Reactions of Ferrocenyl- and Ruthenocenylphosphazenes with Lithiometallocenes and the X-ray Structures of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$, $[N_3P_3F_3\{(\eta\text{-}C_5H_4)_2Fe\}\{(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)\}]$, 1,5-$N_4P_4F_6(\eta\text{-}C_5H_4)_2Fe$, and 1,5,3,7-$N_4P_4F_4[(\eta\text{-}C_5H_4)_2Ru]_2$[1]

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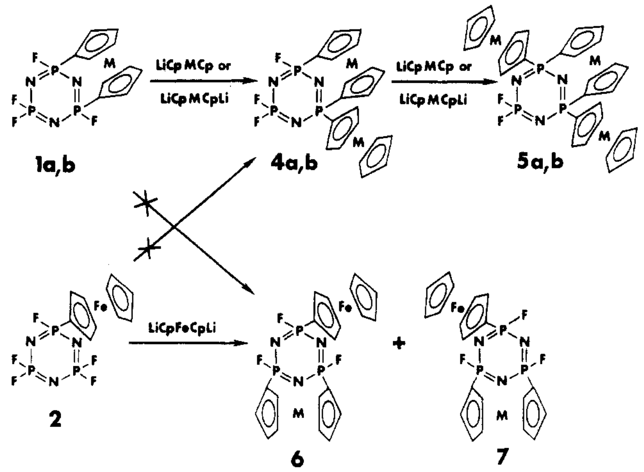
Cyclotri- and cyclotetraphosphazenes that bear fluoro and ferrocenyl or ruthenocenyl side groups undergo fluorine replacement with mono- or dilithioferrocene or mono- or dilithioruthenocene or with methyllithium or phenyllithium. The pattern of fluorine replacement is complex and depends on coordination of the incoming organolithium reagent with the skeletal nitrogen atoms and on steric hindrance factors. An unusual "double-transannular" ruthenocenylphosphazene was isolated from the cyclotetraphosphazene system. Four metallocenylphosphazenes have been studied by X-ray crystallography. Crystals of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (**1a**) are triclinic, space group $P\bar{1}$, with a = 8.074 (1) Å, b = 8.164 (1) Å, c = 11.521 (2) Å, α = 91.37 (2)°, β = 92.31 (2)°, γ = 118.2 (1)°, V = 667.9 Å^3, and Z = 2. The structure was refined to discrepancy indices R = 0.038 and R_w = 0.051. The phosphazene ring is severely distorted in response to the presence of the transannular ferrocenyl unit. *cis-non-gem*-$[N_3P_3F_3\{(\eta\text{-}C_5H_4)_2Fe\}\{(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)\}]$ (**7**) gives orthorhombic crystals, space group $P2_12_12_1$, with a = 10.398 (2) Å, b = 10.644 (2) Å, c = 18.769 (2) Å, V = 2077.3 Å^3, and Z = 4. The structure was refined to discrepancy indices R = 0.042 and R_w = 0.059. The phosphazene ring is highly distorted in this molecule. The ferrocene transannular tetramer 1,5-$N_4P_4F_6(\eta\text{-}C_5H_4)_2Fe$ (**3a**) gives monoclinic crystals, space group $P2_1/n$, with a = 8.668 (1) Å, b = 12.823 (1) Å, c = 14.560 (2) Å, β = 100.86 (1)°, V = 1589.3 Å^3, and Z = 4. The structure was refined to discrepancy indices R = 0.032 and R_w = 0.041. Even more distortion of the phosphazene ring is found in this molecule. Crystals of the double-transannular phosphazene tetramer 1,5,3,7-$N_4P_4F_4\{(\eta\text{-}C_5H_4)_2Ru\}_2$ (**10**) are monoclinic, space group $P2_1$, with a = 7.719 (1) Å, b = 12.151 (5) Å, c = 15.606 (2) Å, β = 101.93 (1)°, V = 1432.1 Å^3, and Z = 2. The eight-membered cyclotetraphosphazene ring is severely puckered to adapt to the constraints imposed by the two ruthenocene systems.

Metallocenylphosphazenes are a new class of organometallic compounds first synthesized in our laboratory.[2-4] These species are of interest for three reasons: (1) The "hybridization" of a metallocene structure with a phosphazene ring or chain allows the structural response of both components to be examined in detail. (2) The organometallic substitution chemistry of phosphazenes is quite complex,[5-12] and it is of some interest to elucidate the influence of metallocenyl groups already attached to a phosphazene ring on the behavior of incoming organometallic nucleophiles and the role played by the incoming nucleophile on substitution patterns. (3) The high polymer chemistry of phosphazenes is becoming increasingly important, with considerable emphasis being placed on the chemistry and uses of the organometallic derivatives. Metallocenylcyclophosphazenes function as "monomers" for the synthesis of such polymers. They also serve as reaction models for their high polymeric counterparts.

Scheme I



In this paper, we will concentrate on the synthesis, reactions, and structure of new metallocenylcyclophosphazenes. The polymerization chemistry will be discussed elsewhere.[13]

The work discussed here involves the substitution chemistry of the small-molecule cyclophosphazenes shown in 1–3. The reagents used for substitution were mono-

(1) This is the fourth paper in a series on metallocenylphosphazene ring systems and high polymers. The preceding papers in the series are listed as ref 2–4.

(2) Allcock, H. R.; Lavin, K. D.; Riding, G. H.; Suszko, P. R.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 2337.
(3) Allcock, H. R.; Lavin, K. D.; Riding, G. H.; Whittle, R. R. *Organometallics* **1984**, *3*, 663.
(4) Allcock, H. R.; Lavin, K. D.; Riding, G. H. *Macromolecules* **1985**, *18*, 1340.
(5) Allcock, H. R.; Allen, R. W.; O'Brien, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 3984.
(6) Allcock, H. R.; Lavin, K. D.; Tollefson, N. M.; Evans, T. L. *Organometallics* **1983**, *2*, 267.
(7) Allcock, H. R.; Harris, P. J.; Nissan, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 2256. Allcock, H. R.; Nissan, R. A.; Harris, P. J.; Whittle, R. R. *Organometallics* **1984**, *3*, 432.
(8) Allcock, H. R.; Scopelianos, A. G.; O'Brien, J. P.; Bernheim, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 350. Allcock, H. R.; Scopelianos, A. G.; Whittle, R. R.; Tollefson, N. M. *J. Am. Chem. Soc.* **1983**, *105*, 1316.
(9) Allcock, H. R.; Greigger, P. P.; Wagner, L. J.; Bernheim, M. Y. *Inorg. Chem.* **1981**, *20*, 717.
(10) Allcock, H. R.; Wagner, L. J.; Levin, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 1321.
(11) Allcock, H. R.; Riding, G. H.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 5561.
(12) Suszko, P. R.; Whittle, R. R.; Allcock, H. R. *J. Chem. Soc., Chem. Commun.* **1982**, 649.
(13) Allcock, H. R.; Lavin, K. D.; Riding, G. H. *Macromolecules*, to be submitted for publication.

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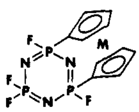
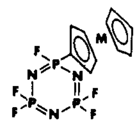


1a,b



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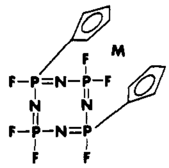


3a,b

a, M = Fe; b, M = Ru

and dilithioferrocene and mono- and dilithioruthenocene, methyllithium, and phenyllithium. The course of the investigation revolved around the following questions. (a) How many metallocenyl units can be attached to a phosphazene ring, and what factors determine the substitution limits? (b) What is the mechanism of substitution of fluorine atoms in 1–3 by lithiometallocenes or simpler organolithium compounds? (c) When dilithiometallocenes are used as reagents for reactions with 1–3, what factors favor transannular cyclization rather than monosubstitution or intermolecular coupling?

Results and Discussion

Substitution Patterns. The course of the reactions of 1 and 2 with mono- or dilithioferrocene or mono- or dilithioruthenocene is summarized in Scheme I. The analogous interactions between 3 and the same reagents are illustrated in Scheme II.

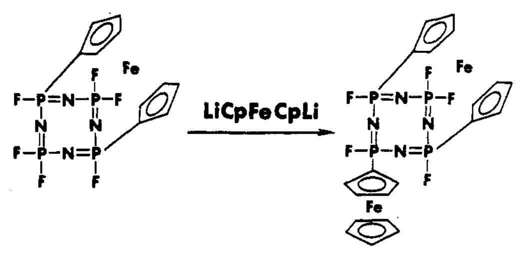
The transannular ferrocenylphosphazene **1a** reacts with 1 equiv of monolithioferrocene to yield the geminally substituted product **4a**. With a 3:1 excess of monolithioferrocene, the same reaction yields significant quantities of **4a**, together with the di-geminal product **5a** (Scheme I). This propensity for replacement of the *geminal* fluorine atoms in **1a** is surprising. In earlier work, we showed that a *non-geminal* pathway prevails when the nontransannular analogue of **1a** (i.e., compound **2a**) reacts with monolithioferrocene, the main product being compound 11.[2] Moreover, we have now found that **2a** reacts with dilithioferrocene to give a mixture of cis- and trans-non-gem transannular products of structure 6 and 7. Thus a pendent metallocenyl group is non-geminal-directing, but a transannular, metallocenyl unit is geminally orienting, at least in the trimeric system.

Dilithioferrocene–TMEDA also reacts with **1a** to yield **4a** and **5a**. No double-transannular products were isolated. This indicates that, after attachment of the first cyclopentadienyl ring to **1a**, ring closure does not take place, probably because of steric restrictions. The pendent lithio function is replaced by hydrogen from the 2-propanol added before isolation of the products.

The transannular ruthenocenyl phosphazene **1b** reacts with a 3:1 mixture of dilithio- or monolithioruthenocene to yield products **4b** and **5b**. Again, a geminal pathway prevails, and no double-transannular species were isolated.

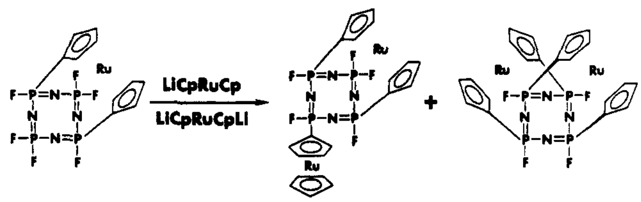
At the cyclic tetrameric phosphazene level, compound **3a** reacted with an excess of dilithioferrocene–TMEDA to yield the non-gem-"pendent" derivative **8a**. No double-transannular derivatives were detected, and, again, the unreacted lithio function was replaced by hydrogen during isolation of the products. Note that there are two possible isomers of **8a**. It was not possible to assign a cis or trans structure on the basis of the spectroscopic data. However, the data are consistent with the presence of only one isomer. Thus, the reaction appears to be stereospecific.

Scheme II



3a **8a**

The ruthenocenyl analogue **3b** reacts with a mixture of monolithio- and dilithioruthenocene to give two main products—the non-gem-pendent derivative **9b** (the major product) and the double-transannular derivative **10**. This



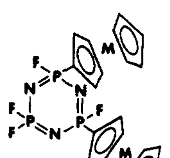
3b **9b** **10**

is the first example reported of a double-transannular phosphazene. The NMR spectra of compound **9b** are compatible with the isolation of only one isomer, but the data did not allow the identification of it as the cis or trans product.

