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Template Synthesis of 1,4,7-Triphosphacyclononanes

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Abstract: Iron(II) templates based on a $[(\eta^5\text{-}Cp^R)Fe]^+$ core have been employed for the successful synthesis of 1,4,7-triphosphacyclononane derivatives (9-ane$P_3R'_3$) from a range of appropriately functionalized coordinated diphosphines and monophosphines. 1,2-Diphosphinoethane (1,2-dpe) or (2-phosphinoethyl)-phenylphosphine (Phdpe) undergo a base-catalyzed Michael-type addition to trivinylphosphine, divinyl-(benzyl)phosphine, or divinyl(phenyl)phosphine in $[(\eta^5\text{-}Cp^R)Fe(diphosphine)(monophosphine)]^+$ complexes (**2a**−**j**) to give $[(\eta^5\text{-}Cp^R)Fe(9aneP_3R'_3)]^+$ derivatives (**4a**−**j**) containing coordinated triphosphacyclononanes bearing one (with Phdpe) or two (with 1,2-dpe) secondary phosphine donors. The rates of macrocyclization show a dependence on the nature of the substituent(s) R on the cyclopentadienyl ligand with increased rates being observed along the series $R = H_5 < (Me_3Si)H_4 < 1,3\text{-}(Me_3Si)_2H_3 \approx Me_5$. For coupling reactions with trivinylphosphine, a pendant vinyl function remains in the macrocyclic product (**4a**−**g**) which is readily hydrogenated to the corresponding ethyl derivatives (**5a**−**g**). Further functionalization of coordinated secondary phosphines in the initially formed macrocycles (**5a**−**g**) is achieved by proton abstraction followed by addition of the appropriate alkyl halide electrophile and gives rise to tritertiary-triphospha-cyclononanes (**7a**−**g**, **7l**, **7m**). All new complexes have been fully characterized by spectroscopic and analytical methods in addition to the structural determination by single-crystal X-ray techniques of $[\{\eta^5\text{-}(Me_3Si)_2C_5H_3)Fe(9\text{-}aneP_3H_2C_2H_3)]PF_6$, **4c**, and $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(9\text{-}aneP_3Et_3)]BF_4$, **7b**. 1,4,7-Triethyl-1,4,7-triphosphacyclononane is released from its metal template (**7a**, **7b**) by treatment with either H_2O_2 or Br_2/H_2O to give the trioxide 9-ane$P_3(O)_3Et_3$ (**8**). Attempts to recover the trivalent phosphorus species, 1,4,7-triethyl-1,4,7-triphosphacyclononane, from the trioxide by reduction proved unsuccessful.

Introduction

The study of the coordination chemistry of small ring macrocycles has been, and continues to be, dominated by homoleptic oxa-, aza-, and thia-carbocyclic systems and some, mostly oxa/aza, mixed donor species. Related phosphorus analogues have, by comparison, been poorly investigated, a surprising anomaly given the importance of acyclic phosphines as ligands in catalysis and in the stabilization of unusual classes of complexes. The scarcity of studies of phosphorus macrocycles is probably due largely to a lack of appropriate precursors for cyclization (e.g., P-tosyl analogues of the N-tosyl derivatives used extensively in the preparation of N_3 and N_4 systems are unstable) and synthetic difficulties arising from the inherent air-sensitivity of most tervalent phosphorus species. There have been significant advancements in the synthesis and coordination chemistry of homoleptic P_3 and P_4 macrocycles. Most of the early preparations of Horner[1] and Kyba[2] were by direct solution methods (nontemplate assisted), which were consequently nonstereoselective, giving all possible isomers of the respective macrocycles. The relative stereochemistry at the phosphorus centers has implications for the coordination behavior in metal complexes of these macrocycles, and control of the stereochemistry is of value. There are examples where the absence of stereoselectivity may be overcome by the inversion of phosphorus centers upon coordination, such as in Kyba's 11-aneP_3 macrocycle, where the *cis*, *cis*, *cis*/*cis*, *cis*, *trans* (or *syn*, *syn*/*syn*, *anti*) mixture could be used directly for the preparation of a number of complexes although elevated temperatures (boiling xylenes) were required to invert the phosphorus and force the facially capping coordination mode of the *syn*, *anti* isomer and formation of the complex.[2] Metal template approaches pioneered by Horner[3] and exploited by a number of groups, including Stelzer,[4] Norman,[5] and more recently us,[6] have for the most part replaced the nontemplate syntheses. Stelzer largely initiated the use of metal templates for the synthesis of tetradentate P_4 systems, and his group has continued to examine the synthesis and complexation chemistry of these interesting ligands.[4] Norman was the first to employ a template for the preparation of terdentate P_3 macrocycles (12-aneP_3R_3 and 15-aneP_3R_3) via intramolecular hydrophosphination reactions of coordinated

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primary alkenyl phosphines, although the ligand was not released from the Mo(0) center upon which it was formed and its coordination chemistry remained unexplored.[5] Functionalization and liberation of Norman's 12-aneP_3H_3 macrocycle was achieved by us and allowed the study of the coordination chemistry of various 12-aneP_3R_3 derivatives.[6] More recently, Gladysz and co-workers have reported very large ring P_3 macrocycles which have also been formed upon a group 6 metal tricarbonyl template although by a ring-closing metathesis reaction of coordinated alkenyl phosphines.[7] Our interest in triphosphorus macrocycles of this nature stems from their ability to facially cap a coordination polyhedron (thus forcing remaining reaction sites into mutually *cis* orientations opposite the *trans*-labilizing phosphine donors) while also forming robust metal−ligand fragments. Our early studies of complexes of 12-aneP_3R_3 ligands do indeed indicate that these principles can lead to unusual structures and reactivity. In this context, we have shown that "simple" (12-aneP_3R_3)MCl_3 complexes (M = Ti, V, Cr) are active in alkene polymerization with selectivity being influenced by the nature of R[8] and that (12-aneP_3Et_3)Mn(I) carbonyl complexes are active ROMP catalysts (for which Mn is not well-known).[9] A disadvantage of the relatively large 12-aneP_3R_3 ligands is that they appear to remain flexible enough to limit stability of complexes of metals not so well suited to forming tertiary phosphine complexes (e.g., f-elements), as might be expected by comparison with related 9-membered and 12-membered N_3 macrocycles, where larger ring sizes lead to increased ligand lability.[10] Thus synthetic routes to smaller ring sizes remain important goals, and our target is the class of ligands based upon the elusive 9-membered triphosphacyclononane core structure.

In related work, Mathey and co-workers prepared 12-aneP_3 macrocycles containing sp^2-type (σ^2,λ^3) phosphorus centers by the nontemplate coupling of azaphosphinines with alkynes.[11] The silicon-based 1,4,7-triphospha-2,3,5,6,8,9-hexasilanonane was the first 9-membered macrocycle with three σ^3,λ^3 phosphorus donors,[12] although the free macrocycle was not isolated; the hydrolytically unstable P−Si linkages are unlikely to survive the conditions required for attempted liberation and will substantially limit coordination chemistry and applications. In view of the potential of triphosphacyclononanes in coordination chemistry and applications, we have continued to investigate alternative metal templates suitable for the closure of smaller ring systems. We have recently reported preliminary results of this study, including the application of cyclopentadienyliron(II) templates, to the synthesis of 9-, 10-, and 12-membered P_3 macrocycles.[13] In this paper, we present full details of the preparation and characterization of the first 1,4,7-triphosphacyclononane derivatives using an Fe(II) template system with variously functionalized Cp ligands.

Results and Discussion

9-aneP_3R_3 Derivatives from Template Reactions of 1,2-Diphosphinoethane and Trivinylphosphine. The starting point for all the macrocycle syntheses described herein is from the [(η^5-Cp^R)Fe(CH_3CN)(diphos)]X (Cp^R = Me_5Cp or Cp*, {Me_3Si}-C_5H_4, 1,3-{Me_3Si}$_2C_5H_3$; X = BF_4^-, PF_6^-) precursor complexes, **1a**−**g**. These are readily obtained from the respective [(η^5-Cp^R)Fe(CH_3CN)(CO)$_2$]X complexes by the photolytically activated substitution of the carbonyl donors in the presence of 1,2-diphosphinoethane (1,2-dpe) or phenyl(2-phosphinoethyl)-phosphine (Phdpe) and in a manner similar to that described by Astruc for related systems.[14] The compounds are red solids that are readily recrystallized from tetrahydrofuran, although they are susceptible to dissociation of coordinated acetonitrile, and reliable, reproducible analytical and mass spectroscopic data were not obtained for the compounds. Coordination of the diphosphine in **1a**−**g** was confirmed by the $^{31}P\{^1H\}$ NMR spectra of the complexes which showed the usual downfield shifts compared to the uncoordinated ligands. The $\nu_{(P-H)}$ and $\nu_{(C\equiv N)}$ stretches were observed in the infrared spectra of the complexes as detailed in the Experimental Section.

In all cases, the acetonitrile−diphosphine complexes decompose in hydrochlorocarbon solvents in which they are initially readily soluble.

The labile acetonitrile in the 1,2-diphosphinoethane complexes [(η^5-Cp^R)Fe(1,2-dpe)(MeCN)]$^+$, **1a**−**d**, may be substituted with trivinylphosphine (tvp), divinylalkylphosphines, or divinylarylphosphines on heating in anisole, 1,2-dichloroethane, or chlorobenzene (Scheme 1). The substitution is conveniently followed by $^{31}P\{^1H\}$ NMR spectroscopy and is accompanied by a color change from the red of the acetonitrile complexes to a lighter orange−yellow of the trivinylphosphine complexes. Isolation of pure **2a**−**d** was compromised by the facile subsequent intramolecular ring-closure (see below), and in all cases, attempts at recrystallization resulted in contamination by the linear triphosphine complexes of type **3**. Typically, the resultant quaternary intermediate complexes [(η^5-Cp^R)Fe(1,2-dpe)(tvp)]$^+$, **2a**−**d**, were not isolated and were characterized only by their $^{31}P\{^1H\}$ NMR spectra, which consist of the expected doublet (2 × RPH_2) and triplet $P(C_2H_3)_3$ ($^2J_{P-P} \sim 50$ Hz) of an A_2B pattern. For the template reactions using 1,2-diphosphinoethane and trivinylphosphine, the first coupling reaction to give the half-cycle (**2** → **3**) proceeds soon after complexation of the tertiary phosphine for the silylated cyclopentadienyl derivatives [(η^5-Me_3SiCp)Fe(1,2-dpe)(tvp)]$^+$, **2b**, and [{η^5-(Me_3Si)$_2$Cp}Fe(1,2-dpe)(tvp)]$^+$, **2c**, as evidenced by the appearance of three distinct multiplets (AMX pattern) in the $^{31}P\{^1H\}$ NMR spectra. The first coupling is somewhat slower for the Cp* derivative (**2d** → **3d**) and considerably slower for the unsubstituted (parent) Cp derivative (**2a** → **3a**). Further heating leads to the disappearance of the signals attributed to **2** and a gradual growth of those of **3** as well as the final product **4**. The second coupling to give the final macrocycle product (**3** → **4**) is slower than the first, but the presence of **4** may be observed before complete conversion of **2** to **3**. The reactions are conveniently monitored by $^{31}P\{^1H\}$ NMR spectroscopy, as

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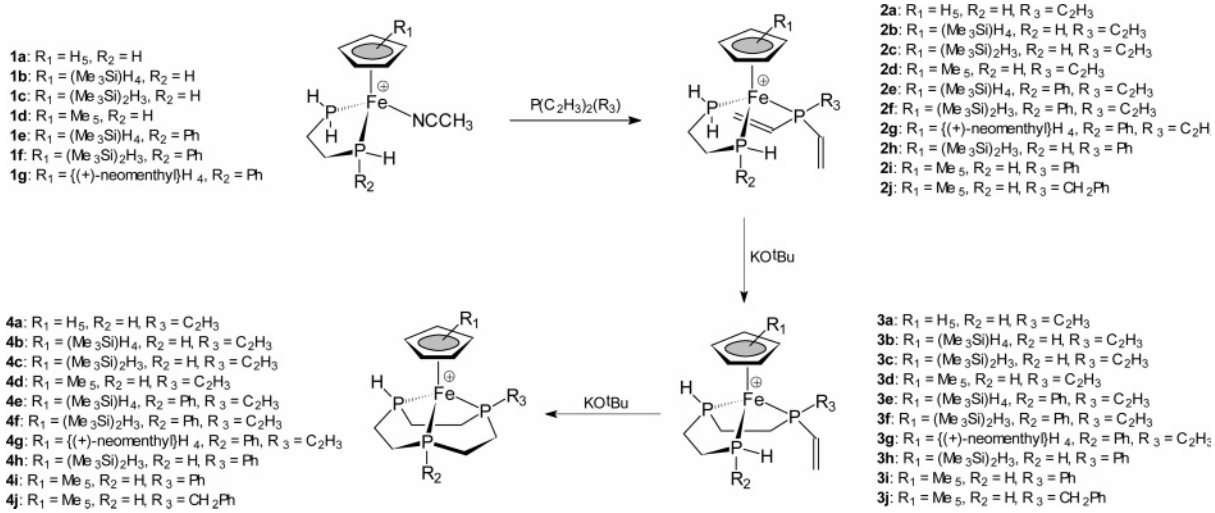
Scheme 1



illustrated in Figure 1. Proton-coupled ^{31}P NMR spectroscopy allows the unequivocal assignment of each signal in the AMX spectra of **3a**−**d** to the appropriate primary, secondary, and tertiary phosphorus centers (Table 1).

While electronic differences between the different Cp^RFe^+ templates may influence the rate of cyclization, these effects are likely to be small, and the observation of faster rates of macrocycle formation with the Cp units bearing bulky fragments may be explained, in part, by steric influences upon the coordinated 1,2-dpe and tvp precursor phosphines. It is reasonable to presume that the presence of bulky groups at the periphery of the Cp ligand will effectively compress the P−Fe−P bond angles, resulting in a closer approach of the vinyl functions of the tvp to the primary phosphines and lead to an enhancement of rate of the hydrophosphination as a result of this "proximity" effect. It is noteworthy that, although the electronic differences between Cp and Me_3SiCp are slight, the relative rates of macrocycle formation for these two templates are significantly different. The greatest yields (and indeed rates of formation) of macrocycle were observed with the bulkier Cp^R derivatives, Cp itself giving the lowest yield of macrocyclic product. For related tris-primary phosphine and 12-aneP_3R_3 complexes of Fe(II), we have demonstrated that increasing the bulk of the *trans* (to P) ligands does indeed reduce the nonbonded P−P distances.[16] This steric compression is also evident in the crystal structures of the macrocyclic products as discussed below.

