures **6a** and **23**, the positional parameters for the hydrogen atoms, given fixed, arbitrary thermal parameters (B = 5.0 Å^2), were located from a difference Fourier electron density map and were refined.

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Registry No. 4, 15599-91-4; **5**, 14700-00-6; **6a**, 84462-63-5; **6b**, 89178-99-4; **7**, 84462-68-0; **8a**, 84462-64-6; **8b**, 89179-00-0; **9a**, 89179-01-1; **9b**, 89179-02-2; **10a**, 89179-03-3; **10b**, 89179-04-4; **11**, 89179-05-5; **12a**, 89179-06-6; **12b**, 89179-17-7; **13a**, 89179-08-8; **13b**, 89179-09-9; **14a**, 84462-65-7; **14b**, 89196-42-9; **15**, 84462-67-9; **16**, 940-71-6; **17**, 2950-45-0; **18a**, 88644-58-0; **18b**, 89179-10-2; **19a**, 88656-94-4; **19b**, 89179-11-3; **20**, 89179-12-4; **21a**, 89196-43-0; **21b**, 89196-44-1; **22a**, 89196-45-2; **22b**, 89196-46-3; **23**, 89196-47-4; **24**, 77589-25-4; **25a**, 89179-13-5; **25b**, 89179-14-6; **28**, 89196-48-5; **29**, 89179-15-7; **30**, 89179-16-8; $Fe(\eta\text{-}C_5H_5)_2$, 102-54-5; $Li(n\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$, 1271-15-4; $Br(n\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$, 1273-73-0; $ClHg(n\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$, 1273-75-2; $Ru(\eta\text{-}C_5H_5)_2$, 1287-13-4; $Li(n\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)$, 89179-17-9; $Li_2(n\text{-}C_5H_4)_2Ru$, 60898-13-7; $Br(n\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)$, 38816-65-8; $N_3P_3F_4(OCH_2CH_3)(n\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$, 89178-97-2; $N_3P_3F_3(OCH_2CH_3)_2(n\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$, 89178-98-3; $Li_2(n\text{-}C_5H_4)_2Fe$, 33272-09-2; $NaOCH_2CF_3$, 420-87-1; CH_3I, 74-88-4; $Cl(n\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$, 1273-74-1; $Cl(n\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)$, 38959-07-8; $LiEt_3BH$, 22560-16-3.

Supplementary Material Available: Includes the positional and thermal parameters from the final cycles of refinement (Tables VI, X, XIV, and XVIII), a list of interatomic distances and bond angles for the four compounds (Tables VII, XI, XV, and XIX), tables of least-squares planes (Tables VIII, XII, XVI, and XX), and calculated structure factors (Tables IX, XIII, XVII, and XXI) (64 pages). Ordering information is given on any current masthead page.

Anionic Alkyne Complexes of Tungsten

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Abstract: Anionic tungsten complexes have been prepared in which the ligand environment is dominated by alkyne ligands. Reduction of $[W(PhC{\equiv}CPh)_3CO]$ with lithium naphthalenide leads to formation of an anionic complex suggested to be $[W(PhC{\equiv}CPh)_3]^{2-}$, the first homoleptic anionic alkyne complex of a transition metal. The dianion has been characterized chemically by derivatization with Ph_3SnCl to form $[W(PhC{\equiv}CPh)_3SnPh_3]^-$, isolated as $[W(PhC{\equiv}CPh)_3SnPh_3]NEt_4$ (**2**) and structurally characterized by a single-crystal X-ray diffraction study. The acetylenic carbons form a tapered trigonal-prismatic coordination sphere for the W, with the Ph_3Sn ligand capping a trigonal face. Dynamic ^{13}C NMR studies have shown that **2** undergoes a rapid fluxional process, with a free energy of activation of 13.0 kcal mol^{-1} at room temperature, which is suggested to involve rotation of the alkyne ligands.

It has been recognized for many years that the reactions of anionic organotransition-metal complexes with electrophiles provide convenient routes to a wide variety of other molecules, but until recently the ligand environment in most common anionic systems has included the strongly π-acidic carbonyl ligand and was frequently dominated by this ligand. Typical examples of such carbonyl metalates include $[Fe(CO)_4]^{2-}$,[1,2] the group 6A carbonyl dianions $[M(CO)_5]^{2-}$,[1,3] $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$,[1] and $[M(\eta^5\text{-}C_5H_5)(CO)_3]^-$ (M = Cr, Mo, W).[1] Jonas and co-workers,[4]

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