A comparison of the spectroscopic data for **8a** and **9b**, particularly the ^{19}F NMR spectra, indicated that these species do not have the same configuration; i.e., one is cis and the other is trans.

Influence of Other Substituent Groups and Organolithium Reagents. Dilithioferrocene–TMEDA reacts with $N_3P_3F_5Ph$ (**12**) to give the cis- and trans-non-geminal isomers of **13** in good yield. No geminal products were detected. Thus, a phenyl group already present on the cyclotriphosphazene ring resembles a pendent metallocenyl group in its substituent-directing effect.

Transannular compound **1a** reacted with 1 or 6 equiv of methyllithium to yield the geminal product **14**. Similarly, **1a** interacted with 1.5 equiv of phenyllithium to give the geminal products **15** and **16**. However, **1a** reacted with 1 equiv of sodium trifluoroethoxide to yield the non-geminal product **17**. No geminal products were detected in this reaction mixture.



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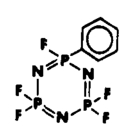

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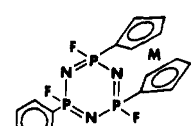

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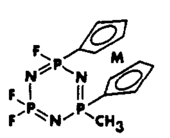

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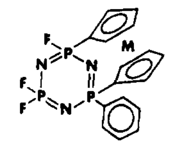

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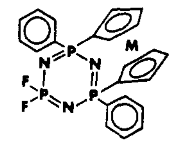

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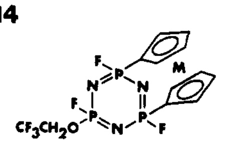

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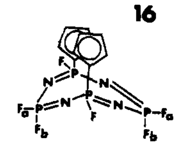

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Explanations for the Reaction Patterns. The experimental facts are as follows. (a) Transannular ferrocenyl or ruthenocenyl groups attached to a trimeric phosphazene ring direct an incoming lithiometallocene, methyllithium, or phenyllithium to one of the geminal substitution sites. (b) A pendent metallocenyl group or a phenyl group attached to a trimeric phosphazene ring directs an incoming lithiometallocene to one of the non-geminal sites. (c) No transannular metallocenyl cyclic trimeric phosphazene has yet been shown to form a double-transannular derivative. (d) The 1,5-transannular ferrocenyl tetramer **3a** has so far failed to form a double-transannular derivative. (e) Only the 1,5-transannular ruthenocenyl tetramer **3b** has yielded a double-transannular derivative.

We believe that geminal substitution, when it occurs in the trimer, is a consequence of prior coordination between the incoming lithium reagent and the skeletal nitrogen atom that lies between the transannular linkage sites. This nitrogen is probably more basic than the other two because (a) it is flanked by less electronegative substituent groups and (b) (see later) it is structurally different because of the distorting influence of the bridging structure. Specifically, that nitrogen atom lies 0.62 Å out of the main phosphazene ring plane, with a P–N–P bond angle of only 111°. Thus, this nitrogen atom has more sp^3 character than its counterparts across the ring and presumably has a greater lone-pair availability. Only when coordination of the incoming reagent to nitrogen is unimportant (for example, when the reagent is sodium trifluoroethoxide) would this influence be lost.

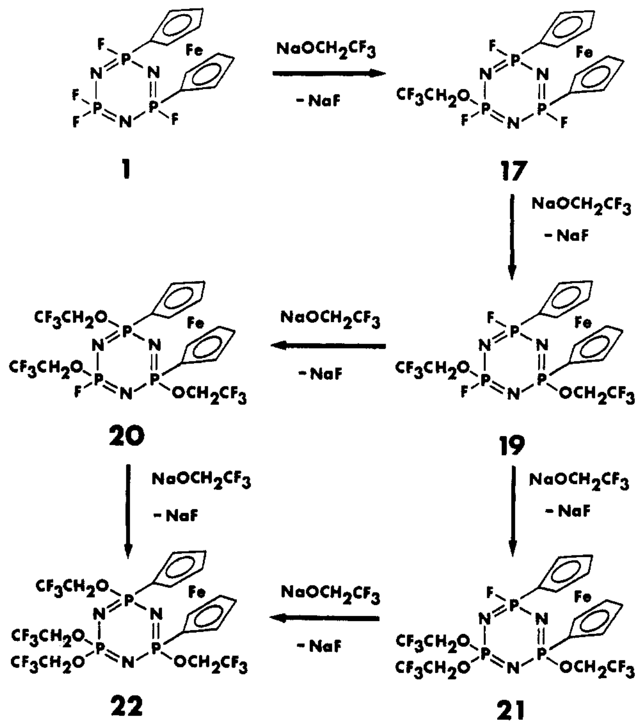
Non-geminal substitution is probably a consequence of an absence of such favored coordination, coupled with the influence of steric hindrance by the substituent group already present. Thus, a pendent metallocenyl group or a phenyl group has a relatively benign influence on the planarity and bond angles of the cyclotriphosphazene ring.[2] Its main effect would be to shield the geminal fluorine atom and the phosphorus atom at that site. Such shielding might be expected to be less serious when the metallocenyl unit forms part of a transannular bridge.

In the cyclic tetrameric phosphazene system **3a,b**, a similar coordination effect may be operating. However, in **3a,b** there is a PCpF and a PF_2 unit adjacent to *every* skeletal nitrogen atom. Thus, if prior coordination does take place between the incoming lithium reagent and a skeletal nitrogen atom, then reaction at the PF_2 unit would probably be more likely for steric reasons. This would lead to the conversion of **3a** to **8a** or **3b** to **9b** and **10**.

The formation of the bis-transannular product with dilithioruthenocene, but not with dilithioferrocene, may be explained by the following interpretation. First, it is possible that, with dilithioferrocene, replacement of fluorine atoms F_a (structure 18) is preferred, i.e., cis-non-gem replacement. If so, cyclization by the second lithio site would be prevented by the shape of the substrate molecule. This view is supported by the spectroscopic data which indicate that **8a** and **9b** have different cis–trans geometries. Second, the difference may be a consequence of the different "spans" of the two dilithio reagents. The span of dilithioferrocene may be too short to bridge the gap between the 3,7-positions of the (now rigid) cyclotetraphosphazene ring.

Earlier work on the mechanism of nucleophilic substitution in halophosphazenes has indicated that an S_N2-type process operates. The transannular linkage in compounds **1a** and **10** might be expected to retard an S_N2-type replacement of the fluorine atoms by organic nucleophiles. Reaction of **1a** with successive equivalents of sodium trifluoroethoxide was found to proceed by the reaction pathway shown in Scheme III (see Appendix A). All substitutions occurred within a few hours at room temperature. By contrast, all attempts to induce **10** to react with sodium trifluoroethoxide were unsuccessful. No reaction was observed when **10** was heated to 75 °C with 10 equiv of sodium trifluoroethoxide in THF solution for 14 days.

Scheme III



It is clear from these results that, when only one face of the ring is protected by a bridging group as in 1, substitution of the remaining halogen atoms occurs relatively easily. However, when both faces of the ring are protected, as in **10**, substitution of the remaining halogen atoms is very difficult, if not impossible. This suggests that in these complexes the attacking nucleophile approaches the phosphorus atom in an axial direction, probably along the *z* axis of an unfilled d_{z^2} orbital. The alternative mechanism, involving attack at the equatorial position, does not appear to occur even when the angle between the two substituents is increased by the strain imposed by the bridging group.

Structure Determination: NMR Spectroscopy. The structures of **3–16** were determined unambiguously by a combination of ^{31}P, ^{1}H, 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 compounds, **1a**, **7**, **3a**, and **10**, were studied by single-crystal X-ray diffraction methods.

X-ray Diffraction: Crystal and Molecular Structure of 1a. An X-ray single-crystal analysis confirmed that the molecule consists of a ferrocenyl unit linked in a non-geminal, transannular manner via two P–C covalent bonds to a cyclotriphosphazene ring. All features of the molecule were identified, including hydrogen atoms attached to the cyclopentadienyl rings. The main structural features of **1a** are summarized in Tables I and II and are illustrated in Figure 1. Positional parameters are listed in Table III.

As in other metallocenylphosphazenes,[2,3] the metallocene portion of the molecule appears to be unaffected by the presence of the phosphazene ring. The cyclopentadienyl groups are planar and virtually coplanar, the dihedral angle

Table I. Summary of Crystal Data and Intensity Collection Parameters

	1a	3a	7	10
formula	$C_{10}H_8N_3P_3F_4Fe$	$C_{10}H_8N_4P_4F_6Fe$	$C_{20}H_{17}N_3P_3F_3Fe_2$	$C_{20}H_{16}N_4P_4F_4Ru_2$
fw, amu	394.96	477.94	560.99	806.55
space group	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$	$P2_1$
cryst system	triclinic	monoclinic	orthorhombic	monoclinic
a, Å	8.074 (1)	8.668 (1)	10.398 (2)	7.719 (1)
b, Å	8.164 (1)	12.823 (1)	10.644 (2)	12.151 (5)
c, Å	11.521 (2)	14.560 (2)	18.769 (2)	15.606 (2)
α, deg	91.37 (1)			
β, deg	92.31 (1)	100.86 (1)		101.93 (1)
γ, deg	118.20 (1)			
V, Å^3	667.9	1589.3	2077.3	1432.1
Z	2	4	4	2
d(calcd), g/cm^3	1.964	2.00	1.79	1.87
F(000)	392	944	1128	696
μ, cm^{-1}	15.2	14.1	16.6	13.1
% loss or gain in I	0.6	1.1	4.2	1.0
decay correctn	0.984–1.025	1.000–1.005	0.903–1.072	0.995–1.000
absorptn correctn, cm^{-1}				
min transmissn		0.6172		0.5793
max transmissn		0.7212		0.8401
θ_{max}, deg	24	25	30	30
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
ω scan width, deg (A + 0.35 tan θ)	1.00	0.60	0.80	0.75
unique data measd	2056	2793	3319	4337
data used	1975 ($I > 2\sigma(I)$)	2259 ($I > 3.5\sigma(I)$)	3074 ($I > 2.5\sigma(I)$)	4064 ($I > 3\sigma(I)$)
data/parameter	8.9	8.8	8.8	8.7
R, $R_w = (\sum\omega\Delta^2/\sum\omega F_o^2)^{1/2}$	0.038, 0.057	0.032, 0.041	0.042, 0.059	0.026, 0.033
max shift/error	0.02	0.00	0.00	0.00

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) for $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (1a)[a]

	Bond Lengths		
Fe–Cp$_1$[b]	1.655	P(2)–F(2)	1.544 (2)
Fe–Cp$_2$[b]	1.655	P(2)–N(1)	1.594 (2)
P(1)–C(1)	1.769 (3)	P(2)–N(2)	1.593 (2)
P(1)–F(1)	1.547 (2)	P(3)–F(3)	1.538 (2)
P(1)–N(1)	1.592 (2)	P(3)–F(4)	1.533 (3)
P(1)–N(3)	1.594 (3)	P(3)–N(2)	1.559 (2)
P(2)–C(6)	1.767 (3)	P(3)–N(3)	1.558 (2)
	Bond Angles		
C(1)–P(1)–F(1)	106.3 (1)	P(1)–N(1)–P(2)	111.0 (2)
N(1)–P(1)–N(3)	115.6 (1)	P(2)–N(2)–P(3)	118.4 (2)
C(6)–P(2)–F(2)	106.1 (1)	P(1)–N(3)–P(3)	118.1 (1)
N(1)–P(2)–N(2)	115.2 (1)	C(2)–C(1)–C(5)	107.8 (3)
F(3)–P(3)–F(4)	97.6 (1)	C(7)–C(6)–C(10)	107.8 (3)
N(2)–P(3)–N(3)	120.5 (1)		

[a] Estimated standard deviation in parentheses. [b] Distance between atom and ring plane.