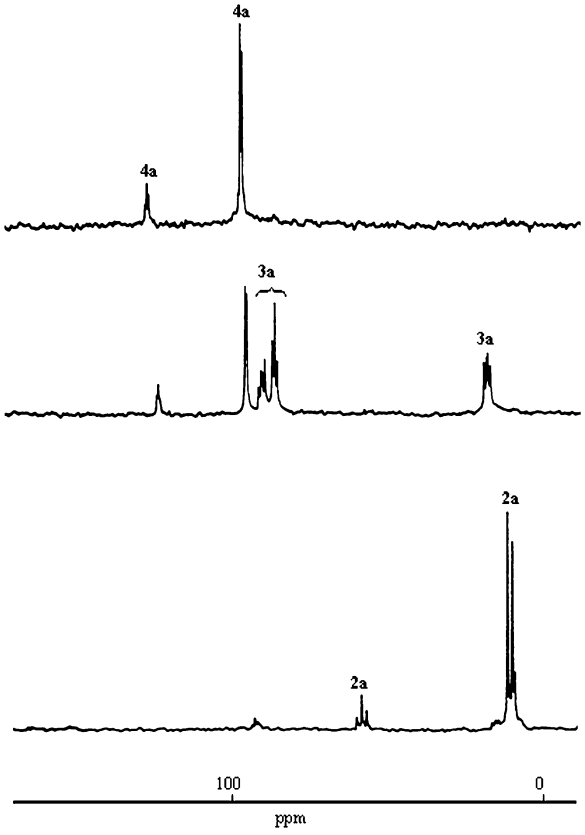


Figure 1. $^{31}P\{^1H\}$ NMR spectra showing the conversion of **2a** into **4a** at 80 °C in the presence of added Et_3N. The bottom trace was recorded after 1 h, the middle trace after 18 h, and the upper trace after 72 h.

As well as being sensitive to the nature of the substituents on the Cp ring, the rate of each coupling reaction (**2** → **3** and **3** → **4**) is also accelerated in the presence of base. Without added base, macrocycle formation was complete after 24 to 48 h at 80 °C with the Cp*, Me_3SiCp, and $(Me_3Si)_2Cp$ templates for the archetypal trivinylphosphine system. If the trivinylphosphine was added in excess, a significant rate enhancement was observed. Rate enhancement was also observed when stoichiometric amounts of triethylamine were added and reaction times were consequently reduced to several hours. In contrast, for the Cp derivative in the absence of added base, only the intermediate complex **3a** and starting material **2a** were observed in the $^{31}P\{^1H\}$ NMR spectrum after 5 days heating at 80 °C, and the final ring closure to form the macrocycle was only achieved after the addition of Et_3N; even then, several days at 80 °C were required for completion (Figure 1). This behavior implies that formation of the linear P_3 intermediates, and subsequently the product 9-aneP_3 macrocycles, requires the generation of an accessible lone pair on a coordinated primary (or secondary) phosphine by proton abstraction. An observable color change (upon addition of base) from yellow to red is consistent with formation of a coordinated phosphide, in accord with the

(15) No attempt was made to isolate the linear P_3 complexes of type **3** as they were only ever observed as mixtures with the respective starting materials (**2**) and macrocyclic products (**4**).

(16) Edwards, P. G.; Malik, K. M. A.; Ooi, L.; Price, A. J. *J. Chem. Soc., Dalton Trans.* **2006**, 433.

Table 1. P{^{1}H} NMR Data for the Complexes[15]

complex	δ_P (J_{PP})	complex	δ_P (J_{PP})
1a	0.5s	**4a**	129.0t (22), 96.0d (22)
1b	3.0s	**4b**	131.0t (21), 98.4d (21)
1c	1.5s	**4c**	126.0t (18), 98.7d (18)
1d	7.0s	**4d**	117.0t (5), 108.2d (5)
1e	74.8d (33), 63.8d (36), 3.7d (36), 2.7d (33)	**4e**	134.2t (21), 129.3t (21), 96.0t (21)
1f	72.5d (36), 61.4d (33), 3.8d (33), 1.6d (36)	**4f**	129.7t (18), 125.7t (18, 100.1t (18)
1g	75.4d (33), 74.7d (33), 63.8d (33), 3.9d (33), 3.1d (33), 2.3d (33)	**4g**	134.6t (18), 133.9t (18), 129.9t (18), 128.6t (18), 100.1t (18), 99.2t (18)
		4h	129.8t (18), 97.0d (18)
2a	51.9t (58), 3.5d (58)	**4i**	119.7t (4), 106.0d (4)
2b	50.8t (59), 4.3d (59)	**4j**	118.9t (4), 106.3d (4)
2c	48.5t (49), 7.0d (49)		
2d	49.5t (47), 15.5d (47)	**5b**	140.2t (21), 97.5d (21)
2h	54.5t (58), 5.9d (58)	**5c**	136.5t (21), 97.1d (21)
2i	57.1t (47), 16.6d (47)	**5e**	139.4t (21), 134.1t (21), 96.4t (21)
2j	51.6t (47), 13.7d (47)	**5f**	136.2t (24), 129.4t (24), 99.6t (24)
3a	90.8dd (36,49), 85.8t (36), 7.2dd (36,49)	**6a**	140.3d (25), 131.1t (25)
3b	87.8m, 8.0dd (42,46)	**6b**	138.9d (25), 128.5t (25)
3c	87.4t (30), 81.6dd (30,38), 8.5dd (30,38)		
3d	95.2t (22), 85.0dd (22,36), 18.8dd (22,36)	**7a**	140.1s
3h	91.4dd (34,48), 87.0dd (34,37), 8.8dd (37,48)	**7b**	139.0s
		7d	124.9s
		7l	139.5t (25), 136.7t (25), 135.3t (25)
		7m	139.5t (27), 136.7d (27)

observations of Wild and co-workers on related systems.[17] The resultant phosphido complex attains an 18-electron configuration at iron (inhibiting π-basic behavior) and thus supporting a σ-bonded phosphido ligand which retains nucleophilic character. The available lone pair may project toward or away from the acceptor orbitals of the vinyl group, as shown schematically in Figure 2. The subsequent coupling chemistry to form the linear P_3 intermediates **3a**−**d** and the final macrocycles **4a**−**d** is only possible when the lone pair of the transient phosphide projects away from the Cp ligand. This extends to the transformation of the linear triphosphorus species (**3**) to the macrocyclic product, and of the four possible diastereoisomers of **3a**−**d** that relate as two enantiomeric pairs, only one of these pairs can form.

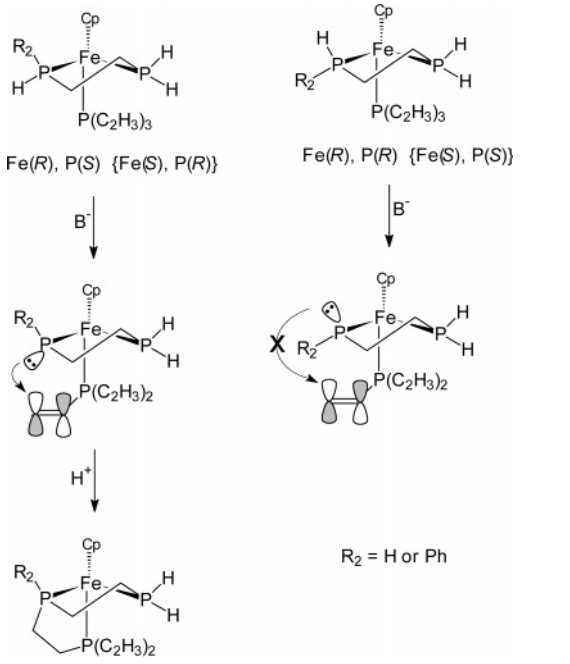


Figure 2. Diastereomeric possibilities and possible reaction pathways for the formation of the linear intermediate **3a** from **2a**. The second ring formation (macrocycle formation) to give **4a** is governed similarly.

The presence of a single AMX pattern in the $^{31}P\{^1H\}$ NMR spectra of **3a**−**d** confirms this, with only one enantiomer (or more likely enantiomeric pair) of the complexes being detected in solution. The selection is kinetic in origin (although the adopted structures may be preferred thermodynamically), as shown in Figure 2. The final ring closure to form the macrocycle is similarly constrained by the selection shown in the figure, so that for all the isolated complexes of $[(\eta^5\text{-Cp}^R)\text{Fe}(9\text{-ane}P_3)]^+$, the substituents at the phosphorus atoms (H, Ph, vinyl, etc.) project toward the Cp fragment.

Although compounds of the type $[(\eta^5\text{-Cp}^R)\text{Fe}(9\text{-ane}P_3H_2\text{-}C_2H_3)]^+$, **4**, were the predominant species observed in solution on completion of the reactions, insoluble deposits of an unknown nature were often formed, and these contribute to the modest isolated yields of products after cyclization. Generally, these precipitates were more prevalent in mixtures that required long reaction times and are likely to be the result of unwanted intermolecular couplings, and since the final macrocycle product contains a pendant vinyl function, this could occur between intermediate as well as product molecules. The macrocyclic complexes **4a**−**d** were isolated as orange−yellow solids that were readily recrystallized from alcohols and are air-stable indefinitely in the solid state but air-sensitive in solution. Ethanolic solutions darken as a result of partial decomposition, whereas in hydrochlorocarbons, the P−H functions are chlorinated; this latter reaction is accelerated upon addition of aqueous base (NaOH).

The $^{31}P\{^1H\}$ NMR spectra (Table 1) reveal a dependence of both δ_P and $^2J_{P-P}$ on the nature of the Cp donor. The coordinated 1,2-dpe in the monoacetonitrile complexes **1a**−**d** resonates between 0 and 8 ppm, ~130 ppm downfield of the signal for the uncoordinated diphosphine, but is typical of formation of a 5-membered chelate.[18] The ^{31}P NMR chemical shifts for **1a**−**c** are similar (δ_P 0.5−3.0 ppm), whereas for the Me_5Cp derivative,

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(18) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Complexes*; Springer-Verlag: Berlin, 1979.

1d, the downfield shift is greater (δ_P 7.0 ppm); this is presumably a consequence of the electronic differences within the series of Cp^R donors. The complexes **2a**−**d** show the expected doublet (RPH_2) and triplet [$P(C_2H_3)_3$] in their $^{31}P\{^1H\}$ NMR spectra, and the absolute difference in chemical shift between the two signals ($\Delta[\delta_1 - \delta_2]$) and $^2J_{P-P}$ decreases along the series Cp > Me_3SiCp > $(Me_3Si)_2Cp$ > Cp*. This trend extends to the complexes **3a**−**d** and **4a**−**d**. Furthermore, although the coordinated trivinylphosphine resonates at δ 50 ± 2 ppm in **2a**−**d**, the vinyl bearing phosphine resonates at a higher field (δ_P 117.0 ppm) in **4d** than in **4a**−**c** (δ_P 126−131 ppm). This is even more pronounced in the perethylated tritertiary phosphine complexes $[(\eta^5\text{-}Cp^R)Fe(9\text{-}aneP_3Et_3]^+$, **7a**,**b**,**d** (Table 1). A possible reason is that increased steric compression about the metal center in **2d** forces the Fe−P(vinyl) bond to lengthen, resulting in the somewhat anomalous δ_P value; this relative bond lengthening is observed in the crystal structure (see below).

In common with the $^{31}P\{^1H\}$ NMR data, the η^5-Cp* derivative **4d** shows some significant differences in its ^1H NMR spectrum with respect to **4a**−**c**. Most notable is the relative chemical shift of the PH protons, which resonate at δ_H 5.55 ppm in the spectrum of **4d** as opposed to 6.24 ± 0.05 ppm for **4a**−**c**. Steric encumbrance at the secondary phosphines is not expected to be large, and it may be that these differences in δ_H (PH) are mainly electronic in origin as (presumably) are the variations in the ^{31}P spectra (see above). Where resolvable, the Cp ring protons of the **1a** → **7a** series appear as quartets in the ^1H NMR spectra with a J_{P-H} coupling of ∼1.5 Hz. The methylene carbons in the macrocycle give three distinct multiplets in the ^{13}C NMR spectra of complexes **4a**−**d**, suggesting pairwise equivalence and hence a plane of symmetry through the P−vinyl phosphorus bisecting the $-HPCH_2CH_2PH-$ carbon−carbon bond and therefore rapid conformational inversion in the 5-membered chelate rings. All the complexes of type **4** containing secondary phosphine donors show a weak but characteristic ν(P−H) stretch in their infrared spectra at approximately 2360 ± 20 cm^{-1}.