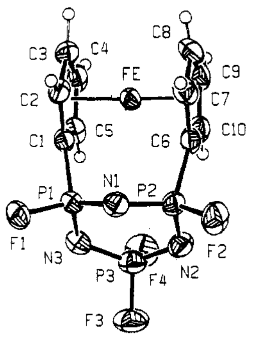


Figure 1. Ortep representation of the molecular structure of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (**1a**).

between the rings being only 2.5°. They are equally separated from the iron atom by a distance of 1.655 Å. This is almost identical with the separation of 1.66 Å found in ferrocene. The average C–C bond distance around the ring of 1.42 Å is close to the value (1.44 Å) found in ferrocene. The P–C distance is 1.77 Å. This is identical with the value found in other metallocenylphosphazenes studied previously.[2]

Table III. Positional Parameters and Their Estimated Standard Deviations for $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (1a)

atom	*x*	*y*	*z*
Fe	0.26534 (4)	0.35227 (5)	0.70812 (3)
P(1)	−0.16618 (9)	0.22261 (9)	0.63212 (6)
P(2)	−0.02823 (9)	0.47931 (9)	0.80223 (7)
P(3)	−0.2816 (1)	0.1276 (1)	0.84896 (7)
F(1)	−0.2824 (2)	0.1824 (2)	0.5150 (2)
F(2)	−0.0205 (2)	0.6672 (2)	0.8356 (2)
F(3)	−0.4821 (3)	0.0613 (3)	0.8885 (2)
F(4)	−0.2326 (3)	0.0007 (3)	0.9226 (2)
N(1)	−0.1111 (3)	0.4316 (3)	0.6706 (2)
N(2)	−0.1526 (3)	0.3335 (3)	0.8931 (2)
N(3)	−0.2939 (3)	0.0684 (3)	0.7180 (2)
C(1)	0.0311 (3)	0.1916 (3)	0.6035 (2)
C(2)	0.1825 (4)	0.3044 (4)	0.5350 (3)
C(3)	0.3304 (4)	0.2578 (4)	0.5579 (3)
C(4)	0.2708 (4)	0.1193 (4)	0.6403 (3)
C(5)	0.0868 (4)	0.0762 (4)	0.6692 (3)
C(6)	0.2066 (4)	0.5184 (4)	0.8154 (4)
C(7)	0.3534 (4)	0.6282 (4)	0.7422 (3)
C(8)	0.5051 (4)	0.5894 (5)	0.7650 (3)
C(9)	0.4546 (4)	0.4580 (4)	0.8503 (3)
C(10)	0.2691 (4)	0.4096 (4)	0.8831 (3)
H(2)	0.196 (4)	0.404 (4)	0.478 (3)
H(3)	0.463 (4)	0.328 (4)	0.525 (3)
H(4)	0.341 (4)	0.063 (4)	0.679 (3)
H(5)	0.005 (4)	−0.018 (4)	0.725 (3)
H(7)	0.361 (4)	0.699 (4)	0.699 (3)
H(8)	0.604 (4)	0.637 (4)	0.721 (3)
H(9)	0.536 (4)	0.412 (4)	0.884 (3)
H(10)	0.196 (4)	0.327 (4)	0.936 (3)

The most unusual feature of the structure is the marked distortion of the phosphazene ring to accommodate the bridging substituent. The phosphazene ring in this molecule is even more distorted than in the analogous ruthenium derivative $N_3P_3F_4(\eta\text{-}C_5H_4)_2Ru$ (**1b**), the structure of which was determined previously.[2] The nitrogen atom between the two phosphorus atoms that bear the cyclopentadienyl groups, N(1), is displaced from the plane of the phosphazene ring by 0.62 Å. A displacement of 0.56 Å was found for $N_3P_3F_4(\eta\text{-}C_5H_4)_2Ru$ (**1b**). The bond lengths and angles also vary considerably from those in $(NPF_2)_3$. The four bonds adjacent to the metallocene

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) for 1,5-$N_4P_4F_6(\eta\text{-}C_5H_4)_2Fe$ (3a)

Bond Lengths			
P(1)–C(1)	1.758 (2)	P(3)–F(4)	1.549 (1)
P(1)–F(1)	1.543 (1)	P(3)–C(6)	1.754 (2)
P(1)–N(1)	1.569 (2)	P(3)–N(2)	1.557 (2)
P(1)–N(4)	1.561 (2)	P(3)–N(3)	1.564 (2)
P(2)–F(2)	1.533 (1)	P(4)–F(5)	1.513 (2)
P(2)–F(3)	1.531 (2)	P(4)–F(6)	1.506 (2)
P(2)–N(1)	1.536 (2)	P(4)–N(3)	1.521 (2)
P(2)–N(2)	1.539 (2)	P(4)–N(4)	1.533 (2)
Bond Angles			
F(1)–P(1)–C(1)	104.01 (8)	N(3)–P(4)–N(4)	125.4 (1)
N(1)–P(1)–N(4)	119.1 (1)	P(1)–N(1)–P(2)	133.2 (1)
F(2)–P(2)–F(3)	97.50 (9)	P(2)–N(2)–P(3)	136.5 (1)
N(1)–P(2)–N(2)	124.2 (1)	P(3)–N(3)–P(4)	135.1 (1)
F(4)–P(3)–C(6)	103.6 (8)	P(1)–N(4)–P(4)	135.7 (1)
N(2)–P(3)–N(3)	120.1 (1)	C(2)–C(1)–C(5)	108.2 (2)
N(3)–P(3)–C(6)	111.7 (1)	C(7)–C(6)–C(10)	108.1 (2)

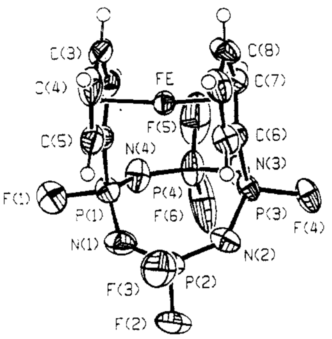


Figure 2. Ortep representation of the molecular structure of 1,5-$N_4P_4F_6(\eta\text{-}C_5H_4)_2Fe$ (**3a**).

linkage sites are longer than expected (1.593 Å average), and the angle at N(1) (111.0 (2)°) is also narrower than those at N(2) and N(3) of 118.4 (1)° and 118.1 (2)°. The angles at P(1) and P(2) (at the bridging site) of 115.6 (1)° and 115.2 (1)° are also narrower than the angle at P(3) of 120.5 (1)°. These distortions are almost certainly a result of the phosphazene unit accommodating to the steric requirements of the bridging ferrocenyl group.

Crystal and Molecular Structure of 3a. An X-ray single-crystal structure analysis confirmed that **3a** consists of a ferrocenyl unit bound through C–P bonds in a transannular manner to the 1,5 phosphorus atoms of the cyclotetraphosphazene ring. All features of the molecule were identified, including the hydrogen atoms attached to the Cp rings. The main structural features of **3a** are summarized in Tables I and IV and are illustrated in Figure 2. Positional parameters are listed in Table V.

The cyclopentadienyl rings in **3a** are planar and virtually coplanar, as in ferrocene, with an average C–C bond distance of 1.415 (3) Å. The cyclophosphazene unit appears to have little or no influence on the metallocene structure as was observed previously for the structure of **3b**.[2] The average C–P bond distance is 1.756 (2) Å. The cyclotetraphosphazene ring is distorted into a boat conformation to accommodate to the steric requirements of the metallocene unit.

The P–N bonds flanking both of the metallocene linkage sites [P(1) and P(3)] (1.563 (2) Å) are longer than the others (1.534 (2) Å). This is in direct contrast to the structure of **3b**, where only the P–N bonds near P(1) were longer.[2] This difference may be attributed to the smaller span in dilithioferrocene vs. dilithioruthenocene.

The phosphazene ring angles in **3a** at the bridgehead sites [P(1) and P(3)] are narrower (119.1 (1)° and 120.1 (1)°, respectively, than the values of 124.2 (1)° and 125.4

Table V. Positional Parameters and Their Estimated Standard Deviations for 1,5-$N_4P_4F_6(\eta\text{-}C_5H_4)_2Fe$ (3a)

atom	*x*	*y*	*z*
Fe	0.65795 (5)	0.20766 (3)	0.13492 (3)
P(1)	0.3015 (1)	0.32763 (7)	0.43430 (6)
P(2)	0.5729 (1)	0.23433 (8)	0.54462 (6)
P(3)	0.3408 (1)	0.08143 (6)	0.56808 (6)
P(4)	0.1772 (1)	0.12423 (7)	0.38306 (6)
F(1)	0.2968 (3)	0.4212 (2)	0.3672 (1)
F(2)	0.7277 (2)	0.2117 (2)	0.5120 (2)
F(3)	0.6422 (3)	0.2941 (2)	0.6339 (2)
F(4)	0.3762 (2)	−0.0285 (1)	0.6109 (1)
F(5)	0.5015 (3)	0.3911 (2)	0.8554 (3)
F(6)	0.2240 (5)	0.0665 (2)	0.3025 (2)
N(1)	0.4810 (3)	0.3115 (2)	0.4741 (2)
N(2)	0.5066 (3)	0.1299 (2)	0.5719 (2)
N(3)	0.2309 (3)	0.0608 (2)	0.4716 (2)
N(4)	0.7090 (4)	0.2593 (2)	0.8718 (2)
C(1)	0.7007 (4)	0.1277 (2)	0.0207 (2)
C(2)	0.5353 (4)	0.1361 (3)	0.0173 (2)
C(3)	0.5024 (4)	0.0879 (3)	0.0988 (3)
C(4)	0.6440 (5)	0.0499 (3)	0.1509 (3)
C(5)	0.2672 (4)	0.4261 (3)	0.6036 (2)
C(6)	0.2393 (3)	0.1433 (2)	0.6463 (2)
C(7)	0.0737 (4)	0.1447 (3)	0.6407 (2)
C(8)	0.0429 (4)	0.2021 (3)	0.7176 (2)
C(9)	0.1870 (5)	0.2379 (3)	0.7697 (2)
C(10)	0.3095 (4)	0.2018 (3)	0.7267 (2)
H(2)	0.472 (3)	0.167 (2)	0.968 (2)
H(3)	0.400 (4)	0.085 (3)	0.113 (2)
H(4)	0.332 (4)	−0.015 (3)	0.791 (2)
H(5)	0.379 (4)	0.440 (3)	0.622 (2)
H(7)	0.496 (3)	0.389 (2)	0.090 (2)
H(8)	0.451 (4)	0.285 (3)	0.234 (3)
H(9)	0.714 (4)	0.221 (3)	0.319 (2)
H(10)	0.425 (4)	0.208 (2)	0.750 (2)

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for *cis-non-gem*-$N_3P_3F_3\{(\eta\text{-}C_5H_4)_2Fe\}\{(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)\}$ (7)[a]

Bond Lengths			
Fe(1)–Cp_1[b]	1.660	P(2)–C(6)	1.776 (4)
Fe(1)–Cp_2[b]	1.651	P(2)–F(2)	1.555 (3)
Fe(2)–Cp_3[b]	1.642	P(2)–N(1)	1.598 (4)
Fe(2)–Cp_4[b]	1.655	P(2)–N(2)	1.594 (4)
P(1)–C(1)	1.771 (5)	P(3)–C(11)	1.758 (4)
P(1)–F(1)	1.557 (3)	P(3)–F(3)	1.567 (3)
P(1)–N(1)	1.602 (4)	P(3)–N(2)	1.602 (4)
P(1)–N(3)	1.598 (3)	P(3)–N(3)	1.582 (4)
Bond Angles			
F(1)–P(1)–C(1)	105.5 (2)	P(2)–N(2)–P(3)	118.4 (2)
N(1)–P(1)–N(3)	116.6 (2)	P(1)–N(3)–P(3)	119.4 (2)
F(2)–P(2)–C(6)	104.3 (2)	C(2)–C(1)–C(5)	107.3 (4)
N(1)–P(2)–N(2)	116.2 (2)	C(7)–C(6)–C(10)	107.7 (4)
F(3)–P(3)–C(11)	100.3 (2)	C(12)–C(11)–C(15)	107.7 (4)
N(2)–P(3)–N(3)	117.5 (2)	C(17)–C(16)–C(20)	109.6 (8)
P(1)–N(1)–P(2)	109.6 (2)		

[a] Estimated standard deviations in parentheses. [b] Distance between atom and ring plane.

(1)° 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 average of 135.1 (1)° being typical. These phosphazene ring angles are similar to those found for **3b**.[2]

X-ray Diffraction: Crystal and Molecular Structure of 7. An X-ray single-crystal analysis confirmed that the molecule consists of a pendent ferrocene unit attached in a cis configuration to a non-geminal phosphorus atom of a cyclotriphosphazene ring in which the other two phosphorus atoms are bound via two P–C covalent bonds to a transannular ferrocene unit. All features of the molecule were identified, including the hydrogen atoms attached to the cyclopentadienyl rings. The main struc-

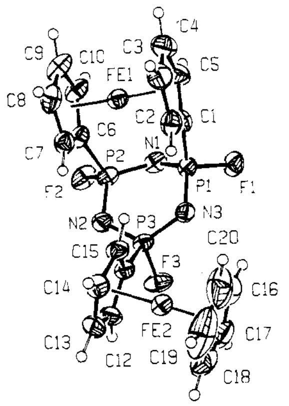


Figure 3. Ortep representation of the molecular structure of *cis-non-gem*-$[N_3P_3F_3\{(\eta\text{-}C_5H_4)_2Fe\}\{(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)\}]$ (7).

Table VII. Positional Parameters and Their Estimated Standard Deviations for $N_3P_3F_3\{(\eta\text{-}C_5H_4)_2Fe\}\{(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)\}$ (7)

atom	x	y	z
Fe(1)	0.80088 (6)	0.00440 (5)	0.02101 (3)
Fe(2)	0.78211 (6)	−0.43391 (5)	−0.22230 (3)
P(1)	0.7140 (1)	0.04865 (9)	−0.14144 (5)
P(2)	0.5264 (1)	−0.0212 (1)	−0.05758 (6)
P(3)	0.6066 (1)	−0.18435 (9)	−0.16172 (5)
F(1)	0.7419 (3)	0.1483 (3)	−0.2002 (2)
F(2)	0.3888 (3)	0.0206 (3)	−0.0354 (1)
F(3)	0.5178 (3)	−0.1954 (3)	−0.2289 (1)
N(1)	0.5811 (4)	0.0907 (3)	−0.1056 (2)
N(2)	0.5147 (4)	−0.1548 (4)	−0.0953 (2)
N(3)	0.7158 (4)	−0.0856 (3)	−0.1795 (2)
C(1)	0.8431 (5)	0.0612 (4)	−0.0803 (2)
C(2)	0.9264 (5)	−0.0385 (5)	−0.0600 (3)
C(3)	0.9982 (5)	−0.0006 (5)	0.0013 (3)
C(4)	0.9570 (6)	0.1250 (6)	0.0194 (3)
C(5)	0.8624 (6)	0.1624 (4)	−0.0301 (3)
C(6)	0.6099 (4)	−0.0382 (4)	0.0244 (2)
C(7)	0.6862 (5)	−0.1470 (4)	0.0435 (2)
C(8)	0.7593 (6)	−0.1161 (5)	0.1048 (3)
C(9)	0.7322 (6)	0.0097 (6)	0.1238 (2)
C(10)	0.6394 (5)	0.0598 (5)	0.0742 (2)
C(11)	0.6630 (4)	−0.3397 (4)	−0.1556 (2)
C(12)	0.5995 (4)	−0.4480 (4)	−0.1846 (2)
C(13)	0.6697 (5)	−0.5566 (4)	−0.1645 (3)
C(14)	0.7764 (5)	−0.5173 (4)	−0.1235 (2)
C(15)	0.7775 (5)	−0.3829 (4)	−0.1175 (2)
C(16)	0.8743 (7)	−0.3127 (7)	−0.2889 (3)
C(17)	0.7803 (7)	−0.3791 (6)	−0.3276 (3)
C(18)	0.8085 (8)	−0.5072 (7)	−0.3222 (3)
C(19)	0.9216 (8)	−0.5171 (8)	−0.2800 (4)
C(20)	0.9567 (7)	−0.391 (1)	−0.2619 (4)
H(2)	0.934	−0.119	−0.084
H(3)	1.062	−0.050	0.026
H(4)	0.989	0.174	0.059
H(5)	0.818	0.242	−0.030
H(7)	0.686	−0.227	0.019
H(8)	0.818	−0.171	0.129
H(9)	0.769	0.055	0.164
H(10)	0.604	0.144	0.074
H(12)	0.522	−0.447	−0.213
H(13)	0.647	−0.642	−0.176
H(14)	0.841	−0.573	−0.103
H(15)	0.838	−0.331	−0.093
H(16)	0.878	−0.223	−0.283
H(17)	0.709	−0.343	−0.353
H(18)	0.761	−0.576	−0.343
H(19)	0.966	−0.594	−0.267
H(20)	1.030	−0.368	−0.233

tural features of 7 are summarized in Tables I and VI and are illustrated in Figure 3. Positional parameters are listed in Table VII.

The metallocene portion of the molecule appears to be unaffected by the presence of the phosphazene ring.[2] The cyclopentadienyl groups are planar and virtually coplanar, the dihedral angle between the rings being only 3.8° (transannular) and 1.2° (monolinked), respectively. They are equally separated from the iron atoms by a distance of 1.66 Å; this is identical with the separation found in ferrocene. The average C–C bond distance around the ring of 1.42 Å is close to the value (1.44 Å) found in ferrocene. The average C–P distance is 1.765 Å. This is almost identical with the distance of 1.77 Å found in other metallocenylphosphazenes studied previously.[2]

The most unusual feature of the structure also is the marked distortion of the phosphazene ring to accommodate the bridging substituent. The phosphazene ring in this molecule is even more distorted than in the iron and ruthenium derivatives **1a,b**. The nitrogen atom between the two phosphorus atoms bearing the cyclopentadienyl groups, N(1), is displaced from the plane formed by the five remaining atoms of the phosphazene ring by 0.67 Å. Displacements of 0.62 and 0.56 Å were detected for **1a** and **1b**, respectively.

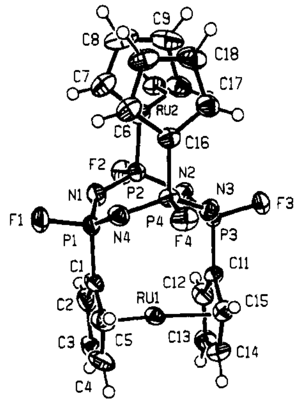


Figure 4. Ortep representation of the molecular structure of 1,5,3,7-$N_4P_4F_4\{(\eta\text{-}C_5H_4)_2Ru\}_2$ (10).

Table VIII. Selected Bond Lengths (Å) and Bond Angles (deg) for 1,5,3,7-$N_4P_4F_4[(\eta\text{-}C_5H_4)_2Ru]_2$ (10)[a]

Bond Lengths			
P(1)–C(1)	1.761 (3)	P(3)–C(11)	1.763 (3)
P(1)–F(1)	1.558 (2)	P(3)–F(3)	1.560 (2)
P(1)–N(1)	1.572 (3)	P(3)–N(2)	1.559 (3)
P(1)–N(4)	1.566 (3)	P(3)–N(3)	1.566 (3)
N(2)–C(6)	1.765 (3)	P(4)–C(16)	1.758 (3)
P(2)–F(2)	1.555 (2)	P(4)–F(4)	1.556 (2)
P(2)–N(1)	1.568 (3)	P(4)–N(3)	1.566 (3)
P(2)–N(2)	1.559 (3)	P(4)–N(4)	1.564 (3)
Bond Angles			
F(1)–P(1)–C(1)	102.3 (1)	N(3)–P(4)–N(4)	122.3 (2)
N(1)–P(1)–N(4)	121.3 (2)	P(1)–N(1)–P(2)	134.3 (2)
F(2)–P(2)–C(6)	102.5 (1)	P(2)–N(2)–P(3)	134.3 (2)
N(1)–P(2)–N(2)	121.5 (2)	P(3)–N(3)–P(4)	135.5 (2)
N(2)–P(2)–C(6)	110.3 (2)	P(1)–N(4)–P(4)	132.8 (2)
F(3)–P(3)–C(11)	102.3 (1)	C(2)–C(1)–C(5)	108.1 (3)
N(2)–P(3)–N(3)	122.5 (2)	C(7)–C(6)–C(10)	108.0 (3)
F(4)–P(4)–C(16)	101.9 (1)		

[a] Estimated standard deviations in parentheses.

X-ray Diffraction: Crystal and Molecular Structure of 10. An X-ray single-crystal analysis confirmed that the molecule consists of two ruthenocene units bonded through C–P bonds in a transannular manner to the 1,5 and 3,7 atoms of the cyclotetraphosphazene ring. All features of the molecule were identified, including the hydrogen atoms attached to the Cp rings. The main structural features of **10** are summarized in Tables I and VIII and are illustrated in Figure 4. Positional parameters are listed in Table IX.