The complex $[\{\eta^5\text{-}(Me_3Si)_2Cp\}Fe(9\text{-}aneP_3H_2C_2H_3]BF_4$, **4c**, crystallizes in the $P2_1/c$ space group with two distinct molecules in the asymmetric unit. The structure of one of the complex cations of **4c** is shown in Figure 3. The iron(II) center is pseudo-octahedral with the usual distortions due to the small "bite" of the carbons in the Cp ring. The macrocycle is facially coordinated with Fe−P bond lengths averaging 2.17 Å (there is little difference between Fe−PH and Fe−P_{vinyl}) and P−Fe−P angles averaging 85.5°. These values compare with those of $1,2\text{-}C_6H_4(PMePh)_2$ in $[(R^*,R^*),(R^*)]\text{-}(\pm)\text{-}[(\eta^5\text{-}C_5H_5)Fe\{1,2\text{-}C_6H_4(PMePh)_2\}(PHMePh)]PF_6$ [19] (Fe−P = 2.176, 2.183 Å; P−Fe−P = 86.3°) and the 11aneP$_2$N macrocycle in $[(\eta^5\text{-Cp})\text{-}Fe(meso\text{-}cis\text{-}2,10\text{-diphenyl-}6\text{-aza-}2,10\text{-diphenylbicyclo}[9.4.0]\text{-pentadeca-}11(1),12,14\text{ triene})]I$ (Fe−P = 2.177, 2.193 Å; P−Fe−P = 86.9°).[20] The bond lengths are shorter and the angles tighter, however, than those in the related $[(\eta^5\text{-Cp})Fe(12\text{-}aneP_3Et_3)]^+$ complexes.[13c] When the structure of the bis-(trimethylsilyl) Cp, **4c**, complex is viewed down the vector connecting the centroid of the Cp ring to the iron, it is evident that the phosphorus donor bearing the vinyl group lies below

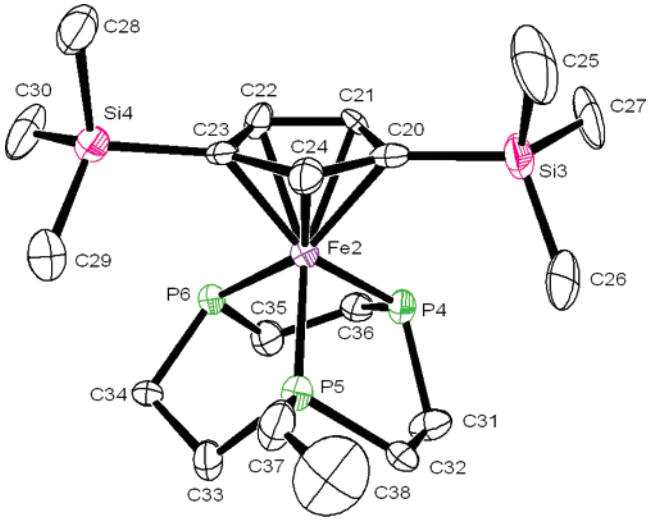

Figure 3. Ortep representation of the structure of **4c**. Ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (°): Fe2−P4 = 2.156(3), Fe2−P5 = 2.168(3), Fe2−P6 = 2.174(3), Fe2−C20 = 2.119(10), Fe2−C21 = 2.094(10), Fe2−C22 = 2.089(11), Fe2−C23 = 2.113(10), Fe2−C24 = 2.090(10), P4−Fe2−P5 = 85.73(12), P4−Fe2−P6 = 84.98(12), P5−Fe2−P6 = 86.25(12).

the C24 carbon of the Cp ring and the vinyl function occupies the space between the two Me_3Si groups. Unsurprisingly, the Fe−C(Si) bond lengths are the longest of the Fe−C bonds, and the C−Si vectors are bent ∼10° out of the C_5 plane. These distortions of the silyl groups out of the C_5 plane of the cyclopentadienyl ligand, coupled with the Fe−P−C_{vin} bond angles being expanded to an average of 122.8°, are evidence for the steric compression discussed above. The vinyl group is located on the same side of the P_3 plane as the $(Me_3Si)_2Cp$ unit, an orientation required by the pathway for ring formation detailed in Figure 2.

9aneP$_3$ Derivatives from Template Reactions of Phenyl(2-phosphinoethyl)phosphine and Trivinylphosphine. As described above, the cyclization chemistry is sensitive to the nature of the peripheral substituents on the Cp^R unit with greater rates being realized with increased bulk at these positions. In the synthesis of nitrogen macrocycles by the Richman−Atkins method,[21] it is well-known that bulky substituents on the nitrogens of acyclic precursor amines helps facilitate ring closure due to the steric influence of the substituents. In view of this, it was of interest to see what effect (if any) the introduction of a substituent at one of the primary phosphines of 1,2-diphosphinoethane (to generate a mixed primary/secondary bidentate phosphine) had on the subsequent cyclization chemistry. To this end, phenyl(2-phosphinoethyl)phosphine, Phdpe, was employed with the most effective of the Cp^RFe^+ templates, that is, the silylated cyclopentadienyl iron(II) fragments, and trivinylphosphine. The precursor complexes $[(\eta^5\text{-}Me_3SiCp)Fe(Phdpe)(MeCN)]PF_6$, **1e**, and $[\{\eta^5\text{-}(Me_3Si)_2Cp\}Fe(Phdpe)(MeCN)]PF_6$, **1f**, were readily prepared in the same manner as their 1,2-dpe analogues (**1a**−**d**), and they were isolated as a mixture of two diastereomeric pairs of enantiomers: Fe(*R*), P(*R*)/Fe(*S*), P(*S*), and Fe(*S*), P(*R*)/Fe(*R*), P(*S*) (see Figure 2). Reaction of complexes **1e**,**f** with trivinylphosphine gives rise to the diphosphine/monophosphine complexes $[(\eta^5\text{-}Cp^R)Fe(Phdpe)(tvp)]PF_6$, **2e** (R = Me_3Si), and $[\{\eta^5\text{-}(Me_3Si)_2Cp\}Fe(Phdpe)(tvp)]PF_6$, **2f**,

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also as a pair of diastereomers. It is clear from Figure 2 that the Fe(*R*), P(*R*)/Fe(*S*), P(*S*) diastereomeric pair will not form the desired 9-ane$P_3HPhC_2H_3$ compounds unless inversion occurs at the P(Ph) center. The chemistry highlighted in Figure 2 relates to the situation where the secondary phosphine reacts to form the first 5-membered chelate; that is, to produce the linear 4-phenyl-1,4,7-triphosphanonane intermediate, the terminal primary phosphine (phosphide) of this intermediate is then available to react with one of the remaining vinyl functions to give the macrocyclic complex in a manner akin to that observed for **3a**−**d**. A second route involving the initial reaction of the primary phosphine (phosphide) to give the 1-phenyl-1,4,7-triphosphanonane intermediate is also possible. The intermediate from this route has a stereogenic terminal secondary phosphine which can only react to form the macrocyclic complexes [(η^5-Cp^R)Fe(9-ane$P_3HPhC_2H_3$)]PF_6, **4e**,**f**, when the orientation is right (cf. Figure 2 and the associated discussion for the **4a**−**d** systems). $^{31}P\{^1H\}$ NMR analysis of the reaction mixtures during the conversions **2e**,**f** → **4e**,**f** suggests that both routes operate. The cyclization reaction for **2e** and **2f** is considerably slower than that for the related systems **2b** and **2c**, and the yields of the desired complexes **4e** and **4f** are lower. As the axial orientation of nonannular groups is not possible in the 9-aneP_3 complexes, the resultant macrocylic complexes **4e**,**f** are formed as a mixture of only two enantiomers. These are characterized in their $^{31}P\{^1H\}$ NMR spectra by three distinct triplets for each of the unique phosphorus centers; two tertiary and one secondary phosphine is confirmed in the ^{31}P NMR spectra. All the phosphorus atoms and the iron(II) center are stereogenic, and the two trimethylsilyl groups of the $(Me_3Si)_2Cp$ unit in [η^5-1,3-bis(trimethylsilyl)cyclopentadienyl](1-phenyl-4-vinyl-1,4,7-triphosphacyclononane)iron(II) hexafluorophosphate, **4f**, are diastereotopic; these are observed as distinct singlets at δ_H 0.07 and 0.05 ppm in the ^1H NMR and δ_C 0.7 and at 0.5 ppm in the $^{13}C\{^1H\}$ NMR spectra of the complex. Similarly, all the cyclopentadienyl protons are inequivalent and give rise to three distinct resonances in the ^1H and $^{13}C\{^1H\}$ NMR spectra of **4f**.

In an effort to introduce some diastereoselectivity into the macrocycle formation, the chiral Cp ligand (+)-neomenthylcyclopentadiene, (+)-neoMenCp, was employed. Following related literature examples,[14] the complex [{(+)-neoMenCp}-Fe(MeCN)(Phdpe)]BF_4, **1g**, was obtained as an approximately equimolar mixture of four diastereomers; because of the predefined chirality of the (+)-neoMenCp, there is no enantiomeric relationship between any of the diastereomers of **1g**. The subsequent cyclization chemistry with Phdpe and tvp was less efficient with this template with respect to the silylated cyclopentadienyl templates, with the consequence that [{(+)-neoMenCp}Fe(9-ane$P_3HPhC_2H_3$)]BF_4, **4g**, was obtained in low yield. The complex **4g** is formed as an equimolar mixture of the two possible diastereoisomers which, unlike the case for the enantiomeric pair of **4e**,**f**, have distinct NMR spectra as detailed in the Experimental Section and Table 1; thus the chiral auxiliary did not induce any enantioselectivity in the cyclization reaction under our conditions.

9aneP_3 Derivatives from Template Reactions of 1,2-Diphosphinoethane and Divinylalkyl(aryl)phosphines. All the reactions discussed thus far have employed trivinylphosphine, and it has been shown that replacing a hydrogen in 1,2-dpe with a phenyl group reduces the efficiency of the macrocyclization

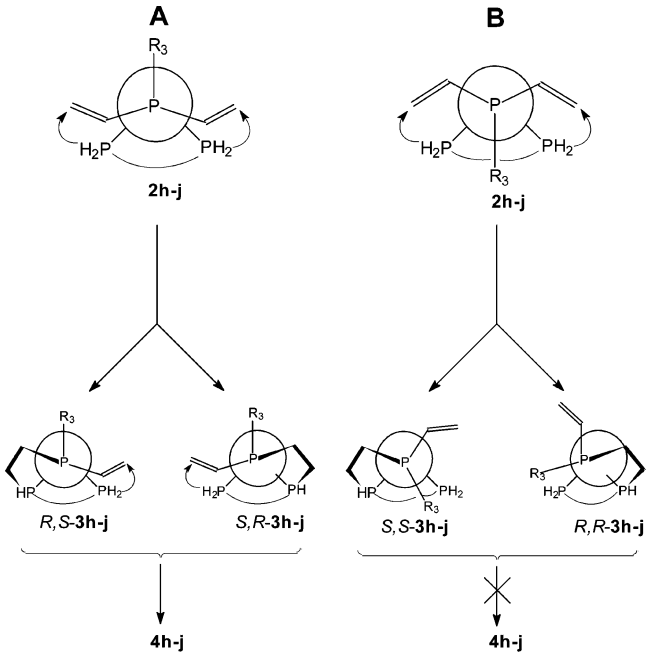
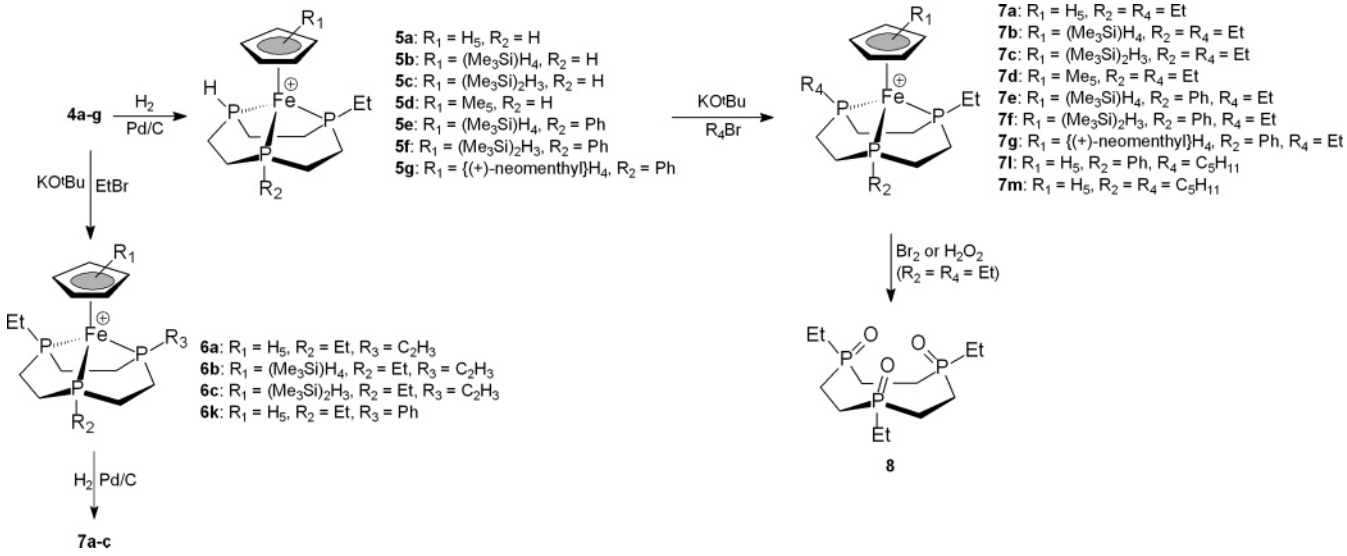


Figure 4. Possible reaction pathways and diastereomeric products in the reactions involving the divinylaryl(alkyl)phosphines.

(see above). It remained of interest to see what effect changing the site of the phenyl substituent from the diphosphine to the monophosphine would have on the subsequent coupling chemistry. Whereas the cyclization was anticipated to be slow for the reactions employing phenyl(2-phosphinoethyl)phosphine and trivinylphosphine, it was originally doubted whether divinyl(alkyl/aryl)phosphines would give any isolable yield of macrocyclic complex. The distinction between the cyclization chemistry here and that for the Phdpe/tvp complement is that, for the latter, linear intermediates with one terminal primary phosphine and a second terminal phosphorus bearing two vinyl functions are accessible (through the initial coupling of the secondary phosphine of Phdpe) enabling complete cyclization akin to reactions using unsubstituted 1,2-dpe and tvp. This is not the case for divinyl(alkyl/aryl)phosphines which necessarily go through linear intermediates with only one vinyl function on a terminal phosphorus. This will lead to stereochemical relationships between the terminal phosphines which may limit complete cyclization (Figure 4). The formation of the first 5-membered chelate to give **3h**−**j** generates two stereogenic phosphorus centers. When the P_{sec} donor has the *S* configuration, macrocycle formation is only possible when P_{tert} has the *R* absolute configuration. Likewise, if P_{sec} is *R*, then P_{tert} must be *S* in order for macrocyclization to occur (Figure 4). The P_{sec}/P_{tert} combinations *S*/*S* and *R*/*R* preclude formation of the macrocycle. The combinations *R*(P_{sec})/*S*(P_{tert}) and *S*(P_{sec})/*R*(P_{tert}) are enantiomers, as are the *R*,*R* and *S*,*S* pair; the relationship between the two sets is diastereomeric. Therefore, two sets of peaks would be expected in the $^{31}P\{^1H\}$ NMR spectrum (one for the *R*,*S*/*S*,*R* pair and one for the *S*,*S*/*R*,*R* pair) if more than one diastereomer of **3h**−**j** were present. Heating a solution of [{η^5-$(Me_3Si)_2Cp$}Fe(1,2-dpe){$PPh(C_2H_3)_2$}]PF_6, **2h**, in chlorobenzene to 80 °C for several days gave no intermediate **3h** or macrocycle complex [{η^5-$(Me_3Si)_2Cp$}Fe(9-aneP_3H_2Ph)]PF_6, **4h**, as determined by $^{31}P\{^1H\}$ NMR spectroscopy. When the reaction was repeated in the presence of 2 molar equiv of triethylamine, the distinctive AMX pattern of the part coupled

Scheme 2



linear acyclic triphosphine intermediate **3h** was observed within several hours. However, only one set of doublets of doublets was observed for each distinct phosphorus center, indicating that only a single isomer (or, more likely, one enantiomeric pair) of **3h** is formed. Further heating leads to complete conversion of **2h** to **3h** with concomitant formation of $[\{\eta^5\text{-}(Me_3Si)_2Cp\}Fe(9\text{-}aneP_3H_2Ph)]PF_6$, **4h**. After 3 days, the reaction is complete and **4h** is isolated in 29% yield. The fact that all the linear intermediate (**3h**) is converted to the macrocycle product **4h** confirms the assignment of the former as the *R,S*/*S,R* mixture. The rate of cyclization is much slower than the analogous reaction with trivinylphosphine (**2c** to **4c**), and consequently yields are lower as deleterious intermolecular side reactions compete with the desired coupling. The observation of only one enantiomeric pair of **3h** may reflect a preferred orientation of the divinylphenylphosphine in **2h**, that is, **A** in Figure 4, which is, fortunately, an orientation that favors macrocyclization. The complexes **4i** and **4j** were prepared similarly, again in low to modest yield. To assess the efficiency or otherwise of radical induced coupling, $[(\eta^5\text{-Cp*})Fe(1,2\text{-dpe})(dvpp)]^+$ and $[(\eta^5\text{-Cp*})Fe(1,2\text{-dpe})(dvbp)]^+$, where dvpp is divinylphenylphosphine and dvbp is divinylbenzylphosphine, were cyclized in the presence of AIBN (no base), but under these conditions, intermolecular coupling predominates and the desired compounds are isolated in very low yield (5%).