The metallocene portion of the molecule appears to be unaffected by the presence of the phosphazene ring.[2] The

Table IX. Positional Parameters and Their Estimated Standard Deviations for 1,5,3,7-$N_4P_4F_4[(\eta\text{-}C_5H_4)_2Ru]_2$ (10)

atom	x	y	z
Ru(1)	0.11465 (3)	0.82916 (3)	0.10374 (2)
Ru(2)	0.44912 (3)	1.25000	0.39055 (2)
P(1)	0.0423 (1)	1.0898 (1)	0.1833 (1)
P(2)	0.4076 (1)	1.1419 (1)	0.1823 (1)
P(3)	0.4564 (1)	0.9272 (1)	0.2609 (1)
P(4)	0.1989 (1)	1.0120 (1)	0.3554 (1)
F(1)	−0.1145 (3)	1.1728 (2)	0.1616 (2)
F(2)	0.4714 (3)	1.1780 (2)	0.0983 (1)
F(3)	0.6423 (3)	0.8832 (2)	0.3069 (1)
F(4)	0.1039 (3)	0.9396 (2)	0.4139 (1)
N(1)	0.2009 (4)	1.1527 (3)	0.1565 (2)
N(2)	0.4990 (4)	1.0287 (3)	0.2077 (2)
N(3)	0.3522 (4)	0.9373 (3)	0.3365 (2)
N(4)	0.0477 (4)	1.0560 (3)	0.2806 (2)
C(1)	−0.0328 (4)	0.9802 (3)	0.1114 (2)
C(2)	−0.0026 (5)	0.9686 (4)	0.0240 (2)
C(3)	−0.0889 (5)	0.8675 (4)	−0.0105 (3)
C(4)	−0.1695 (5)	0.8209 (4)	0.0522 (3)
C(5)	−0.1366 (5)	0.8895 (4)	0.1285 (3)
C(6)	0.5005 (4)	1.2437 (3)	0.2587 (2)
C(7)	0.4251 (5)	1.3479 (3)	0.2713 (3)
C(8)	0.5436 (7)	1.4009 (4)	0.3404 (3)
C(9)	0.6880 (5)	1.3327 (5)	0.3704 (3)
C(10)	0.6648 (4)	1.2340 (4)	0.3209 (2)
C(11)	0.3718 (4)	0.8175 (3)	0.1908 (2)
C(12)	0.3923 (4)	0.8043 (3)	0.1009 (2)
C(13)	0.2963 (6)	0.7085 (4)	0.0676 (3)
C(14)	0.2186 (6)	0.6629 (4)	0.1355 (3)
C(15)	0.2645 (5)	0.7302 (3)	0.2100 (3)
C(16)	0.2842 (5)	1.1195 (3)	0.4272 (2)
C(17)	0.4522 (6)	1.1206 (4)	0.4868 (2)
C(18)	0.4703 (6)	1.2235 (4)	0.5299 (2)
C(19)	0.3172 (6)	1.2871 (4)	0.4988 (2)
C(20)	0.2007 (5)	1.2234 (3)	0.4346 (2)
C(21)	−0.214 (1)	0.5208 (8)	0.2036 (5)
C(22)	−0.0546 (8)	0.4522 (6)	0.2488 (5)
C(23)	0.041 (1)	0.4950 (6)	0.3193 (7)
C(24)	−0.0032 (10)	0.5878 (8)	0.3545 (6)
C(25)	−0.1313 (13)	0.6521 (8)	0.3206 (8)
C(26)	−0.2336 (9)	0.6142 (6)	0.2437 (5)
C(27)	−0.2914 (14)	0.4760 (13)	0.1363 (6)
H(2)	0.061	1.018	−0.005
H(3)	−0.090	0.837	−0.067
H(4)	−0.236	0.754	0.046
H(5)	−0.177	0.877	0.181
H(7)	0.316	1.376	0.239
H(8)	0.527	1.472	0.362
H(9)	0.786	1.349	0.417
H(10)	0.743	1.173	0.328
H(12)	0.458	0.851	0.070
H(13)	0.286	0.680	0.010
H(14)	0.149	0.598	0.131
H(15)	0.229	0.719	0.264
H(17)	0.536	1.062	0.496
H(18)	0.570	1.246	0.573
H(19)	0.296	1.359	0.518
H(20)	0.088	1.246	0.402
H(22)	−0.026	0.382	0.227
H(23)	0.147	0.459	0.347
H(24)	0.068	0.609	0.412
H(25)	−0.155	0.721	0.345
H(26)	−0.328	0.660	0.217
H(271)	−0.388	0.521	0.110
H(272)	−0.211	0.469	0.098
H(273)	−0.331	0.407	0.150

cyclopentadienyl groups are planar and virtually coplanar. The average C–C bond distance around the ring of 1.42 Å is close to the value of 1.43 Å found in ruthenocene.[14] The average C–P distance is 1.762 Å. This is almost identical with the distance of 1.77 Å found in other metallocenylphosphazenes studied previously.[2]

The most unusual feature of the structure is the marked distortion of the phosphazene ring to accommodate the two bridging substituents. All the P–N bond lengths were found to be long and similar in length (average 1.565 (3) Å) in contrast to the structure of **3a**. The phosphazene ring angles at P(1), P(2), P(3), and P(4) are narrow and similar in length (average 121.9 (2)°), again in contrast to the structure of **3a**. The angles at N(1), N(2), N(3), and N(4) are also significantly wider than those at phosphorus, with an average of 134.2 (2)° being typical.

Experimental Section

Materials. Species $(NPF_2)_3$, $(NPF_2)_4$, and $N_3P_3F_5Ph$ were prepared by procedures in the literature.[15,16] Ferrocene (Aldrich), $RuCl_3(III)\cdot H_2O$ (Strem), zinc dust (Aldrich), methyllithium (1.5 M solution in diethyl ether), *n*-butyllithium (1.6 M solution in hexane) (Aldrich), and phenyllithium (2.7 M solution in 70/30 cyclohexane/diethyl ether) were used as received. Ruthenocene was prepared by a literature procedure.[17] Tetrahydrofuran (THF) (MCB Reagents), hexane (Fisher), and diethyl ether (Fisher) were distilled under nitrogen from sodium benzophenone ketyl. Tetramethylethylenediamine (TMEDA) was dried over CaH_2 and then distilled (bp 120–122 °C) from sodium benzophenone ketyl. Column chromatography was carried out with the use of silica gel (230–400 mesh) (VWR) as packing material. All reactions were carried out under an atmosphere of dry nitrogen using standard airless-ware (Kontes).

Equipment. ^1H, ^{31}P, and ^{19}F NMR spectra were recorded on Varian EM 360 and CFT-20 NMR, JEOL PS-100 and FX 90Q FT NMR, and Bruker WP-200 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 shifts were referenced to internal $CHCl_3$ or acetone. The ^{19}F NMR shifts were referenced to external C_6H_5F in chloroform or acetone solution. Infrared (KBr disk or NaCl plate) spectra were recorded on a Perkin-Elmer 283B grating spectrometer. Electron-impact mass spectral results were obtained by using an AEI MS 950 spectrometer and were tabulated by a linked computer.

Metallocenylphosphazenes—Starting Materials. Compounds **1a,b** and **2a** were prepared as described previously.[2] Species 1,5-$N_4P_4F_6(\eta\text{-}C_5H_4)_2Ru$ (**3b**) and 1,5-$N_4P_4F_6(\eta\text{-}C_5H_4)_2Fe$ (**3a**) and 1,3-$N_4P_4F_6(\eta\text{-}C_5H_4)_2Fe$ were also prepared as described in a previous paper.[2] The reaction of dilithioferrocene with $(NPF_2)_4$ gave almost equimolar amounts of the 1,5 and 1,3 transannular isomers. These two isomers proved impossible to separate by chromatography or fractional recrystallization. However, the 1,5-isomer **3a** was obtained pure by treatment of the mixture of isomers with 1 equiv of dilithioferrocene–TMEDA. Only the 1,3-isomer reacted, leaving the 1,5-isomer unaffected. This was then purified by chromatography.

Reaction of Lithioferrocene (1.0 Equiv) with $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$. A solution of lithioferrocene was prepared via a transmetalation reaction[18] between chloromercuriferrocene (2.1 g, 5.06 mmol) and *n*-butyllithium (1.6 M) (3.1 mL, 1.0 equiv) in diethyl ether (50 mL) at room temperature. This solution was then added to a solution of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (**1a**) (2.0 g, 5.06 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. 2-Propanol (10 mL) was added, and the mixture was stirred for 10 min. The solvent was removed and the residue chromatographed. Elution with hexane gave ferrocene, identified by ^1H NMR. Further elution with dichloromethane–hexane (5:3) gave a yellow band which yielded orange crystals of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (**1a**) (0.050 g). Further elution with dichloromethane gave a yellow band which yielded orange crystals of *gem*-$N_3P_3F_3\{(\eta\text{-}C_5H_4)_2Fe\}\{(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)\}$ (**4a**) (1.2 g, 42%; mp 232 °C).

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For **4a**: IR 3080 (w, CH), 1200 (vs, br, PN) cm^{-1}; ^1H NMR δ 5.02 (m, 1 H), 4.94 (m, 2 H), 4.78 (m, 1 H), 4.69 (m, 2 H), 4.66 (m, 1 H), 4.51 (m, 1 H), 4.45 (m, 2 H), 4.42 (m, 1 H), 4.30 (m, 1 H), 4.23 (s, 5 H); ^{31}P NMR 46.75 (ddm, J_{PF} 912 Hz J_{PNP} = 71.6 Hz), 35.46 (m), 11.26 (ttm, J_{PF} = 880 Hz, J_{PNP} = 40.6 Hz) ppm; ^{19}F NMR 65.5 (dm, J_{PF} = 865 Hz), 56.3 (dd, J_{PF} = 900 Hz), 50.4 (dm, J_{PF} = 911 Hz) ppm; MS Calcd for $C_{20}H_{17}N_3F_3P_3Fe_2$: 560.9285. Found: 560.9271 (deviation 2.5 ppm). Anal. Calcd: C, 42.82; H, 3.05; N, 7.49. Found: C, 42.69; H, 3.18; N, 7.50.

Reaction of Lithioferrocene (3.0 Equiv) with $N_3P_3F_4(\eta$-$C_5H_4)_2Fe$. A solution of lithioferrocene was prepared as described above from chloromercuriferrocene (6.3 g, 15.2 mmol) and *n*-butyllithium (9.3 mL, 3.0 equiv) in diethyl ether (50 mL) at room temperature. This was then added to a solution of $N_3P_3F_4(\eta$-$C_5H_4)_2Fe$ (**1a**) (2.0 g, 5.06 mmol) in diethyl ether (75 mL) at −78 °C, as above. The mixture was allowed to warm to room temperature, and the reaction was then stirred for 17 h. The solvent was removed and the residue chromatographed. Elution with hexane gave ferrocene, identified by ^1H NMR. Further elution with dichloromethane–hexane (5:3) gave a yellow band which yielded small quantities of orange crystals of $N_3P_3F_4(\eta$-$C_5H_4)_2Fe$ (**1a**) (0.050 g). Further elution with dichloromethane gave a yellow band which yielded small quantities of orange crystals of *gem*-$N_3P_3F_3\{(\eta$-$C_5H_4)_2Fe\}\{(\eta$-$C_5H_4)Fe(\eta$-$C_5H_5)\}$ (**4a**) (0.130 g, 5.0%). Further elution with dichloromethane gave a yellow band which yielded orange crystals of *gem*-$N_3P_3F_2\{(\eta$-$C_5H_4)_2Fe\}\{(\eta$-$C_5H_4)Fe$-$(\eta$-$C_5H_5)\}_2$ (**5a**) (0.720 g, 20.0%, mp 250 °C).

For **5a**: IR 2975 (w, CH), 1180 (vs, br, PN) cm^{-1}; ^1H NMR δ 4.92 (m, 2 H), 4.67 (m, 4 H), 4.55 (m, 2 H), 4.52 (m, 2 H), 4.38 (m, 4 H), 4.34 (m, 2 H), 4.25 (s, 10 H); ^{31}P NMR 29.8 (m, J_{PNP} = 30.1 Hz), 7.69 (tt, J_{PF} = 910 Hz); ^{19}F NMR 55.4 (d, J_{PF} = 890 Hz), 44.7 (d, J_{PF} = 906 Hz) ppm. MS Calcd for $C_{30}H_{26}N_3F_2P_3Fe_3$: 726.9355. Found: 726.9379 (deviation 3.3 ppm). Anal. Calcd: C, 49.58; H, 3.59; N, 5.78. Found: C, 48.44; H, 3.76; N, 5.42.