Further Functionalization of Secondary Phosphine Complexes of Type 4. For complexes of 12-aneP_3H_3 macrocycles coordinated to Cr(0) or Mo(0), it is possible to convert the PH groups to tertiary phosphines by either a stepwise process of deprotonation and electrophilic alkylation or by radical-induced hydrophosphination. In preliminary studies, we have shown that deprotonation and alkylation can lead to 1,4,7-triethyl-1,4,7-triphosphacyclononane (9-aneP_3Et_3) complexes of iron(II).[13b] There are two possible routes for the formation of the 1,4,7-triethyl-1,4,7-triphosphacyclononane complexes (**7a**−**d**) from the 1-vinyl derivatives (**4a**−**d**) as indicated in Scheme 2.

The first, which has been used successfully for the preparation of $[\{\eta^5\text{-Cp*}\}Fe(9\text{-}aneP_3Et_3)]BF_4$, **7d**,[13b] involves hydrogenation of the vinyl group proceeded by alkylation of the secondary phosphine functions with KO^{t}Bu/EtBr. This is the preferred route for the pentamethyl- and trimethylsilyl-substituted cyclopentadienyl complexes. However, the unsubstituted Cp derivative, with a single vinyl function (**4a**), is poorly soluble in ethanol (the solvent of choice for the hydrogenation), resulting in slow rates and/or the need for large volumes of solvent. For this complex, the second route, whereby the secondary phosphines in $[(\eta^5\text{-Cp})Fe(9\text{-}aneP_3H_2C_2H_3)]BF_4$, **4a**, are ethylated to give the 1,4-diethyl-7-vinyl derivative **6a** which is subsequently hydrogenated to the 1,4,7-triethyl species **7a**, is preferred as $[(\eta^5\text{-Cp})Fe(9\text{-}aneP_3Et_2C_2H_3)]BF_4$, **6a**, is much more soluble in ethanol than is **4a**. This route is not the first choice for all the complexes as the reactive vinyl group can interfere with the alkylation, and in the synthesis of **6a**, the amount of added base must be carefully controlled in order to prevent dimerization of **4a** by an intermolecular Michael-type addition. The trimethylsilyl groups in **4b**, **4c**, **5b**, and **5c** are unstable under the basic conditions required for ethylation. Thus, attempts to isolate $[(\eta^5\text{-}\{Me_3Si\}_2Cp)Fe(9\text{-}aneP_3Et_2C_2H_3)]BF_4$, **6c**, were unsuccessful as partial loss of one or both Me_3Si functions from the Cp ring was observed with the formation of a mixture of $[(\eta^5\text{-Cp})Fe(9\text{-}aneP_3Et_2C_2H_3)]BF_4$ (**6a**) and $[(\eta^5\text{-}Me_3SiCp)Fe(9\text{-}aneP_3Et_2C_2H_3)]BF_4$ (**6b**). Furthermore, this loss is accompanied by partial reduction of the vinyl group of the resultant **6a**/**6b** to give variable amounts of $[(\eta^5\text{-Cp})Fe(9\text{-}aneP_3Et_3)]BF_4$, **7a**, and $[(\eta^5\text{-}Me_3SiCp)Fe(9\text{-}aneP_3Et_3)]BF_4$, **7b**, and so an overall mixture of **6a**, **6b**, **7a**, and **7b** was obtained. Fortunately, both like pairs **6a**/**7a** and **6b**/**7b** could be isolated and the mixtures hydrogenated to give reasonable yields of pure **7a** and **7b**.

Although the extent of desilylation was less for the monosilylcyclopentadienyl complex $[(\eta^5\text{-}Me_3SiCp)Fe(9\text{-}aneP_3H_2C_2H_3)]BF_4$, **4b**, with respect to the disilyl derivative $[(\eta^5\text{-}\{Me_3Si\}_2Cp)Fe(9\text{-}aneP_3H_2C_2H_3)]BF_4$, **4c**, complex mixtures were still observed and **6b** was isolated in only modest yield. These Me_3Si eliminations were also observed on ethylating $[(\eta^5\text{-}Me_3SiCp)Fe(9\text{-}aneP_3H_2Et)]BF_4$, **5b**, and $[(\eta^5\text{-}\{Me_3Si\}_2Cp)Fe(9\text{-}aneP_3H_2Et)]PF_6$, **5c**. Although careful control of reaction temperature and amount of added base gave good yields of the perethylated complex $[(\eta^5\text{-}Me_3SiCp)Fe(9\text{-}aneP_3Et_3)]BF_4$, **7b**, the analogous $(Me_3Si)_2Cp$ complex, **7c**, was not obtained pure. Efforts to obtain **7c** by ethylation of **5c** using Et_3N and EtBr were only partly successful; although no desilylation was observed, bromination of the secondary phosphines did occur as a

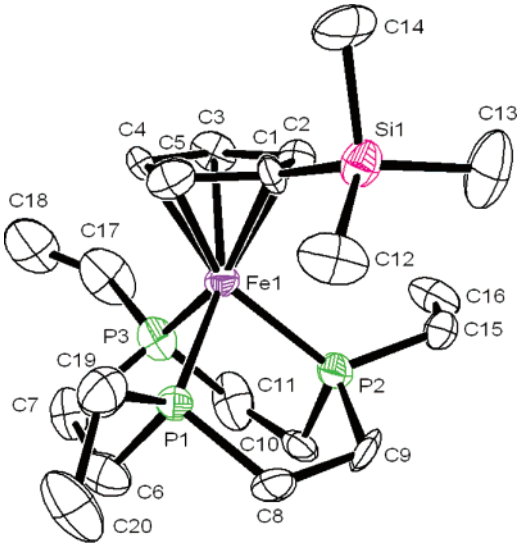


Figure 5. Ortep representation of the structure of **7b**. Ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (°): Fe1−P1 = 2.178(4), Fe1−P2 = 2.196(5), Fe1−P3 = 2.153(4), Fe1−C1 = 2.140(14), Fe1−C2 = 2.114(16), Fe1−C3 = 2.088(15), Fe1−C4 = 2.090(16), Fe1−C5 = 2.071(16); P1−Fe1−P2 = 81.86(17), P1−Fe1−P3 = 86.47(18), P2−Fe1−P3 = 87.25(18), Fe1−P1−C19 = 120.2(6), Fe1−P2−C15 = 123.0(6), Fe1−P3−C17 = 123.1(7).

competing reaction and it proved difficult to separate the desired complex **7c** from the $[(\eta^5\text{-}\{Me_3Si\}_2Cp)Fe(9\text{-}aneP_3Et_2Br)]PF_6$ byproduct. The desilylation extended to the complex $[(\eta^5\text{-}Me_3SiCp)Fe(9\text{-}aneP_3HEtPh\}]PF_6$, **5e**, which, upon deprotonation and subsequent alkylation with 1-bromopentane, eliminated the trimethylsilyl fragment to give $[(\eta^5\text{-}Cp)Fe(9\text{-}aneP_3EtPhC_5H_{11})]PF_6$, **7l**. In addition, when complex $[(\eta^5\text{-}\{Me_3Si\}_2Cp)Fe(9\text{-}aneP_3H_2Et)]PF_6$, **5c**, was treated with an excess of potassium *tert*-butoxide, and subsequently reacted with >2 molar equiv of 1-bromopentane, only $[(\eta^5\text{-}Cp)Fe(9aneP_3Et\{C_5H_{11}\}_2)]PF_6$, **7m**, was isolated. The tritertiary complexes **6a**−**c**,**k** and **7a**,**b**,**l** are all bright yellow, air-stable crystalline solids that retain their stability to air and moisture when in solution. The symmetrical $9\text{-}aneP_3Et_3$ derivatives (**7a**,**b**,**d**) are soluble in hydrochlorocarbons, and alcohols and may be crystallized from these with or without additional solvents. The structure of $[(\eta^5\text{-}Me_3SiCp)Fe(9\text{-}aneP_3Et_3)]^+$ (**7b**) is shown in Figure 5.

The structure is as expected with a pseudo-octahedral iron atom facially capped by the Cp ligand and the P_3 macrocycle. The Fe−C($SiMe_3$) bond is significantly longer [2.14(1) Å] than the remainder [av. 2.09(2) Å] as is the Fe−P2 bond: 2.196(5) Å compared to 2.153(4) and 2.178(4) for the other two. The longest Fe−P bond is comparable to those of **7d** (av. 2.194 Å) and to the phosphorus whose ethyl substituent is in closest contact with the bulky Me_3Si group on the Cp fragment. The P1−Fe1−P2 angle is the smallest of the P−Fe−P angles due, presumably, to the steric influence of the trimethylsilyl group on the two phosphorus atoms. The average Fe−P−C_{ethyl} angle is again expanded to 122.6°, reflecting the steric compression in the complex. The average of the Fe−P bonds is longer here at 2.175 Å than in complex **4c**. In addition, the C−Si bond is bent 14° out of the C_5 plane of the Cp ring, appreciably more than in $[(\eta^5\text{-}\{Me_3Si\}_2Cp)Fe(9\text{-}aneP_3H_2C_2H_3)]^+$, **4c**, or for the methyl groups in $[(\eta^5\text{-}\ Cp^*)Fe(9\text{-}aneP_3Et_3)]^+$, **7d**.

Liberation of $9\text{-}aneP_3Et_3$ as the Trioxide. When **7b** (or **7a**) was treated with aqueous hydrogen peroxide under acidic conditions or bromine in dichloromethane and water in a modification of the liberation conditions of Stelzer,[22] the free macrocycle was isolated as the trioxide, **8** (Scheme 2). Use of either liberation technique results in excellent recovery of $9\text{-}aneP_3(O)_3Et_3$, although the bromine method is the preferred one. The resultant $9\text{-}aneP_3(O)_3Et_3$ is a hygroscopic white solid that is freely soluble in water, sparingly soluble in alcohols, and insoluble in other common organic solvents. The $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at δ_P = 65.2 ppm confirming the all *syn* arrangement of the P═O functions as indicated in Scheme 1. The chemical shift is similar to those for related P_4 macrocycle oxides.[22] ^1H and ^{13}C NMR spectra are consistent with the proposed structure. A strong absorption at 1145 cm^{-1} in the infrared spectrum is assigned to the ν(P═O) stretch. It is of interest to note that the mass spectrum of the trioxide only gave a peak for $[9\text{-}aneP_3(O)_3Et_3 + M^+]$ where M = Li, Na, suggesting a high affinity of the compound for hard metal ions. To date, all efforts to reduce the trioxide to the phosphine using $LiAlH_4$ and $PhSiH_3$ have proved fruitless, possibly due to the very poor solubility of the compound in appropriate solvents. Work is continuing on the development of methods for the reduction of the trioxide and/or release of the macrocycle from the template without ligand oxidation.

In conclusion, a general method for the synthesis of $9\text{-}aneP_3$ macrocycles using CpFe(II) units as templates has been established. The rate of formation of the macrocycles is dependent on the nature and position of the substituents on the Cp ring and the phosphorus donors. The triethyl macrocycle has been released from the template by oxidation using H_2O_2 to give the trioxo derivative. We are currently examining the stereoselective reduction of the $9\text{-}aneP_3(O)_3Et_3$ compound to obtain the free phosphine with a view to investigating the chemistry of this and related systems with a range of metal ions.

Experimental Section

The complexes were synthesized under nitrogen using standard inert atmosphere (Schlenk) techniques. The tertiary macrocycle complex salts are indefinitely stable in air in the solid state and in solution; solutions of macrocycle complexes containing secondary phosphines were manipulated and stored under nitrogen. All solvents were freshly distilled from sodium (toluene and anisole) or calcium hydride (acetonitrile and 1,2-dichloroethane) under nitrogen before use. The ^{31}P NMR spectra were recorded on JEOL FX90Q, Bruker AM360, and JEOL Eclipse 300 spectrometers operating at 36.2, 145.1, and 121.7 MHz, respectively, and referenced to 85% H_3PO_4 (δ = 0 ppm). ^1H (400.13 or 300 MHz) and ^{13}C (100 or 75.6 MHz) NMR spectra were obtained on Bruker DPX400 and JEOL Eclipse 300 spectrometers and are referenced to tetramethylsilane (δ = 0 ppm). Infrared spectra were recorded as KBr disks on a Nicolet 510 FT-IR spectrophotometer. Mass spectra were obtained on a VG Fisons Platform II spectrometer at Cardiff or through Warwick Analytical Service Ltd. Microanalyses were performed within the School of Chemistry at Cardiff or by Warwick Analytical Service Ltd. 1,2-Bis(phosphino)ethane,[23] phenyl(2-phosphinoethyl)phosphine,[24] trivinylphosphine,[25] $[\{\eta^5\text{-}(Me_3Si)Cp\}Fe(CO)_2]_2$,[26] $[\{\eta5\text{-}(Me_3Si)_2Cp\}Fe(CO)_2]_2$,[27] and $[\{(+)\text{-neomenthyl})Cp\}Fe(CO)_2]_2$[28]

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(27) Clark, J. T.; Killian, C. M.; Luthra, S.; Nile, T. A. *J. Organomet. Chem.* **1993**, *462*, 247.

were prepared as described. All other chemicals were of reagent grade and were used as supplied unless otherwise stated. Complexes **1d**, **4d**, **5d**, and **7d** were synthesized by the reported methods.[13b]

(Acetonitrile)dicarbonyl(η^5-trimethylsilylcyclopentadienyl)-iron(II) tetrafluoroborate. This compound was prepared from [{η^5-(Me_3Si)Cp}$Fe(CO)_2$]$_2$ (1.00 g, 2.01 mmol) and ferrocenium tetrafluoroborate using the method of Astruc.[14] Large golden-brown crystals were grown from acetone/diethyl ether at −30 °C. Yield = 1.32 g (87%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.63 (s, 2H, Cp), 5.42 (s, 2H, Cp), 2.41 (s, 3H, CH_3CN), 0.34 (s, 9H, SiCH_3). Elemental analysis calcd for $C_{12}H_{16}NSiO_2BF_4Fe$: C, 38.22; H, 4.29; N, 3.72. Found: C, 37.9; H, 4.2; N, 3.5. IR (KBr): 2328w (ν_{CN}), 2066, 2021vs (ν_{CO}).

(Acetonitrile)dicarbonyl{η^5-1,3-bis(trimethylsilyl)cyclopentadienyl}-iron(II) hexafluorophosphate. This compound was prepared as above using [{η^5-(Me_3Si)$_2$Cp}$Fe(CO)_2$]$_2$ (1.00 g, 1.56 mmol) and ferrocenium hexafluorophosphate and obtained as a yellow microcrystalline solid by crystallization from from acetone/diethyl ether mixtures. Yield = 1.30 g (82%). ^{1}H NMR {(CD_3)$_2$CO, 300 MHz}: δ = 5.53 (s, 1H, Cp), 5.40 (s, 2H, Cp), 2.36 (s, 3H, CH_3CN), 0.29 (s, 18H, SiCH_3). Elemental analysis calcd for $C_{15}H_{24}NSi_2O_2PF_6Fe$: C, 35.50; H, 4.78; N, 2.76 Found: C, 35.1; H, 4.7; N, 2.6 IR (KBr): 2316w (ν_{CN}), 2076, 2036vs (ν_{CO}).

(Acetonitrile)dicarbonyl{η^5-(+)-neomenthylcyclopentadienyl}-iron(II) hexafluorophosphate. This compound was prepared from [{η^5-(+)-neomenthylCp}$Fe(CO)_2$]$_2$ (1.00 g, 1.58 mmol) using a method similar to those above. The pure compound was obtained after two recrystallizations from acetone/diethyl ether mixtures at −30 °C. Yield = 0.90 g (57%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 5.45 (s, 1H, Cp), 5.24 (s, 1H, Cp), 5.19 (s, 1H, Cp), 5.14 (s, 1H, Cp), 2.80 (s br, 1H), 2.29 (s, 3H, CH_3CN), 1.8−0.8 (m, 9H), 0.86 (d, 3H, 5.0 Hz), 0.85 (d, 3H, 5.0 Hz), 0.72 (d, 3H, 6.2 Hz). Elemental analysis calcd for $C_{19}H_{26}NO_2PF_6Fe$: C, 45.52; H, 5.24; N, 2.79. Found: C, 45.1; H, 5.2; N, 2.5. IR (KBr): 2336w (ν_{CN}), 2061, 2024vs (ν_{CO}).

(Acetonitrile)(η^5-cyclopentadienyl)(1,2-diphosphinoethane)-iron(II) hexafluorophosphate, 1a. A solution of [(η^5-Cp)Fe(η^6-C_6H_6)]-PF_6 (1.00 g, 2.91 mmol) and 1,2-diphosphinoethane (0.30 mL, 3.1 mmol) in acetonitrile (50 mL) was irradiated for 12 h with a 100 W tungsten lamp. The solvent was subsequently removed and the resultant residue crystallized from hot tetrahydrofuran/acetonitrile to give complex **1a** as orange−red crystals. Yield = 1.00 g (85%). ^{31}P{^{1}H} NMR ($CDCl_3$, 36.23 MHz): δ = 0.5. ^{1}H NMR {(CD_3)$_2$CO, 300 MHz}: δ = 5.67 (d, 2H, PH_2, $^1J_{PH}$ = 356 Hz), 4.92 (d, 2H, PH_2, $^1J_{PH}$ = 340 Hz), 4.58 (s, 5H, Cp), 2.29 (s, 3H, CH_3CN), 2.05 (br, 4H, CH_2). Elemental analysis calcd for $C_9H_{16}NP_3F_6Fe$: C, 26.95; H, 4.03; N, 3.49. Found: C, 26.6; H, 3.8; N, 3.1. IR (KBr): 2352, 2317m (ν_{PH}), 2265m (ν_{CN}).

(Acetonitrile)(η^5-trimethylsilylcyclopentadienyl)(1,2-diphosphinoethane)iron(II) tetrafluoroborate, 1b. A solution of [{η^5-(Me_3Si)Cp}$Fe(CO)_2$(CH_3CN)]BF_4 (1.00 g, 2.65 mmol) and 1,2-diphosphinoethane (0.25 mL, 2.7 mmol) in acetonitrile (100 mL) was irradiated for 12 h with a Hanovia 125W UV lamp. The solvent was subsequently removed and the resultant residue crystallized from hot tetrahydrofuran to give **1b** as a red crystalline solid. Yield = 0.90 g (82%). ^{31}P{^{1}H} NMR ($CDCl_3$, 36.23 MHz): δ = 3.0. ^{1}H NMR ($CDCl_3$, 300 MHz}: δ = 5.81 (d br, 2H, PH_2, $^1J_{PH}$ = 356 Hz), 4.67 (d, 2H, PH_2, $^1J_{PH}$ = 340 Hz), 4.50 (s br, 2H, Cp), 4.12 (s br, 2H, Cp), 2.23 (s br, 3H, CH_3CN), 2.2−1.8 (m br, 4H, CH_2), 0.26 (s, 9H, SiCH_3). Elemental analysis calcd for $C_{12}H_{24}NSiP_2BF_4Fe$: C, 34.72; H, 5.84; N, 3.37. Found: C, 34.3; H, 5.5; N, 2.9. IR (KBr): 2334m (ν_{PH}), 2269m (ν_{CN}).

(Acetonitrile){η^5-1,3-bis(trimethylsilyl)cyclopentadienyl}(1,2-diphosphinoethane)iron(II) hexafluorophosphate, 1c. This was prepared as for **1b** using [{η^5-(Me_3Si)$_2$Cp}$Fe(CO)_2$(CH_3CN)]PF_6 (1.00 g, 1.97 mmol) and 1,2-diphosphinoethane (0.2 mL, 2.1 mmol). After removing the solvent, the residue was triturated with diethyl ether to give **1c** as an orange solid. Yield = 0.81 g (70%). ^{31}P{^{1}H} NMR ($CDCl_3$, 36.23 MHz): δ = 1.5. ^{1}H NMR {(CD_3)$_2$CO, 300 MHz}: δ = 5.50 (d br, 2H, PH_2, $^1J_{PH}$ = 343 Hz), 5.32 (s, 1H, Cp), 5.05 (d br, 2H, PH_2, $^1J_{PH}$ = 341 Hz), 4.71 (s, 2H, Cp), 2.27 (s, 3H, CH_3CN), 2.20 (br, 2H, CH_2), 1.94 (br, 2H, CH_2), 0.28 (s, 18H, SiCH_3). Reproducible elemental analysis was not possible for this complex due to excessive decomposition by loss of acetonitrile prior to combustion. IR (KBr): 2330m (ν_{PH}), 2269m (ν_{CN}).

The BF_4^- salt was prepared as follows. A solution of η^5-(Me_3Si)$_2$CpFe$(CO)_2$I (0.50 g, 1.12 mmol) and $AgBF_4$ (0.22 g, 1.12 mmol) in acetonitrile (50 mL) was stirred in the absence of light for 24 h. After filtering, the solution was diluted 2-fold and the BF_4^- salt prepared and isolated in an analogous manner to that of the PF_6^- salt above. Yield = 0.39 g (72%). Spectroscopic data as above.

(Acetonitrile)(η^5-trimethylsilylcyclopentadienyl){phenyl-(2-phosphinoethyl)phosphine}iron(II) hexafluorophosphate, 1e. This compound was prepared as for **1b** but using phenyl(2-phosphinoethyl)-phosphine and [{η^5-(Me_3Si)Cp}$Fe(CO)_2$(CH_3CN)]PF_6. Removal of the solvent gave a red solid which was washed with diethyl ether to remove residual phosphine. Yield = 1.25 g (99%). ^{31}P{^{1}H} NMR (CD_3CN, 121.7 MHz): δ = 74.8 (d, 33 Hz), 63.8 (d, 36 Hz), 3.7 (d, 36 Hz), 2.7 (d, 33 Hz). ^{1}H NMR (CD_3CN, 300 MHz): δ = 7.8−7.2 (m, 5H, Ph), 6.5−3.6 (m, 7H, PH, PH_2, Cp), 2.6−1.6 (m, 7H, CH_2, CH_3CN), 0.24 and 0.20 (2 × s, 9H, SiCH_3). Elemental analysis calcd for $C_{18}H_{28}NSiP_3F_6Fe$: C, 39.34; H, 5.10; N, 2.55. Found: C, 40.4; H, 5.5; N, 2.1. Analytical data were variable, reflecting the instability of the compound with respect to loss of CH_3CN; the data listed here are the closest to required values obtained. IR (KBr): 2314m (ν_{PH}), 2262w (ν_{CN}).

(Acetonitrile){η^5-1,3-bis(trimethylsilyl)cyclopentadienyl}{phenyl-(2-phosphinoethyl)phosphine}iron(II) hexfluorophosphate, 1f. This compound was prepared as for **1c** but using phenyl(2-phosphinoethyl)-phosphine. Removal of the solvent gave a red solid which was washed with diethyl ether to remove residual phosphine. Yield = 1.09 g (89%). ^{31}P{^{1}H} NMR (CD_3CN, 121.7 MHz): δ = 72.5 (d, 36 Hz), 61.4 (d, 33 Hz), 3.8 (d, 33 Hz), 1.6 (d, 36 Hz). ^{1}H NMR (CD_3CN, 300 MHz): δ = 7.7−7.3 (m, 5H, Ph), 6.7−4.3 (m, 6H, PH, PH_2, Cp), 2.5−1.6 (m, 7H, CH_2, CH_3CN), 0.33, 0.16, 0.14 and 0.13 (4 × s, 18H, SiCH_3). Reproducible elemental analytical data were not obtained for this complex due to excessive decomposition by loss of acetonitrile prior to combustion. IR (KBr): 2336m (ν_{PH}), 2269w (ν_{CN}).

(Acetonitrile){η^5-(+)-neomenthylcyclopentadienyl}{phenyl(2-phosphinoethyl)phosphine}iron(II) tetrafluoroborate, 1g. A solution of [{η^5-(+)-neomenthylCp}$Fe(CO)_2$(CH_3CN)]PF_6 (1.00 g, 2.0 mmol) and phenyl(2-phosphinoethyl)phosphine (0.35 mL, 2.06 mmol) in acetonitrile (100 mL) was irradiated for 12 h with a Hanovia 125 W UV lamp. The solvent was subsequently removed in vacuo to give a red solid which was washed once with diethyl ether, dried in vacuo, and used for the subsequent reactions without further purification. Yield = 0.90 g (82%). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz): δ = 75.4 (d, 33 Hz), 74.7 (d, 33 Hz), 63.8 (d, 33 Hz), 63.6 (d, 33 Hz), 3.9 (d, 33 Hz), 3.1 (d, 33 Hz), 2.3 (d, 33 Hz), 2.2 (d, 33 Hz). Reproducible elemental analytical data were not obtained for this complex due to excessive decomposition by loss of acetonitrile prior to combustion. IR (KBr): 2327m (ν_{PH}), 2274w (ν_{CN}).

(η^5-Cyclopentadienyl)(1-vinyl-1,4,7-triphosphacyclononane)-iron(II) hexafluorophosphate, 4a. A solution of [(η^5-Cp)Fe(1,2-dpe)(CH_3CN)]PF_6, **1a** (1.00 g, 2.49 mmol), and trivinylphosphine (0.28 mL, 2.5 mmol) in 1,2-dichloroethane (50 mL) was heated at 80 °C for 2 h. After cooling, the volatiles were removed in vacuo to give **2a** as a yellow solid. The yellow residue was dissolved in chlorobenzene (100 mL) containing excess triethylamine (0.5 mL) and the resulting solution heated at 80 °C for 60 h. ^{31}P{^{1}H} NMR spectroscopy showed the successive formation of **3a** and **4a**, and the mixture was worked up

(28) Malische, W.; Gunzelmann, N.; Thirase, K.; Neumayer, M. *J. Organomet. Chem.* **1998**, *571*, 215.

upon complete conversion of **3a** to **4a**. The mixture was filtered hot, cooled, and concentrated to small volume. After standing at −20 °C overnight, the bright orange crystals of **4a** were isolated by filtration. Yield = 0.42 g (36%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 36.23 MHz): $\delta = 129.0$ (t, $J = 22$ Hz), 96.0 (d, $J = 22$ Hz). ^1H NMR (CD_2Cl_2, 400 MHz): $\delta = 6.51$ (m, 1H, PC*H*:CH_2), 6.00 (dd, 1H, PCH:C*H*$_2$), 6.19 (d br, 2H, 362 Hz, P*H*), 5.73 (t, 1H, PCH:C*H*$_2$), 4.38 (s, 5H, Cp), 2.2−1.5 (m, 12H, C*H*$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, DEPT, 100 MHz): $\delta = 135.3$ (d, 34 Hz, P*C*H:CH_2), 128.6 (d, 3 Hz, PCH:*C*H$_2$), 78.6 (s, Cp), 29.0 (dt, 30 and 7 Hz, CH_2), 24.7 (t, 22 Hz, CH_2), 23.9 (m, CH_2). IR (KBr): 2334m (ν_{PH}). MS (APCI) *m*/*z*: 327 (100) [(η^5-Cp)Fe(9-ane$P_3H_2C_2H_3$)]$^+$. Elemental analysis calcd for $C_{13}H_{22}F_6P_4Fe$: C, 33.07; H, 4.71. Found: C, 33.2; H, 4.6.