Reaction of Dilithioferrocene–TMEDA with $N_3P_3F_4(\eta$-$C_5H_4)_2Fe$. 1,1′-Dilithioferrocene–TMEDA was prepared by a published procedure.[19] A solution of *n*-butyllithium (1.6 M) (20.5 mL, 2.2 equiv) was added to a solution of TMEDA (4.6 mL, 2.2 equiv) in hexane (10 mL). This mixture was stirred for 5 min and was then added to a solution of ferrocene (2.8 g, 15.0 mmol) in hexane (50 mL). The mixture was then stirred for 5 h at room temperature. A solution of $N_3P_3F_4(\eta$-$C_5H_4)_2Fe$ (3.0 g, 7.6 mmol) in diethyl ether (50 mL) was then added at −78 °C. The reaction was allowed to warm to room temperature, and the mixture was stirred for 17 h. 2-Propanol (10 mL) was added to quench any excess anion. The solvent was removed and the residue chromatographed. Elution with hexane gave ferrocene, identified by ^1H NMR. Further elution with dichloromethane–hexane (5:3) gave a yellow band which yielded small quantities of orange crystals of $N_3P_3F_4(\eta$-$C_5H_4)_2Fe$ (**1a**) (0.025 g). Further elution with dichloromthane gave a yellow band which yielded orange crystals of *gem*-$N_3P_3F_3\{(\eta$-$C_5H_4)_2Fe\}\{(\eta$-$C_5H_4)Fe(\eta$-$C_5H_5)\}$ (**4a**) (0.650 g, 15.0%). Further elution with dichloromethane gave a yellow band which yielded orange crystals of *gem*-$N_3P_3F_2\{(\eta$-$C_5H_4)_2Fe\}\{(\eta$-$C_5H_4)Fe(\eta$-$C_5H_5)\}_2$ (**5a**) (0.800 g, 14.0%). A similar reaction with dilithioferrocene, prepared from *tert*-butyllithium (1.9 M in pentane) (17.5 mL, 33.0 mmol) and ferrocene (2.8 g, 15.0 mmol) in diethyl ether (50 mL), gave similar results.

Reaction of Mono- and Dilithioruthenocene with $N_3P_3F_4(\eta$-$C_5H_4)_2Ru$ (1b). Ruthenocene (2 g, 8.62 mmol) was dissolved in diethyl ether (75 mL) and *n*-butyllithium (16.8 mL, 3.0 equiv) was added. The reaction was allowed to proceed for 48 h at 25 °C. This resulted in a 3:1 mixture of di- to monolithioruthenocene. This solution was then added to a solution of $N_3P_3F_4(\eta$-$C_5H_4)_2Ru$ (**1b**) (2.0 g, 4.54 mmol) in diethyl ether (75 mL) at −78 °C, and the mixture was heated at 35 °C for 17 h. The solvent was removed and the residue chromatographed. Elution with hexane gave ruthenocene, identified by ^1H NMR. Further elution with dichloromethane–hexane (1:5) gave a colorless band, which yielded crystals of *gem*-$N_3P_3F_3\{(\eta$-$C_5H_4)_2Ru\}\{(\eta$-$C_5H_4)Ru$-$(\eta$-$C_5H_5)\}$ (**4b**) (1.5 g, 50%). Further elution with dichloromethane–hexane (1:1) gave a colorless band which yielded a mixture of **4b** and *gem*-$N_3P_3F_2\{(\eta$-$C_5H_4)_2Ru\}\{(\eta$-$C_5H_4)Ru(\eta$-$C_5H_5)\}_2$ (**5b**) (0.5 g, 12.7%). These two compounds were separated by preparative thin-layer chromatography with dichloromethane as the eluent.

For **4b**: IR 3100 (w, CH), 1275 (vs, br, PN) cm^{-1}; ^1H NMR δ 5.37 (m, 1 H), 5.26 (m, 1 H), 5.20 (m, 2 H), 5.09 (m, 1 H), 4.98 (m, 2 H), 4.95 (m, 1 H), 4.89 (m, 1 H), 4.76 (m, 2 H), 4.72 (m, 1 H), 4.56 (s, 5 H); ^{31}P NMR 46.5 (ddm, J_{PF} = 840 Hz, J_{PNP} = 70 Hz), 33.5 (m), 11.2 (ttm, J_{PF} = 880 Hz, J_{PNP} = 72 Hz) ppm; ^{19}F NMR: 50.0 (dm, J = 890 Hz), 42.9 (dd, J_{PF} = 920 Hz), 35.6 (dm, J_{PF} = 930 Hz) ppm. MS Calcd for $C_{20}H_{17}N_3F_3P_3Ru_2$: 653. Found: 653.

For **5b**: ^1H NMR δ 5.35 (m, 2 H), 5.31 (m, 2 H), 5.19 (m, 2 H), 5.06 (m, 2 H), 5.00 (m, 4 H), 4.78 (m, 4 H), 4.70 (s, 10 H); ^{31}P NMR 25.6 (m, J_{PNP} = 70 Hz), 7.1 (tm, J_{PF} = 830 Hz) ppm. MS calcd for $C_{30}H_{26}N_3F_2P_3Ru_3$: 864.8437. Found: 864.8429 (deviation 0.9 ppm).

Reaction of Dilithioferrocene–TMEDA with $N_3P_3F_5(\eta$-$C_5H_4)Fe(\eta$-$C_5H_5)$ (2a). 1,1′-Dilithioferrocene–TMEDA was prepared by a published procedure.[19] A solution of *n*-butyllithium (1.6 M) (20.0 mL, 2.2 equiv) was added to a solution of TMEDA (4.8 mL, 2.2 equiv) in hexane (10 mL). This mixture was stirred for 5 min and was then added to a solution of ferrocene (2.7 g, 14.4 mmol) in hexane. The mixture was then stirred for 17 h at room temperature. This was then added to a solution of $N_3P_3F_5(\eta$-$C_5H_4)Fe(\eta$-$C_5H_5)$ (**2a**) (5.0 g, 12.0 mmol) in diethyl ether (150 mL) at −78 °C. The reaction was allowed to warm to room temperature, and the mixture was stirred for 17 h. 2-Propanol (10 mL) was added to quench any excess anion. The solvent was removed and the residue chromatographed. Elution with hexane gave ferrocene, identified by ^1H NMR. Further elution with dichloromethane–hexane (1:9) gave unreacted starting material $N_3P_3F_5(\eta$-$C_5H_4)Fe(\eta$-$C_5H_5)$ (**2a**) (1.0 g), identifed by ^1H, ^{31}P NMR, and mass spectrometry. Elution with dichloromethane–hexane (3:7) gave a small quantity of *non-gem*-$N_3P_3F_4\{(\eta$-$C_5H_4)Fe(\eta$-$C_5H_5)\}_2$ (**11**) (0.2 g, 2.4%; mp 95 °C), identified by ^{31}P NMR and mass spectrometry and elemental analysis. Further elution with dichloromethane–hexane (8:2) have a yellow band which yielded yellow crystals of *trans-non-gem*-$N_3P_3F_3\{(\eta$-$C_5H_4)_2Fe\}\{(\eta$-$C_5H_4)$-$Fe(\eta$-$C_5H_5)\}$ (**6**) (2.0 g, 24.4%; mp 300 °C). Elution with dichloromethane gave a yellow band which yielded orange crystals of *cis-non-gem*-$N_3P_3F_3\{(\eta$-$C_5H_4)_2Fe\}\{(\eta$-$C_5H_4)Fe(\eta$-$C_5H_5)\}$ (**7**) (1.0 g, 12.2%; mp 240 °C.

For **6**: IR 3100 (w, CH), 1220 (vs, br, PN) cm^{-1}; ^1H NMR δ 5.10 (m, 2 H), 5.02 (m, 2 H), 4.70 (m, 4 H), 4.69 (m, 2 H), 4.43 (s, 5 H), 4.39 (m, 2 H); ^{31}P NMR 48.3 (dm, J_{PF} = Hz), 44.9 (J_{PF} = 940 Hz) ppm; ^{19}F NMR 69.8 (d, J_{PF} = 930 Hz), 40.3 (d, J_{PF} = 920 Hz) ppm. MS Calcd for $C_{20}H_{17}N_3F_3P_3Fe_2$: 560.9285. Found: 560.9281 (deviation 0.7 ppm). Anal. Calcd: C, 42.82; H, 3.05; N, 7.49. Found: C, 42.64; H, 3.14; N, 7.41.

For **7**: IR 3100 (w, CH), 1220 (vs, br, PN) cm^{-1}; ^1H NMR δ 4.99 (m, 2 H), 4.86 (m, 2 H), 4.79 (m, 2 H), 4.57 (m, 2 H), 4.56 (m, 2 H), 4.42 (s, 5 H), 4.28 (m, 2 H); ^{31}P NMR 48.2 (dm, J_{PF} = 1005 Hz), 45.7 (dm, J_{PF} = 910 Hz) ppm; ^{19}F NMR 66.9 (d, J_{PF} = 1000 Hz), 45.6 (d, J_{PF} = 940 Hz) ppm. MS Calcd for $C_{20}H_{17}N_3F_3P_3Fe_2$: 560.9285. Found: 560.9277 (deviation 1.5 ppm). Anal. Calcd: C, 42.82; H, 3.05; N, 7.49. Found: C, 42.61; H, 3.03; N, 7.50.

Reaction of Dilithioferrocene–TMEDA with 1,5-$N_4P_4F_6$-$(\eta$-$C_5H_4)_2Fe$. An excess of dilithioferrocene–TMEDA (5.0 g, 16.7 mmol) was dissolved in diethyl ether (100 mL) and added to a solution of 1,5-$N_4P_4F_6(\eta$-$C_5H_4)_2Fe$ (**3a**) (2.0 g, 4.2 mmol) in diethyl ether (100 mL) at 25 °C. The mixture was then stirred for 72 h at room temperature. The solvent was removed and the residue chromatographed. Elution with hexane gave ferrocene, identified by ^1H NMR. Further elution with dichloromethane–hexane (1:9) gave a yellow band which gave orange crystals of 1,5-$N_4P_4F_6(\eta$-$C_5H_4)_2Fe$ (**3a**) (0.5 g, 25.0%). Further elution with dichloromethane–hexane (1:1) gave a yellow band which yielded orange crystals of 1,5-3-$N_4P_4F_5(\eta$-$C_5H_4)_2Fe\{(\eta$-$C_5H_4)Fe(\eta$-$C_5H_5)\}$ (**8a**) (1.0 g, 37.0%; mp 209 °C).

For **8a**: IR 3100 (w, CH), 1340 (vs, br, PN) cm^{-1}. ^1H NMR δ 4.73 (m, 10 H), 4.49 (m, 2 H), 4.43 (s, 5 H); ^{31}P NMR 19.9 (dm, J_{PF} = 930 Hz), 17.6 (dm, J_{PF} = 890 Hz), −11.7 (tm, J_{PF} = 913 Hz) ppm; ^{19}F NMR 72.1 (d, J_{PF} = 923 Hz, 1 F), 60.0 (d, J_{PF} = 804 Hz, 2 F), 47.7 (d, J_{PF} = 868 Hz, 1 F), 45.2 (d, J_{PF} = 907 Hz, 1 F) ppm. MS Calcd for $C_{20}H_{17}N_4F_5P_4Fe_2$: 643.9022. Found: 643.9058 (deviation 5.5 ppm). Anal. Calcd: C, 37.30; H, 2.66; N, 8.70.

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Found: C, 37.11; H, 2.81; N, 8.44.

Reaction of Mono- and Dilithioruthenocene with 1,5-$N_4P_4F_6(\eta\text{-}C_5H_4)_2Ru$. A solution of mono- and dilithioruthenocene was prepared from ruthenocene (2.0 g, 8.62 mmol) and *n*-butyllithium (16.8 mL, 3.0 equiv) in diethyl ether (75 mL) at 25 °C for 48 h. This mixture was added to a solution of 1,5-$N_4P_4F_6(\eta\text{-}C_5H_4)_2Ru$ (**3b**) (1.5 g, 2.87 mmol) in diethyl ether (100 mL) at −78 °C. The mixture was allowed to warm to room temperature and was then stirred for 17 h. The solvent was removed, and the residue was chromatographed. Elution with hexane gave ruthenocene and biruthenocene ($C_{20}H_{18}Ru_2$), identified by ^1H NMR and mass spectrometry, respectively. Further elution with dichloromethane–hexane (1:9) gave a colorless band, which yielded crystals of 1,5-$N_4P_4F_6(\eta\text{-}C_5H_4)_2Ru$ (**3b**) (0.1 g). Further elution with dichloromethane–hexane (1:5) gave another colorless band, which yielded crystals of 1,5-3-$N_4P_4F_5(\eta\text{-}C_5H_4)_2Ru\{(\eta\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)\}$ (**9b**) (0.13 g, 6.3%; mp 180 °C.) Finally, elution with dichloromethane–hexane (1:3) yielded a colorless band which gave white crystals of 1,5,3,7-$N_4P_4F_4\{(\eta\text{-}C_5H_4)_2Ru\}_2$ (**10**) (0.02 g, 1.0%; mp 165–166 °C).

For **9b**: ^1H NMR δ 4.75 (m, 4 H), 4.69 (m, 4 H), 4.56 (m, 2 H), 4.52 (m, 2 H), 4.51 (s, 5 H); ^{31}P NMR 18.3 (d, J_{PF} = 961 Hz, J_{PNP} = 56 Hz), 13.3 (dm, J_{PF} = 845 Hz, J_{PNP} = 80 Hz), −12.7 (tm, J_{PF} = 870 Hz, J_{PNP} = 112 Hz) ppm; ^{13}F NMR 56.3 (dm, J_{PF} = 840 Hz, 2 F), 47.7 (dm, J_{PF} = 860 Hz, 1 F), 43.4 (dm, J_{PF} = 870 Hz, 1 F), 41.5 (dm, J_{PF} 900 Hz, 1 F) ppm. MS Calcd for $C_{20}H_{17}N_4F_5P_4Ru_2$: 735.8410. Found: 735.8414 (deviation 4.6 ppm).

For **10**: ^1H NMR δ 4.89 (m, 8 H), 4.20 (m, 8 H); ^{31}P NMR 15.9 (dm, J_{PF} = 850 Hz, J_{PNP} = 93 Hz) ppm; ^{19}F NMR 64.5 (dm, J_{PF} = 861 Hz) ppm. MS Calcd for $C_{20}H_{16}N_4F_4P_4Ru_2$: 715.8348. Found: 715.8292 (deviation 7.8 ppm). Anal. Calcd: C, 33.63; H, 2.26. Found: C, 34.18; H, 2.50.

Reaction of Dilithioferrocene–TMEDA and $N_3P_3F_5Ph$. 1,1′-Dilithioferrocene–TMEDA was prepared by a published procedure,[19] isolated, and stored in a glovebox. A quantity of dilithioferrocene–TMEDA (4.5 g, 14.3 mmol) was added to diethyl ether (150 mL) and was cooled to −78 °C. An equimolar quantity of $N_3P_3F_5Ph$ (**12**) (4.5 g, 14.3 mmol) in diethyl ether (100 mL) was slowly added to this solution. The reaction was allowed to warm to room temperature and was stirred at 25 °C for 17 h. 2-Propanol (10 mL) was then added and the solution filtered. The solvent was removed and the residue chromatographed. Elution with hexane gave ferrocene, identified by ^1H NMR. Further elution with dichloromethane–hexane (1:1) gave an orange band which yielded orange crystals of *cis*- and *trans-non-gem*-$N_3P_3F_3(Ph)(\eta\text{-}C_5H_4)_2Fe$ (**13**) (5.2 g, 78.8%; mp 170 °C).

For **13**: IR 3050, 3070 (w, CH), 1200 (vs, br, PN) cm^{-1}; ^1H NMR δ 8.13 (m, 2 H), 7.69 (m, 3 H), 5.02 (m, 1 H), 4.99 (m, 2 H), 4.70 (m, 1 H), 4.62 (m, 2 H), 4.37 (m, 1 H), 4.16 (m, 1 H); ^{31}P NMR 46.5 (dm, J_{PF} = 930 Hz, J_{PNP} = 20 Hz), 38.1 (dt, J_{PF} = 1010 Hz, J_{PNP} = 20 Hz) ppm; ^{19}F NMR 67.2 (d, J_{PF} = 1010 Hz, 1 F), 45.5 (d, J_{PF} = 940 Hz, 2 F) for cis and 61.1 (d, J_{PF} = 940 Hz, 1 F), 39.0 (d, J_{PF} = 920 Hz, 2 F) ppm for trans. MS Calcd for $C_{16}H_{13}N_3F_3P_3Fe$: 452.9623. Found: 452.9635 (deviation 2.4 ppm). Anal. Calcd: C, 42.42; H, 2.89; N, 9.27. Found: C, 42.32; H, 2.88; N, 9.14.

Reaction of Methyllithium (1.0 and 6.0 Equiv) with 1a. A sample of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (**1a**) (1.0 g, 2.53 mmol) was prepared as described previously.[2] This was dissolved in diethyl ether (50 mL) and methyllithium (1.0 equiv, 0.94 mmol) was added. The reaction was stirred at 25 °C for 17 h. The solvent was removed, and the residue was chromatographed. Elution with dichloromethane gave an orange band which yielded orange crystals of *gem*-$N_3P_3(CH_3)F_3(\eta\text{-}C_5H_4)_2Fe$ (**14**) (0.85 g, 85.9%; mp 137 °C). The reaction of 6 equivs of methyllithium with **1a** did not lead to any higher substituted products.

For **14**: IR 3080, 2920 (w, CH), 1210 (vs, br, PN) cm^{-1}; ^1H NMR δ 4.95 (m, 1 H), 4.88 (m, 2 H), 4.76 (m, 1 H), 4.67 (m, 1 H), 4.61 (m, 1 H), 4.38 (m, 1 H), 4.29 (m, 1 H), 1.84 (dt, 3 H, J_{PCH} = 15.6 Hz, J_{PNPCH} = 3.4 Hz); ^{31}P NMR 48.0 (dm, J_{PF} = 952 Hz), 38.4 (m), 10.5 (tm, J_{PF} = 910 Hz) ppm; ^{19}F NMR 50.8 (d, J_{PF} = 890 Hz), 42.5 (d, J_{PF} = 920 Hz), 35.6 (d, J_{PF} = 930 Hz) ppm. MS Calcd for $C_{11}H_{11}N_3F_3P_3Fe$: 390.9467. Found: 390.9482 (deviation 3.7 ppm). Anal. Calcd: C, 33.79; H, 2.84; N, 10.75. Found: C, 35.50; H, 2.74; N, 10.50.

Reaction of Phenyllithium with 1a. A sample of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ (**1a**) (1.0 g, 2.5 mmol) was prepared as described previously.[2] This was dissolved in diethyl ether (50 mL) and phenyllithium (1.5 equiv, 3.8 mmol) was added. The mixture was stirred at 25 °C for 17 h. The solvent was removed and the residue chromatographed. Elution with dichloromethane–hexane (1:1) gave an orange band which yielded orange crystals of *gem*-$N_3P_3F_3(Ph)(\eta\text{-}C_5H_4)_2Fe$ (**15**) (0.5 g, 43.9%; mp 200 °C). Elution with dichloromethane gave an orange band which yielded orange crystals of *gem*-$N_3P_3F_2(Ph)_2(\eta\text{-}C_5H_4)_2Fe$ (**16**) (0.1 g, 7.7%; mp 144–145 °C).

For **15**: IR 3060 (w, CH), 1200 (vs, br, PN) cm^{-1}, ^1H NMR δ 7.91 (m, 2 H), 7.53 (m, 3 H), 5.10 (m, 1 H), 4.94 (m, 2 H), 4.69 (m, 2 H), 4.61 (m, 1 H), 4.41 (m, 1 H), 4.34 (m, 1 H); ^{31}P NMR 48.3 (dm, J_{PF} = 930 Hz, J_{PNP} = 70 Hz), 30.9 (m), 11.0 (tm, J_{PF} = 960 Hz) ppm; ^{19}F NMR 42.5 (d, J_{PF} = 930 Hz, 1 F), 35.6 (d, J_{PF} = 940 Hz, 2 F) ppm. MS Calcd for $C_{16}H_{13}N_3F_3P_3Fe$: 452.9623. Found: 452.9651 (deviation 6.2 ppm). Anal. Calcd: C, 42.42; H, 2.89; N, 9.27. Found: C, 41.76; H, 3.13; N, 8.69.

For **16**: IR 3080 (w, CH), 1200 (vs, br, PN) cm^{-1}; ^1H NMR δ 7.99 (m, 4 H), 7.51 (m, 6 H), 5.02 (m, 2 H), 4.57 (m, 4 H), 4.40 (m, 2 H); ^{31}P NMR 27.5 (dm, J_{PNP} = 30 Hz), 6.5 (tt, J_{PF} = 900 Hz, J_{PNP} = 30 Hz) ppm; ^{19}F NMR 55.7 (d, J_{PF} = 900 Hz), 44.3 (d, J_{PF} = 910 Hz) ppm. MS Calcd for $C_{22}H_{18}N_3F_2P_3Fe$: 511.0031. Found: 510.9996 (deviation 6.8 ppm). Anal. Calcd: C, 51.69; H, 3.55; N, 8.22. Found: C, 51.15; H, 3.55; N, 7.89.

Reaction of Sodium Trifluoroethoxide with 1a. A sample of **1a** (1.0 g, 2.53 mmol) was prepared as described previously.[2] This was dissolved in THF (50 mL), and a solution of sodium trifluoroethoxide, prepared from sodium (0.06 g, 2.53 mmol) and trifluoroethanol (0.26 g, 2.61 mmol) in THF (10 mL), was added. This reaction was heated at reflux for 17 h. The product was isolated by removing the solvent under reduced pressure followed by chromatography on silica gel. Elution with dichloromethane–hexane (3:1) gave an orange band which yielded yellow needle-shaped crystals of *non-gem*-$N_3P_3F_3(OCH_2CF_3)(\eta\text{-}C_5H_4)_2Fe$ (**17**) (0.50 g, 41.7%; mp 174 °C).