(η^5-Trimethylsilylcyclopentadienyl)(1-vinyl-1,4,7-triphosphacyclononane)iron(II) tetrafluoroborate, 4b. A solution of [(η^5-Me_3SiCp)Fe(1,2-dpe)(CH_3CN)]BF_4, **1b** (1.00 g, 2.41 mmol), and trivinylphosphine (0.28 mL, 2.50 mmol) in 1,2-dichloroethane (50 mL) was heated at 80 °C for 24 h. After cooling, the mixture was filtered, the volatiles were removed in vacuo, and the orange−yellow residue was extracted into ethanol (150 mL) and filtered. The ethanol was removed in vacuo and the residue chromatographed on neutral alumina (10 × 1 cm) using 0.3% MeOH in dichloromethane as eluent. The fractions containing **4b** were dried ($MgSO_4$) and the solvents removed in vacuo giving **4b** as a yellow solid. Yield = 0.50 g (43%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): $\delta = 131.0$ (t, $J = 21$ Hz), 98.4 (d, $J = 21$ Hz) ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 6.58$ (m, 1H, PC*H*:CH_2), 6.22 (d br, 2H, 354 Hz, P*H*), 6.04 (dd, 1H, PCH:C*H*$_2$), 5.80 (t, PCH:C*H*$_2$), 4.56 (br, 2H, Cp), 4.46 (br, 2H, Cp), 2.3−1.6 (m, 12H, C*H*$_2$), 0.12 (s, 9H, SiC*H*$_3$) $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT, 75.6 MHz): $\delta = 134.5$ (dd, 34 and 2.3 Hz, P*C*H:CH_2), 127.4 (d, 3.5 Hz, PCH:*C*H$_2$), 88.3 (s, CH), 78.0 (s, CH), 27.7 (dt, 29 and 6 Hz, CH_2), 23.7 (t, 23 Hz, CH_2), 23.2 (dd, 29 and 14 Hz, CH_2), 0.2 (s, Si*C*H$_3$) IR (KBr): 2340m (ν_{PH}). MS (APCI) *m*/*z*: 399 (100) [(η^5-Me_3SiCp)Fe(9aneP_3−$H_2C_2H_3$)]$^+$. Elemental analysis calcd for $C_{16}H_{30}BSiF_4P_3Fe$: C, 39.53; H, 6.23. Found: C, 39.4; H, 6.2.

{η^5-1,3-Bis(trimethylsilyl)cyclopentadienyl}(1-vinyl-1,4,7-triphosphacyclononane)iron(II) tetrafluoroborate, 4c. A solution of [{η^5-(Me_3Si)$_2$Cp}Fe(1,2-dpe)(CH_3CN)]BF_4, **1c** (1.00 g, 2.05 mmol), and trivinylphosphine (0.23 mL, 2.05 mmol) in 1,2-dichloroethane (50 mL) was heated at 80 °C for 48 h. After cooling, the mixture was filtered, and the volatiles were removed in vacuo to give an orange−brown solid. The solid was exhaustively extracted into toluene (4 × 100 mL) before concentrating the extracts in vacuo to crystallize **4c** as a bright yellow solid. Yield = 0.71 g (62%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 145.8 MHz): $\delta = 126.0$ (t, $J = 18$ Hz), 98.7 (d, $J = 18$ Hz). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 6.54$ (m, 1H, PC*H*:CH_2), 6.28 (d br, 2H, 354 Hz, P*H*), 6.11 (dd, 1H, PCH:C*H*$_2$), 5.80 (t, PCH:C*H*$_2$), 4.58 (d, 2H, Cp), 4.38 (d, 1H, Cp), 2.3−1.7 (m, 12H, C*H*$_2$), 0.16 (s, 18H, SiC*H*$_3$) $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT, 100 MHz): $\delta = 134.7$ (d, 32 Hz, P*C*H:CH_2), 127.4 (d, 5 Hz, PCH:*C*H$_2$), 96.1 (s, CH), 86.0 (s, CH), 80.5 (s, C), 28.5 (dt, 30 and 7 Hz, CH_2), 23.4 (t, 23 Hz, CH_2), 22.3 (dd, 27 and 14 Hz, CH_2), 0.2 (s, Si*C*H$_3$) IR (KBr): 2383m (ν_{PH}). MS (APCI) *m*/*z*: 471 (100) [{η^5-(Me_3Si)$_2$Cp}Fe(9-ane$P_3H_2C_2H_3$]$^+$. Elemental analysis calcd for $C_{19}H_{38}BSi_2F_4P_3Fe$: C, 40.87; H, 6.87. Found: C, 40.8; H, 6.8.

{η^5-Trimethylsilylcyclopentadienyl}(1-phenyl-4-vinyl-1,4,7-triphosphacyclononane)iron(II) hexafluorophosphate, 4e. A solution of [(η^5-Me_3SiCp)Fe(Phdpe)(CH_3CN)]PF_6, **1e** (1.00 g, 1.82 mmol), and trivinylphosphine (0.21 mL, 1.90 mmol) in chlorobenzene (40 mL) containing triethylamine (0.2 mL) was heated at 90 °C for 36 h. After cooling, the mixture was filtered, the volatiles were removed in vacuo and the orange-yellow residue was extracted into ethanol (2 × 75 mL) and filtered. The ethanol was removed in vacuo and the residue chromatographed on neutral alumina (10 × 1 cm) using 0.15% MeOH in dichloromethane as eluent. The fractions containing **4e** were dried ($MgSO_4$) and the solvents removed in vacuo giving **4e** as a yellow solid. Yield = 0.41 g (36%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): $\delta = 134.2$ (t, 21 Hz), 129.3 (t, 21 Hz), 96.0 (t, 21 Hz). ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.48$ (m, 5H, Ph), 6.67 (m, 1H, PC*H*:CH_2), 6.35 (d br, 2H, 357 Hz, P*H*), 6.07 (dd, 1H, PCH:C*H*$_2$), 5.87 (t, PCH:C*H*$_2$), 4.36 (br, 1H, Cp), 4.23 (br, 1H, Cp), 4.12 (br, 1H, Cp), 4.08 (br, 1H, Cp), 2.4−1.6 (m, 12H, C*H*$_2$), 0.11 (s, 9H, SiC*H*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT, 75.6 MHz): $\delta = 137.0$ (d, 39 Hz, *ipso*-Ph), 135.2 (d, 36 Hz, P*C*H:CH_2), 130.7 (s, Ph), 129.6 (d, 8 Hz, Ph), 129.5 (d, 11 Hz, PCH:*C*H$_2$), 128.0 (s, Ph), 89.7 (s, CH), 89.0 (s, CH), 79.5 (s, CH), 79.0 (CH), 29.0 (obs, 3 × CH_2), 27.7 (dd, 28 and 11 Hz, CH_2), 23.7 (dd, 31 and 17 Hz, CH_2), 0.3 (s, Si*C*H$_3$). IR (KBr): 2363m (ν_{PH}). MS (APCI) *m*/*z*: 475 (100) [(η^5-Me_3SiCp)Fe(9-aneP_3HPhC_2H_3)]$^+$. Elemental analysis calcd for $C_{22}H_{34}SiF_6P_4Fe$: C, 42.58; H, 5.48. Found: C, 42.3; H, 5.9.

{η^5-1,3-Bis(trimethylsilyl)cyclopentadienyl}(1-phenyl-4-vinyl-1,4,7-triphosphacyclononane)iron(II) hexafluorophosphate, 4f. A solution of [{η^5-(Me_3Si)$_2$Cp}Fe(Phdpe)(CH_3CN)]PF_6, **1f** (1.02 g, 1.64 mmol), and trivinylphosphine (0.19 mL, 1.69 mmol) in chlorobenzene (30 mL) containing Et_3N (0.2 mL) was heated at 105 °C for 24 h. After cooling, the mixture was filtered, and the volatiles were removed in vacuo to give an orange−brown solid. The solid was extracted into ethanol (2 × 100 mL), filtered, and the volatiles were removed in vacuo. The yellow solid was purified by passage through a short column (1 × 7 cm) of neutral alumina using 0.5% methanol in dichloromethane as eluent. Yield = 0.401 g (35%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): $\delta = 129.7$ (t, $J = 18$ Hz), 125.7 (t, 18 Hz), 100.1 (t, 18 Hz). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.47$ (m, 5H, Ph), 6.69 (m, 1H, PC*H*:CH_2), 6.41 (d br, 2H, 352 Hz, P*H*), 6.03 (dd, 1H, PCH:C*H*$_2$), 5.82 (t, 1H, PCH:C*H*$_2$), 4.54 (br, 1H, Cp), 4.24 (br, 1H, Cp), 4.09 (br, 1H, Cp), 2.4−1.7 (m, 12H, C*H*$_2$), 0.07 (s, 9H, SiC*H*$_3$), 0.05 (s, 9H, SiC*H*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT, 75.6 MHz): $\delta = 137.4$ (d, 36 Hz, *ipso*-Ph), 135.5 (d, 31 Hz, P*C*H:CH_2), 130.7 (s, Ph), 130.3 (d, 8 Hz, Ph), 129.3 (d, 7 Hz, PCH:*C*H$_2$), 128.0 (s, Ph), 98.6 (s, *C*H), 90.4 (s, CH), 86.0 (s, CH), 81.0 (s, C), 80.0 (s, C), 31.0 (m, CH_2), 29.9 (m, CH_2), 28.4 (m, CH_2), 26.9 (m, CH_2), 24.0 (m, CH_2), 22.2 (m, CH_2), 0.7 (s, Si*C*H$_3$), 0.5 (s, Si*C*H$_3$). IR (KBr): 2347m (ν_{PH}). MS (APCI) *m*/*z*: 547 (100) [{η^5-(Me_3Si)$_2$Cp}Fe(9-aneP_3HPhC_2H_3)]$^+$. Elemental analysis calcd for $C_{25}H_{42}Si_2F_6P_4Fe$: C, 43.35; H, 6.12. Found: C, 43.4; H, 6.5.

{η^5-(+)-Neomenthylcyclopentadienyl}(1-phenyl-4-vinyl-1,4,7-triphosphacyclononane)iron(II) hexafluorophosphate, 4g. A solution of [{η^5-(+)-neomenthylCp)Fe(Phdpe)(CH_3CN)]PF_6, **1g** (0.32 g, 0.51 mmol), and trivinylphosphine (0.15 mL of a 50% solution in toluene, 0.67 mmol) in chlorobenzene (40 mL) containing triethylamine (0.1 mL) was heated at 120 °C for 72 h. After cooling, the mixture was filtered, the volatiles were removed in vacuo, and the orange−yellow residue was extracted into ethanol (2 × 75 mL) and filtered. The ethanol was removed in vacuo and the residue chromatographed on neutral alumina (20 × 1 cm) using gradient elution from 0.5% to 5% MeOH in dichloromethane. The fractions containing **4g** were dried ($MgSO_4$) and the solvents removed in vacuo giving **4g** as a yellow solid. Yield = 0.06 g (17%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): $\delta = 134.6$ (t, 18 Hz), 133.9 (t, 18 Hz), 129.9 (t, 18 Hz), 128.6 (t, 18 Hz), 100.1 (t, 18 Hz), 99.2 (t, 18 Hz). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.46$ (m, 5H, Ph), 6.65 (m, 1H, PC*H*:CH_2), 6.23 (d br, 1H, 357 Hz, P*H*), 6.04 (dd, 0.5H, PCH:C*H*$_2$), 5.95 (dd, 0.5H, PCH:C*H*$_2$), 5.80 (t, 0.5H, PCH:C*H*$_2$), 5.79 (t, 0.5H, PCH:C*H*$_2$), 4.36 (br, 0.5H, Cp), 4.16 (br, 0.5H, Cp), 4.14 (br, 0.5H, Cp), 4.01 (br, 0.5H, Cp), 3.98 (br, 0.5H, Cp), 3.92 (br, 0.5H, Cp), 3.88 (br, 0.5H, Cp), 3.83 (br, 0.5H, Cp), 2.6−0.5 (m, 31H, C*H*, C*H*$_2$, C*H*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT, 75.6 MHz): $\delta = 137.4$ (d, 31 Hz, *ipso*-Ph), 136.9 (d, 31 Hz, *ipso*-Ph), 135.5 (d, 33 Hz, P*C*H:CH_2), 134.9 (d, 31 Hz, P*C*H:CH_2), 130.6 (s, Ph), 129.6 (obs, Ph and PCH:*C*H$_2$), 127.7 (s br, Ph), 98.9, (s, CH), 98.6 (s, CH), 86.7 (s, CH), 85.9 (s, CH), 82.5 (s, CH), 81.4 (s, CH), 81.0.5 (s, CH), 80.9 (s, CH), 69.4 (s, C), 48.4 (s), 43.1 (d, 14 Hz), 35.4 (s), 34.7 (s), 34.6 (s), 28.5 (obs), 23.5 (s), 23.1 (s), 22.0 (d, 11 Hz), 20.5 (s). IR (KBr): 2363m (ν_{PH}). MS (APCI) *m*/*z*: 541 (40) [{η^5-(+)-neomenthylCp}Fe(9-aneP_3-

$HPhC_2H_3)]^+$. Elemental analysis calcd for $C_{29}H_{44}F_6P_4Fe$: C, 50.74; H, 6.47. Found: C, 50.5; H, 6.8.

{η^5-1,3-Bis(trimethylsilyl)cyclopentadienyl}(1-phenyl-1,4,7-triphosphacyclononane)iron(II) hexafluorophosphate, 4h. A solution of [{η^5-$(Me_3Si)_2Cp$}Fe(dpe)(CH_3CN)]PF_6, **1c** (1.00 g, 1.97 mmol), divinylphenylphosphine (0.32 mL, 1.97 mmol) and triethylamine (1 mL) in 1,2-dichloroethane (50 mL) was heated at 80 °C for 60 h. After cooling, the mixture was filtered, and the volatiles were removed in vacuo to give a dark brown solid. The solid was extracted into ethanol (100 mL), filtered, and the solvent removed in vacuo. The residue was chromatographed on neutral alumina (15 × 1 cm), the yellow complex being eluted with dichloromethane. The solution was dried ($MgSO_4$) and the solvent removed in vacuo to give **4h**. Yield = 0.40 g (29%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ = 129.8 (t, J = 18 Hz), 97.0 (d, J = 18 Hz). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.5−7.4 (m, Ph), 6.36 (d br, 2H, 360 Hz, P*H*), 4.43 (s br, 2H, CH), 4.12 (s br, 1H, CH), 2.35−1.70 (m, 12H, CH_2), 0.07 (s, 18H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT, 75.6 MHz): δ = 136.8 (d, 36 Hz, C), 130.7 (s, CH), 130.0 (d, 9 Hz, CH), 129.3 (d, 9 Hz, CH), 95.1 (s, CH), 87.4 (s, CH), 82.3 (s, C), 30.1 (dt, 29 and 4.5 Hz, CH_2), 24.1 (t, 23 Hz, CH_2), 23.2 (dd, 29 and 14 Hz, CH_2), 0.42 (s, Si*C*H_3). IR (KBr): 2383m (ν_{PH}). MS (APCI) *m*/*z*: 521 (100) [{η^5-$(Me_3Si)_2Cp$}Fe(9-ane$P_3H_2Ph]^+$. Elemental analysis calcd for $C_{23}H_{39}Si_2F_6P_4Fe$: C, 41.50; H, 5.92. Found: C, 41.0; H, 5.6.

(η^5-1,2,3,4,5-Pentamethylcyclopentadienyl)(1-phenyl-1,4,7-triphosphacyclononane)iron(II) hexafluorophosphate, 4i. A solution of [(η^5-Cp*)Fe(1,2-dpe)(CH_3CN)]PF_6, **1d** (1.00 g, 2.12 mmol), divinylphenylphosphine (0.36 mL, 2.20 mmol) and triethylamine (1 mL) in 1,2-dichloroethane (50 mL) was heated at 80 °C for 60 h. After cooling, the mixture was filtered, and the volatiles were removed in vacuo to give a dark brown solid. The solid was extracted into ethanol (100 mL), filtered, and the solvent was removed in vacuo. The residue was chromatographed on neutral alumina (15 × 1 cm), the yellow complex being eluted with dichloromethane. The solution was dried ($MgSO_4$) and the solvent removed in vacuo to give **4i**. Yield = 0.20 g (16%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ = 119.7 (t, 4 Hz), 106.0 (d, 4 Hz). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.42 (m, 3H, Ph), 7.04 (m br, 2H, Ph), 5.50 (d br, 2H, 344 Hz, P*H*), 2.1−1.1 (m, 12H, CH_2), 1.38 (s, 15H, CH_3). IR (KBr): 2322m (ν_{PH}). MS (APCI) *m*/*z*: 447 (100) [(η^5-Me_5Cp)Fe(9-ane$P_3H_2Ph)]^+$. Elemental analysis calcd for $C_{22}H_{34}F_6P_4$-Fe: C, 44.61; H, 5.80. Found: C, 44.4; H, 5.8.

(η^5-1,2,3,4,5-Pentamethylcyclopentadienyl)(1-benzyl-1,4,7-triphosphacyclononane)iron(II) hexafluorophosphate, 4j. A solution of [(η^5-Cp*)Fe(1,2-dpe)(CH_3CN)]PF_6, **1d** (1.00 g, 2.12 mmol), divinylbenzylphosphine (0.39 mL, 2.20 mmol), and triethylamine (1 mL) in 1,2-dichloroethane (50 mL) was heated at 80 °C for 60 h. After cooling, the mixture was worked up as for **4i**. Yield = 0.28 g (22%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ = 118.9 (t, 4 Hz), 106.3 (d, 4 Hz). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.22 (t, 7.8 Hz, 2H, Ph), 7.17 (t obs, 1H, Ph), 7.04 (d, 8.0 Hz, 2H, Ph), 5.57 (d br, 2H, 344 Hz, P*H*), 3.29 (d, 10.9 Hz, 2H, CH_2), 2.1−1.0 (m, 12H, CH_2), 1.77 (s, 15H, CH_3). IR (KBr): 2315m (ν_{PH}). MS (APCI) *m*/*z*: 461 (100) [(η^5-Me_5Cp)Fe(9-ane$P_3H_2Bz)]^+$. Elemental analysis calcd for $C_{23}H_{36}F_6P_4Fe$: C, 45.56; H, 6.00. Found: C, 45.7; H, 6.1.

(η^5-Trimethylsilylcyclopentadienyl)(1-ethyl-1,4,7-triphosphacyclononane)iron(II) tetrafluoroborate, 5b. A solution of [(η^5-Me_3-SiCp)Fe(9-ane$P_3H_2C_2H_3$)]BF_4, **4b** (1.00 g, 2.41 mmol), in ethanol (100 mL) containing 0.01 g of 10% palladium on carbon and several drops of water was hydrogenated at room temperature and atmospheric pressure for 2 days. After filtering off the catalyst, the volatiles were removed in vacuo and the orange−yellow residue was crystallized from ethanol (10 mL) at 4 °C. Yield = 0.85 g (85%). $^{31}P\{^1H\}$ NMR ($\{CD_3\}_2$-CO, 121.7 MHz): δ = 140.2 (t, 21 Hz), 97.5 (d, 21 Hz). ^1H NMR ($\{CD_3\}_2CO$, 300 MHz): δ = 6.31 (d br, 2H, 356 Hz, P*H*), 4.78 (s br, 2H, Cp), 4.74 (s br, 2H, Cp), 2.28 (m, 2H, CH_2CH_3), 2.2−1.6 (m br, 12H, CH_2), 1.28 (dt, 15 and 8 Hz, CH_2CH_3), 0.18 (s, 9H, SiCH_3). $^{13}C\{^1H\}$ NMR ($\{CD_3\}_2CO$, DEPT, 75.6 MHz): δ = 88.1 (s, CH), 78.5 (s, CH), 26.7 (dt, 27 and 6 Hz, CH_2), 24.3 (t, 23 Hz, CH_2), 23.9 (dd, 26 and 10 Hz, CH_2), 9.2 (d, 5 Hz, CH_3), 0.2 (s, SiCH_3). IR (KBr): 2357m (ν_{PH}). MS (APCI) *m*/*z*: 399 (100) [(η^5-Me_3SiCp)Fe(9-aneP_3H_2-Et)]$^+$. Elemental analysis calcd for $C_{16}H_{32}BSiF_4P_3Fe$: C, 39.37; H, 6.62. Found: C, 39.5; H, 6.6.

{η^5-1,3-Bis(trimethylsilyl)cyclopentadienyl}(1-ethyl-1,4,7-triphosphacyclononane)iron(II) hexafluorophosphate, 5c. This was prepared in an analogous fashion to the monosilylcyclopentadienyl derivative **5b** using [{η^5-$(Me_3Si)_2Cp$)Fe(9-ane$P_3H_2C_2H_3$)]PF_6, **4c**, as precursor. Yield = 0.91 g (91%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.7 MHz): δ = 136.5 (t, 21 Hz), 97.1 (d, 21 Hz). ^1H NMR (CD_2Cl_2, 400 MHz): δ = 6.24 (d br, 2H, 357 Hz, P*H*), 4.56 (s br, 2H, Cp), 4.49 (s br, 1H, Cp), 2.09 (m, 2H, CH_2CH_3), 2.2−1.5 (m, 12H, CH_2), 1.26 (dt, 3H, 15 and 8 Hz, CH_2CH_3), 0.17 (s, 18H, SiCH_3). $^{13}C\{^1H\}$ NMR (CD_2-Cl_2, DEPT, 100 MHz): δ = 95.1 (s, CH), 86.3 (s, CH), 81.8 (s, C), 27.5 (dt, 28 and 6 Hz, CH_2), 25.7 (d, 22 Hz, CH_2), 24.2 (t, 23 Hz, CH_2), 23.7 (dd, 27 and 13 Hz, CH_2), 9.6 (d, 6 Hz, CH_3), 0.5 (s, SiCH_3). IR (KBr): 2344m (ν_{PH}). MS (APCI) *m*/*z*: 471 (100) [{η^5-$(Me_3Si)_2Cp$}-Fe(9-ane$P_3H_2Et]^+$. Elemental analysis calcd for $C_{19}H_{40}Si_2F_6P_4Fe$: C, 36.89; H, 6.53. Found: C, 37.3; H, 6.6.

(η^5-Trimethylsilylcyclopentadienyl)(1-ethyl-4-phenyl-1,4,7-triphosphacyclononane)iron(II) Hexafluorophosphate, 5e. A solution of [(η^5-Me_3SiCp)Fe(9-ane$P_3HPhC_2H_3$)]PF_6, **4e** (0.40 g, 0.65 mmol), in a mixture of ethanol (150 mL) and methanol (50 mL) containing 0.02 g of 10% palladium on carbon was hydrogenated at room temperature and atmospheric pressure for 10 days. After filtering off the catalyst, the volatiles were removed in vacuo, and the orange−yellow residue was recrystallized from ethanol (10 mL) at 4 °C. Yield = 0.25 g (63%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ = 139.4 (t, 21 Hz), 134.1 (t, 21 Hz), 96.4 (t, 21 Hz). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.41 (m, 5H, Ph), 6.23 (d br, 1H, 352 Hz, P*H*), 4.33 (s br, 1H, Cp), 4.26 (s br, 1H, Cp), 4.00 (s br, 1H, Cp), 3.69 (s br, 1H, Cp), 2.13 (m, 2H, CH_2-CH_3), 2.1−1.2 (m br, 12H, CH_2), 1.14 (m, CH_2CH_3), 0.08 (s, 9H, SiCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT, 75.6 MHz): δ = 137.3 (d, 36 Hz, *ipso*-Ph), 130.5 (s, Ph), 129.8 (d, 8 Hz, Ph), 129.4 (d, 8 Hz, Ph), 89.3 (s, CH), 87.1 (s, CH), 79.7 (s, CH), 78.5 (s, CH), 30.3 (dd, 28 and 14 Hz, CH_2), 29.3 (dd, 28 and 14 Hz), 27.6 (m, 2 × CH_2), 25.2 (d, 22 Hz, CH_2), 24.2 (dd, 31 and 14 Hz, CH_2), 23.6 (dd, 31 and 17 Hz, CH_2), 9.7 (d, 5 Hz, CH_3), 0.5 (s, SiCH_3). IR (KBr): 2357m (ν_{PH}). MS (APCI) *m*/*z*: 477 (100) [(η^5-Me_3SiCp)Fe(9-ane$P_3HPhEt)]^+$. Elemental analysis calcd for $C_{22}H_{36}SiF_6P_4Fe$: C, 42.45; H, 5.84. Found: C, 42.1; H, 6.0.

{η^5-1,3-Bis(trimethylsilyl)cyclopentadienyl}(1-ethyl-4-phenyl-1,4,7-triphosphacyclononane)iron(II) hexafluorophosphate, 5f. A solution of [{η^5-$(Me_3Si)_2Cp$}Fe(9-ane$P_3HPhC_2H_3$)]PF_6, **4f** (0.60 g, 0.87 mmol), in ethanol (150 mL) containing 0.20 g of 10% palladium on carbon was hydrogenated at room temperature and atmospheric pressure for 5 days. After filtering off the catalyst, the volatiles were removed in vacuo, and the orange-yellow residue was recrystallized from ethanol at 4 °C. Yield = 0.45 g (75%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ = 136.2 (t, 24 Hz), 129.4 (t, 24 Hz), 99.6 (t, 21 Hz). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.46 (m, 5H, Ph), 6.43 (d br, 1H, 356 Hz, P*H*), 4.61 (s br, 1H, Cp), 4.26 (s br, 1H, Cp), 4.13 (s br, 1H, Cp), 2.4−1.6 (m, 14H, CH_2), 1.29 (m, CH_2CH_3), 0.07 (s, 9H, SiCH_3), 0.05 (s, 9H, SiCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT, 75.6 MHz): δ = 137.7 (d, 33 Hz, *ipso*-Ph), 130.7 (s, Ph), 130.2 (d, 8 Hz, Ph), 129.3 (d, 8 Hz, Ph), 97.6 (s, CH), 89.5 (s, CH), 85.8 (s, CH), 81.0 (s, C), 79.8 (s, C), 31.3 (dd, 28 and 14 Hz, CH_2), 27.8 (dd, 28 and 14 Hz), 26.9 (dd, 28 and 14 Hz, CH_2), 26.5 (dd obs, CH_2), 25.9 (d, 22 Hz, CH_2), 23.6 (dd, 31 and 14 Hz, CH_2), 23.1 (dd, 31 and 14 Hz, CH_2), 9.7 (d, 5 Hz, CH_3), 0.7 (s, SiCH_3), 0.6 (s, SiCH_3). IR (KBr): 2348m (ν_{PH}). MS (APCI) *m*/*z*: 549 (100) [{η^5-$(Me_3Si)_2Cp$}Fe(9-ane$P_3HPhEt)]^+$. Elemental analysis calcd for $C_{25}H_{44}Si_2F_6P_4Fe$: C, 43.23; H, 6.40. Found: C, 43.5; H, 6.7.

Preparation of [(η^5-Cp)Fe(9-aneP_3Et_2,C_2H_3)]BF_4 (6a), [(η^5-Me_3SiCp)Fe(9-aneP_3Et_2,C_2H_3)]BF_4 (6b), and [(η^5-Cp)Fe(9-aneP_3Et_2,-Ph)]PF_6 (6k). These complexes were prepared by the same procedure.

To a solution of [(η^5-Cp)Fe(9-ane$P_3H_2C_2H_3$)]BF_4, **4a**, [(η^5-Me_3SiCp)-Fe(9-ane$P_3H_2C_2H_3$)]BF_4, **4b**, or [(η^5-Cp)Fe(9-ane$P_3H_2C_2H_3$)]PF_6, **4h** (300 mg), in THF (25 mL, 100 mL for **4a**) at −78 °C was added potassium *tert*-butoxide (2.2 molar equiv), and the mixture was stirred for 5 min at this temperature before warming to −20° for 15 min. The mixture was cooled to −78 °C and excess ethyl bromide (0.5 mL) added thereto. The mixture was stirred at −78 °C for 30 min then at ambient temperature overnight. After filtering, the solvent was removed in vacuo, and the orange−yellow solids were partitioned between CH_2Cl_2 (20 mL) and water (20 mL). The organic phase was separated, dried over $MgSO_4$, and the solvent removed in vacuo to yield yellow solids that were recrystallized from ethanol.