For **17**: IR 3100 (w, CH), 1180 (vs, br, PN) cm^{-1}. ^1H NMR δ 5.01 (m, 4 H), 4.72 (m, 2 H), 4.49 (dq, J_{PCH} = 8 Hz, J_{FCH} = 9 Hz), 4.37 (m, 2 H); ^{31}P NMR 46.3 (dm, J_{PF} = 986 Hz, J_{PNP} = 80 Hz), 20.5 (dm, J_{PF} = 876 Hz, J_{PNP} = 80 Hz) ppm; ^{19}F NMR 48.6 (dm, J_{PF} = 860 Hz), 39.4 (dm, J_{PF} = 920 Hz), 38.6 (s) ppm. MS Calcd for $C_{12}H_{10}N_3F_6FeOP_3$: 474.9290. Found: 474.9288 (deviation 0.4 ppm). Anal. Calcd: C, 30.34; H, 2.12; N, 8.85. Found: C, 30.00; H, 2.17; N, 8.87.

Reaction of Sodium Trifluoroethoxide (1.0 and 2.0 Equiv) with 17. A sample of *gem*-$N_3P_3F_3(OCH_2CF_3)\{(\eta\text{-}C_5H_4)_2Fe\}$ (1 g, 2.11 mmol) was dissolved in THF (25 mL). A solution of sodium trifluoroethoxide, prepared from sodium (50 mg, 2.17 mmol) and trifluoroethanol (250 mg, 2.50 mmol) in THF (20 mL), was added dropwise. The reaction was stirred at room temperature for 24 h. The product was isolated by removing the solvent under reduced pressure, followed by chromatography on silica gel. Elution with dichloromethane–hexanes (4:1) gave an orange band which yielded a yellow oil of $N_3P_3F_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ (**19**) (860 mg, 74%).

The reaction of 2 equiv of sodium trifluoroethoxide, prepared from sodium (100 mg, 4.34 mmol) and trifluoroethanol (500 mg, 5.0 mmol), with **17** (1 g, 4.22 mmol) was performed in a similar manner to the above. The products were separated by chromatography on silica gel. Elution with dichloromethane–hexanes (3:1) developed an orange band which yielded yellow crystals of $N_3P_3F(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ (**20**) (320 mg, 24%; mp 83 °C). Further elution with the same solvent gave a pale yellow band which yielded a small quantity of orange crystals of $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$ (**22**) (22 mg, 1.5%), identified by ^{31}P and ^{19}F NMR spectroscopy. Elution with dichloromethane–hexane (4:1) gave a yellow band which yielded a yellow oil of $N_3P_3F_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ (**19**) (56 mg, 5%). Elution with dichloromethane brought about the separation of an orange band which yielded orange crystals of $N_3P_3F(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ (**21**) (420 mg, 31%; mp 104 °C).

For **19**: IR 3080, 2940 (w, CH), 1215, 1180 (vs, PN) cm^{-1}; ^1H NMR δ 4.96 (m, 3 H), 4.90 (m, 1 H), 4.71 (m, 1 H), 4.67 (m, 1 H), 4.48 (dq, J_{HCOP} = 10 Hz, J_{HCCF} = 8 Hz, 2 H), 4.35 (dq, J_{HCOP} = 8 Hz, J_{HCCF} = 8 Hz, 2 H), 4.32 (m, 2 H); ^{31}P NMR 57.5 (dm, J_{PF}

= 965 Hz), 41.8 (m), 20.1 (dm, J_{PF} = 881 Hz) ppm; ^{19}F NMR 50.2 (dm, J_{PF} = 878 Hz, 1 F), 38.7 (t, J_{FH} = 8 Hz, 3 F), 38.5 (t, J_{FH} = 8 Hz, 3 F), 36.0 (dm, J_{PF} = 947 Hz, 1 F) ppm. MS Calcd for $C_{14}H_{12}F_8FeN_3O_2P_3$: 555. Found: 555. Anal. Calcd: C, 30.30; H, 2.18; N, 7.57. Found: C, 30.36; H, 2.24; N, 7.68.

For **20**: IR 3080, 3060, 2940 (w, CH), 1180 (vs, PN) cm^{-1}; ^{1}H NMR δ 4.92 (m, 2 H), 4.89 (m, 2 H), 4.65 (m, 2 H), 4.46 (dq, J_{HCOP} = 10 Hz, J_{HCCF} = 8 Hz, 2 H), 4.34 (m, 4 H), 4.32 (m, 2 H); ^{31}P NMR 39.2 (m), 16.7 (dm, J_{PF} = 877 Hz) ppm; ^{19}F NMR 56.1 (dm, J_{PF} = 879 Hz, 1 F), 38.4 (t, J_{FH} = 8 Hz, 6 F), 38.1 (t, J_{FH} = 8 Hz, 3 F) ppm. MS Calcd for $C_{16}H_{14}F_{10}FeN_3O_3P_3$: 635. Found: 635. Anal. Calcd: C, 30.26; H, 2.22; N, 6.61. Found: C, 30.22; H, 2.07; N, 6.69.

For **21**: IR 3080, 2940 (w, CH), 1170 (vs, PN) cm^{-1}; ^{1}H NMR δ 4.95 (m, 1 H), 4.91 (m, 2 H), 4.88 (m, 1 H), 4.67 (m, 1 H), 4.64 (m, 1 H), 4.52 (dq, J_{HCOP} = 10 Hz, J_{HCCF} = 8 Hz, 2 H), 4.51 (dq, J_{HCOP} = 10 Hz, J_{HCCF} = 8 Hz, 2 H), 4.35 (m, 2 H), 4.33 (m, 2 H); ^{31}P NMR 46.9 (dm, J_{PF} = 942 Hz), 41.1 (m), 21.7 (m) ppm; ^{19}F NMR 39.6 (dm, J_{PF} = 942 Hz, 1 F), 37.9 (t, J_{FH} = 8 Hz, 3 F), 37.8 (t, J_{FH} = 8 Hz, 6 F) ppm. MS Calcd for $C_{16}H_{14}F_{10}FeN_3O_3P_3$: 635. Found: 635. Anal. Calcd: C, 30.26; H, 2.22; N, 6.61. Found: C, 30.36; H, 2.31; N, 6.55.

Attempted Reaction of Sodium Trifluoroethoxide (10 Equiv) with 10. A sample of $N_4P_4F_4(\eta\text{-}C_5H_4)_4Ru_2$ (**10**) (100 mg, 0.19 mmol) was dissolved in THF–benzene-d_6 (4:1, 2 mL) in a 10-mm NMR tube. Sodium trifluoroethoxide (1.9 mmol) in THF (2 mL) was added. The tube was degassed, sealed under vacuum, and heated to 75 °C for 14 days. No reaction was observed by both ^{31}P and ^{19}F NMR spectroscopy. In addition, no precipitate of NaF, an insoluble byproduct of the substitution reaction, was observed in the tube.

X-ray Structure Determination for 1a, 3a, 7, and 10. Our general X-ray structure technique has been described in earlier papers[2], and only the details related to the present work will be given here.

Crystals of **1a**, **3a**, and **7** were obtained from dichloromethane–hexane solutions and were mounted along the longest axis. Crystals of **10** were grown from toluene. The structures of **1a**, **3a**, and **7** were solved by direct methods, and that of **10** was resolved by Patterson and Fourier techniques. In the final cycles of full-matrix least-squares refinement, all non-hydrogen atom positional parameters and anisotropic thermal parameters were refined. The positional parameters for the hydrogen atoms of **1a**, given fixed, arbitrary thermal parameters (B = 5.0 Å^2), were located from a difference Fourier electron density map and were refined. The positional parameters and thermal parameters for the hydrogen atoms of **3a**, **7**, and **10** (B = 5.0 Å^2) were fixed in calculated positions (C–H = 0.97 Å) during the later cycles of refinement.

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Registry No. **1a**, 89179-03-3; **1b**, 89179-04-4; **2a**, 84462-63-5; **3a**, 89179-06-6; **3b**, 89179-07-7; **4a**, 102735-99-9; **4b**, 102736-11-8; **5a**, 102736-00-5; **5b**, 102736-12-9; **6**, 102849-13-8; **7**, 102736-01-6; **8a**, 102736-02-7; **9b**, 102736-03-8; **10**, 103002-51-3; **12**, 2713-48-6; *cis*-**13**, 102849-14-9; *trans*-**13**, 102736-04-9; **14**, 102736-05-0; **15**, 102736-06-1; **16**, 102745-11-9; **17**, 102736-07-2; **19**, 102736-08-3; **20**, 102736-09-4; **21**, 102736-10-7; **22**, 95784-56-8; lithioferrocene, 1271-15-4; 1,1′-dilithioferrocene, 33272-09-2; dilithioruthenocene, 60898-13-7; lithioruthenocene, 89179-17-9; chloromercuriferrocene, 1273-75-2; ruthenocene, 1287-13-4.

Supplementary Material Available: Appendix A, analysis of NMR spectra, and tables of interatomic distances and bond angles (Tables X, XIV, XVII, and XXI), least-squares planes (Tables XII and XIX), anisotropic thermal parameters (Tables XI, XV, XVIII, and XXII), and calculated structure factors (Tables XIII, XVI, XX, and XXIII) (126 pages). Ordering information is given on any current masthead page.

Formation and Molecular Structures of η^5-Pentabenzylcyclopentadienyl and η^5-Pentaphenylcyclopentadienyl Dicarbonyl Derivatives of Cobalt and Rhodium

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Improved synthetic routes to pentabenzylcyclopentadiene (**1**) and pentaphenylcyclopentadiene (**2**) have been developed. Reactions of **1** and **2** with $Co_2(CO)_8$ in refluxing toluene have afforded (η^5-C_5Bz_5)Co(CO)$_2$ (**3**) and (η^5-C_5Ph_5)Co(CO)$_2$ (**5**) in yields of 67% and 9%, respectively. Reaction of **1** with n-butyllithium in THF at 0 °C has produced C_5Bz_5Li (**7**), whereas reaction of **2** with sodium amide in refluxing toluene has afforded C_5Ph_5Na (**8**) in 84% yield. Both **7** and **8** react with [Rh(CO)$_2$Cl]$_2$ in THF to produce (η^5-C_5Bz_5)Rh(CO)$_2$ (**4**) and (η^5-C_5Ph_5)Rh(CO)$_2$ (**6**), respectively. Single-crystal X-ray diffraction studies on **3** and **5** have been undertaken. Compound **3** crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions a = 12.753 (7) Å, b = 14.877 (8) Å, c = 18.28 (1) Å, β = 108.58 (5)°, and Z = 4 for d_{calcd} = 1.28 g cm^{-3}. Compound **5** crystallizes in the orthorhombic space group $Pbca$ with unit cell dimensions a = 13.66 (1) Å, b = 20.44 (4) Å, c = 20.600 (5) Å, and Z = 8 for d_{calcd} = 1.30 g cm^{-3}. Full-matrix least-squares refinement led for **3** to a final R value of 0.042 for 2398 observed reflections and for **5** to a final R value of 0.054 for 1779 observed reflections. Compound **3** exhibits a nonsymmetric placement of the benzyl substituents, while the phenyl substituents of **5** are symmetrically placed and canted an average of 55.8° with respect to the cyclopentadienyl ring.

Since the first definitive study on η^5-pentamethylcyclopentadienyl derivatives of the metals in 1967,[2] the η^5-C_5Me_5 ligand has played an important role in the development of organometallic chemistry. Replacement of