6a: Yield = 0.29 g (87%). $^{31}P\{^1H\}$ NMR {$(CD_3)_2CO$, 121.7 MHz}: δ = 140.3 (d, 25 Hz), 131.1 (t, 25 Hz) ppm. ^1H NMR {$(CD_3)_2$-CO, 400 MHz}: δ = 6.63 (m, 1H), 5.84 (dd, 1H), 5.67 (t, 1H), 4.20 (q, 5H), 2.07 (m, 4H), 1.56 (m, 12H), 1.02 (m, 6H). MS (APCI) *m*/*z*: 383 (100) [(η^5-Cp)Fe(9-ane$P_3Et_2C_2H_3$)]$^+$. Elemental analysis calcd for $C_{17}H_{30}BF_4P_3Fe$: C, 43.44; H, 6.45. Found: C, 43.4; H, 6.5.

6b: Yield = 0.18 g (53%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ = 139.9 (d, 24 Hz), 128.5 (t, 24 Hz). ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.59 (m, 1H), 6.04 (dd, 1H), 5.80 (t, 1H), 4.42 (s br, 2H), 4.37 (s br, 2H), 2.12 (m, 4H), 1.76 (m, 12H), 1.27 (m, 6H), 0.15 (s, 9H). MS (APCI) *m*/*z*: 455 (100) [(η^5-Me_3SiCp)Fe(9-ane$P_3Et_2C_2H_3$)]$^+$. Elemental analysis calcd for $C_{20}H_{38}SiP_3BF_4Fe$: C, 44.30; H, 7.08. Found: C, 44.4; H, 7.1.

6k: Yield = 0.11 g (96%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ = 139.6 (d, 25 Hz), 135.4 (t, 25 Hz). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.46 (m, 5H), 4.12 (s, 5H), 2.21 (m, 4H), 1.77 (m, 12H), 1.27 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT, 75.6 MHz): δ = 137.9 (d, 38 Hz, C), 130.4 (d, 2 Hz, CH), 129.4 (d, 8 Hz, CH), 129.3 (d, 8 Hz, CH), 77.3 (s, CH), 28.9 (dt, 28 and 6 Hz, CH_2), 26.9 (m 2 × CH_2), 24.7 (m, CH_2), 9.2 (s, CH_3). MS (APCI) *m*/*z*: 433 (100) [(η^5-Cp)Fe(9-aneP_3-Et_2Ph)]$^+$. Elemental analysis calcd for $C_{21}H_{32}P_4F_6Fe$: C, 43.62; H, 5.59. Found: C, 43.2; H, 5.3.

(η^5-Cyclopentadienyl)(1-phenyl-4-pentyl-7-ethyl-1,4,7-triphosphacyclononane)iron(II) hexafluorophosphate, 7l. To a solution of [(η^5-Me_3SiCp)Fe(9-aneP_3HPhEt)]PF_6, **5e** (0.20 g, 0.32 mmol), in THF (20 mL) at −78 °C was added potassium *tert*-butoxide (0.20 g, 1.77 mmol), and the mixture was stirred for 5 min at this temperature before warming to −20° for 15 min. The mixture was cooled to −78 °C and excess 1-bromopentane (0.1 mL) added thereto. The mixture was stirred at −78 °C for 30 min then at ambient temperature overnight. After filtering, the solvent was removed in vacuo, and the orange−yellow solids were partitioned between CH_2Cl_2 (20 mL) and water (20 mL). The organic phase was isolated, dried over $MgSO_4$, and the solvent removed to yield a yellow solid that was purified by passage through a column (10 × 1.5 cm) of basic alumina using dichloromethane as eluent followed by evaporation of solvent in vacuo. Yield = 0.12 g (53%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ = 139.5 (t, 25 Hz), 136.7 (t, 25 Hz), 135.3 (t, 25 Hz). ^1H NMR (CDCl, 300 MHz): δ = 7.45 (m, 5H), 4.10 (d, 1.3 Hz, 5H), 2.2−1.2 (m, 25H), 0.92 (t, 6.6 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz): δ = 137.9 (d, 36 Hz, *ipso*-Ph), 130.4 (s, Ph), 129.4 (d, 6 Hz, Ph), 129.3 (d, 6 Hz, Ph), 68.1 (s, Cp), 34.9 (s, CH_2), 33.5 (d, 11 Hz, CH_2), 31.7 (d, 22 Hz, CH_2), 28.8 (dd, 28 and 14 Hz, CH_2), 27.1 (m obs), 25.7 (s, CH_2), 24.8 (d, 6 Hz, CH_2), 24.6 (d, 14 Hz, CH_2), 22.3 (s, CH_2), 19.0 (s, CH_2), 14.0 (s, CH_3), 9.1 (d, 5 Hz, CH_3). MS (APCI) *m*/*z*: 475 (100) [(η^5-Cp)Fe(9-aneP_3-$EtPhC_5H_{11}$)]$^+$. Elemental analysis calcd for $C_{24}H_{38}F_6P_4Fe$: C, 46.46; H, 6.19. Found: C, 46.7; H, 6.2.

(η^5-cyclopentadienyl)(1,4-dipentyl-7-ethyl-1,4,7-triphosphacyclononane)iron(II)] bromide/hexafluorophosphate, 7m. To a solution of the hexafluorophosphate salt of **5b** (0.70 g, 1.28 mmol) in THF (40 mL) at −78 °C was added potassium *tert*-butoxide (0.4 g, 3.54 mmol), and the mixture was stirred for 5 min at this temperature before warming to 0 °C for 15 min. The mixture was cooled to −78 °C and excess 1-bromopentane (1 mL) added thereto. The mixture was stirred at −78 °C for 30 min then at room temperature overnight. After filtering, the solvent was removed in vacuo, and the orange−yellow solids were partitioned between CH_2Cl_2 (20 mL) and water (20 mL). The organic phase was isolated, dried over $MgSO_4$, and the solvent removed to yield a yellow solid that was purified by passage through a column (10 × 1.5 cm) of neutral alumina using dichloromethane as eluent. Yield = 0.54 g (62%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ = 139.5 (t, 27 Hz), 136.7 (d, 27 Hz). ^1H NMR (CDCl, 300 MHz): δ = 4.34 (d, 1.3 Hz, 5H), 2.2−1.2 (m, 33H), 0.92 (t, 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz): δ = 76.4 (s, Cp), 33.5 (s br, CH_2), 31.9 (m, CH_2), 27.5 (m, CH_2), 24.8 (d obs, CH_2), 24.7 (s, CH_2), 22.3 (s, CH_2), 14.0 (s, CH_3), 9.1 (s, CH_3). MS (APCI) *m*/*z*: 469 (100) [(η^5-Cp)Fe{9-aneP_3-$Et(C_5H_{11})_2$}]$^+$. Elemental analysis calcd for $C_{23}H_{44}F_{1.8}P_{3.3}Br_{0.7}Fe$: C, 48.56; H, 7.81. Found: C, 49.0; H, 8.0.

Preparation of [(η^5-Cp)Fe(9-aneP_3Et_3)]BF_4 (7a) and [(η^5-Me_3SiCp)-Fe(9-aneP_3Et_3)]BF_4 (7b). These complexes were prepared by the same procedure. Hydrogen was bubbled through a solution of [(η^5-Cp)Fe(9-ane$P_3Et_2C_2H_3$)]BF_4, **6a**, or [(η^5-Me_3SiCp)Fe(9-ane$P_3Et_2C_2H_3$)]BF_4, **6b** (300 mg), in ethanol (75 mL) containing 10% palladium on carbon (20 mg) for 24 h. After filtering, the solvent was removed in vacuo and the residue crystallized from ethanol.

7a: Yield = 0.29 g (97%). $^{31}P\{^1H\}$ NMR {$(CD_3)_2CO$, 121.7 MHz}: δ = 140.1 (s). ^1H NMR {$(CD_3)_2CO$, 300 MHz}: δ = 4.55 (q, 5H), 2.30 (m, 6H), 1.86 (m, 12H), 1.26 (m, 9H). $^{13}C\{^1H\}$ NMR {-$(CD_3)_2CO$, 75.6 MHz}: δ = 77.4 (s, Cp), 27.6 (dd, 11 and 5 Hz, CH_2), 27.4 (dd, 13 and 5 Hz, CH_2), 24.9 (dd, 16 and 10 Hz, CH_2), 9.2 (s, CH_3). MS (APCI) *m*/*z*: 385 (100) [(η^5-Cp)Fe(9-aneP_3Et_3)]$^+$. Elemental analysis calcd for $C_{17}H_{32}BF_4P_3Fe$: C, 43.25; H, 6.85. Found: C, 43.1; H, 6.8.

7b: Yield = 0.29 g (96%). $^{31}P\{^1H\}$ NMR {$(CD_3)_2CO$, 121.7 MHz}: δ = 139.0 (s). ^1H NMR {$(CD_3)_2CO$, 300 MHz}: δ = 4.65 (q, 4H), 2.28 (m, 6H), 1.86 (m, 12H), 1.28 (m, 9H), 0.21 (s, 9H). $^{13}C\{^1H\}$ NMR {$(CD_3)_2CO$, 75.6 MHz}: δ = 89.8 (s, CH), 75.4 (s, C), 26.5 (m, CH_2), 24.8 (dd, 16 and 8 Hz, CH_2), 8.6 (d, 5 Hz, CH_3), 0.26 (s, SiCH_3). MS (APCI) *m*/*z*: 457 (100) [(η^5-Me_3SiCp)Fe(9-aneP_3Et_3)]$^+$. Elemental analysis calcd for $C_{20}H_{40}SiP_3BF_4Fe$: C, 44.13; H, 7.42. Found: C, 44.1; H, 7.5.

P,P′,P″-Trioxo-1,4,7-triethyl-1,4,7-triphosphacyclononane, 8. To a stirred solution of [(η^5-Me_3SiCp)Fe(9-aneP_3Et_3)]BF_4, **7b** (0.08 g, 0.15 mmol), in dichloromethane (10 mL) in air was added bromine (0.5 mL) whereupon the solution got hot. The dark brown solution was layered with water (10 mL) and the mixture stirred for 2 days. The dichloromethane was removed on a rotary evaporator and the dark aqueous suspension filtered through Celite. After taking the solution to a pH of approximately 11 with aq. NaOH, the suspension was filtered to remove iron oxides and the filtrate stirred with Dowex 50 × 8 resin in the H^+ form for 2 h. The resin was removed by filtration and the aqueous solution taken to dryness. The residue was dried by azeotroping with EtOH (2 × 10 mL) before being triturated with dry acetone to give a hygroscopic off-white solid. Yield = 0.04 g (85%). $^{31}P\{^1H\}$ NMR (D_2O, 121.7 MHz): δ_P 65.2. ^1H NMR (D_2O, 300 MHz): δ_H 2.24 (m, 12H), 1.97 (m, 6H), 1.19 (m, 9H). MS (ES) *m*/*z*: 335 (40) [9-ane$P_3(O)_3Et_3$ + Na]$^+$. Elemental analysis calcd for $C_{12}H_{27}P_3O_3$: C, 46.15; H, 8.73. Found: C, 45.8; H, 8.8. IR (KBr): 1145 cm^{-1} (υ_{PO}).

X-ray Crystallography. All crystallographic measurements were made on an Enraf Nonius CAD4 diffractometer. The structures were solved via direct methods[29] and refined on F_o^2 by full matrix least squares[22] using all unique data corrected for Lorentz and polarization factors.[30] With the exception of C30 and C39 (**7b**), all non-hydrogen atoms were anisotropic. The hydrogen atoms were inserted in idealized positions with U_{iso} set at 1.2 or 1.5 times the U_{eq} of the parent atom.

(29) Sheldrick, G. M. *SHELX97 [Includes SHELXS97, SHELXL97, CIFTAB]*—Programs for Crystal Structure Analysis (Release 97−2); Tammanstrasse 4, D-3400; Institüt für Anorganische Chemie der Universität: Göttingen, Germany, 1998.

(30) Harms, K.; Wocadlo, S. *XCAD4*−*CAD4 Data Reduction*; University of Marburg: Marburg, Germany, 1995.

The weighting scheme used was $w = 1/[\sigma^2(F_o)^2 + (0.0999P)^2]$, where $P = [\max(F_o)^2 + 2(F_c)^2]/3$; this gave satisfactory agreement analyses. Empirical absorption corrections were carried out by the XABS[31] and DIFABS[32] methods.

Crystal data for complex **4c**, $C_{38}H_{76}B_2F_8Fe_2P_6Si_4$, $M = 1116.49$, monoclinic, space group $P2_1/c$, $a = 20.252(4)$, $b = 8.595(2)$, $c = 31.418(6)$ Å, $\beta = 101.56(3)°$, $V = 5357.9(19)$ Å^3, $Z = 4$, $D = 1.384$ g cm^{-3}, μ(Mo Kα) = 0.865 mm^{-1}, $F(000) = 2336$, $T = 293(2)$ K, yellow blocks, crystal size 0.15 × 0.15 × 0.15 mm; 8058 independent measured reflections, F^2 refinement, $R_1 = 0.1047$ $wR_2 = 0.2262$, 5905 independent observed absorption corrected reflections [$|F_o| > 2\sigma(|F_o|)$, $2\theta_{maz} = 48°$], 570 parameters.

Crystal data for complex **7b**, $C_{20}H_{40}F_6FeP_4Si$, $M = 602.34$, monoclinic, space group $P2_1$, $a = 8.226(3)$, $b = 21.665(5)$, $c = 15.256(5)$ Å, $\beta = 99.48(8)°$, $V = 2681.7(13)$ Å^3, $Z = 4$, $D = 1.492$ g cm^{-3}, μ(Mo Kα) = 0.896 mm^{-1}, $F(000) = 1256$, $T = 293(2)$ K, yellow plates, crystal size 0.2 × 0.2 × 0.15 mm; 4964 independent measured reflections, F^2 refinement, $R_1 = 0.0868$ $wR_2 = 0.2156$, 2820 independent observed absorption corrected reflections [$|F_o| > 2\sigma(|F_o|)$, $2\theta_{maz} = 50°$], 582 parameters, 133 restraints.

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Supporting Information Available: Crystallographic data (CIF) are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) *DIFABS*; Walker, N.; Stuart, D. *Acta Crystallogr., Sect A* **1983**, *39*, 158−166.