Synthesis and Characterization of Iron(II) Complexes of 10- and 11-Membered Triphosphamacrocycles

Andrew R. Battle, Peter G. Edwards,* Robert Haigh, David E. Hibbs, Dongmei Li, Sam M. Liddiard,† and Paul D. Newman

School of Chemistry, Cardiff University, Park Place, Cardiff, CF10 3AT, U.K.

Received September 1, 2006

The complex $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(10aneP_3\text{-}H_2,C_2H_3)]^+$, where $Me_3SiC_5H_4$ is trimethylsilylcyclopentadienyl and 10-aneP_3-H_2,C_2H_3 is 1-vinyl-1,4,8-triphosphacyclodecane, has been prepared by the base-catalyzed template cyclization of 1,3-bis(phosphino)propane (1,3-bpp) and trivinylphosphine (tvp) at the metal center. A related radical-initiated iron-template reaction between 1,2-bis(phosphino)ethane (1,2-bpe) and triallylphosphine (tap) gave $[(\eta^5\text{-}C_5Me_5)Fe(Me\text{-}10aneP_3\text{-}H_2,C_3H_5)]^+$, where C_5Me_5 is 1,2,3,4,5-pentamethylcyclopentadienyl and Me-10aneP_3-H_2,C_3H_5 is the unsymmetric 10-aneP_3 derivative 1-allyl-3-methyl-1,4,7-triphosphacyclodecane. This macrocycle is the result of two intramolecular hydrophosphination reactions, one that generates a five-membered (chelate) ring with an exo-methyl group and one a six-membered chelate. The $[(\eta^5\text{-}Cp^R)Fe]^+$ fragment also controls the cyclization of 1,2-bis(diallylphosphino)-ethane with phenylphosphine to give a ternary complex containing the symmetrical 11-membered macrocycle 1-phenyl-4,8-diallyl-1,4,8-triphosphacycloundecane, in addition to the unsymmetrical 10-aneP_3 derivative.

Introduction

Unlike their nitrogen analogues, homoleptic macrocyclic phosphines represent a rare class of ligand. Some of the apparent lack of interest relates to the difficulty, perceived or otherwise, of their preparation and, for most derivatives, their inherent instability to air. Small-ring macrocyclic phosphines are likely to be prized ligands, as it is anticipated that they will produce highly robust metal complexes capable of outperforming similar complexes of acyclic derivatives already employed so successfully in coordination chemistry and homogeneous catalysis. As the majority of metal-promoted catalysis requires mutually *cis* coordination sites in order to facilitate the desired transformations, triphosphamacrocycles are preferred to tetraphosphorus species, as the latter, unless they are sufficiently flexible, tend to coordinate in a square plane.

The first triphosphorus macrocycles were prepared by Kyba using high-dilution techniques to give 12- to 14-membered cyclo-P_3 ligands as isomeric mixtures.[1] Kyba noted that the tertiary phosphines in his ligands inverted at high temperature, enabling the preparation of a number of metal complexes with facially capping 11-aneP_3 ligands.[1] Although this remains a significant landmark in the development of homoleptic phosphorus macrocycle chemistry, template methods have largely superseded the high-dilution techniques as the method of choice for the preparation of P-containing macrocycles. Template methods offer the advantage of controlling the stereochemistry of the resultant ligand as the desired *syn, syn* all-*cis* form. This is crucial in smaller and/or more rigid systems containing bulky groups where the barrier to inversion at the phosphorus centers may be prohibitively high. However, the template method has one major drawback; as the metal−macrocycle unit is very robust, it is not easy to remove the product macrocycle from its template.

There are three main methods for the template synthesis of triphosphamacrocycles, namely, the 1+1+1, 2+1, and 3+0 approaches. In the 1+1+1 closure, all three chelate rings of the macrocycle are formed successively at the metal center from three appropriately functionalized monodentate phosphines. The 2+1 approach requires the formation of only two chelate rings, as one is already present in a prebound bidentate diphosphine, while the 3+0 approach utilizes a coordinated terdentate P_3 ligand and requires just one ring closure to give the macrocycle. Surprisingly, although this latter approach would appear to be the simplest, no literature examples exist for this kind of chemistry. One restriction may be the lack of suitable linear triphosphorus ligands as necessary precursors.

The first example of the use of a template method for the preparation of a P_3 macrocycle was that of Norman and coworkers.[2] The synthesis of 12-aneP_3H_3 was achieved by the radical-induced 1+1+1 coupling of three allylphosphine ligands in *cis*-$[Mo(CO)_3(H_2PC_3H_5)_3]$.[2] This elegant chemistry established the template method for the preparation of triphosphorus macrocycles. However, Norman was unable to exploit the ligand system, as methods for the removal of the macrocycle from the template eluded him. Our group was able to achieve the liberation of tritertiary derivatives of the type 12-aneP_3-R_3, enabling a study of the rich coordination chemistry of these intriguing ligands.[3] Aside from this incipient example, there are only two further examples of the successful synthesis of P_3 macrocycles by the 1+1+1 method: the first uses a modification of the Norman procedure employing $[(\eta^5\text{-}C_5H_5)Fe]^+$ as the template,[4] while the second generates a unique 45-aneP_3 ligand

* Author for correspondence. E-mail: Edwardspg@cardiff.ac.uk.
† Deceased

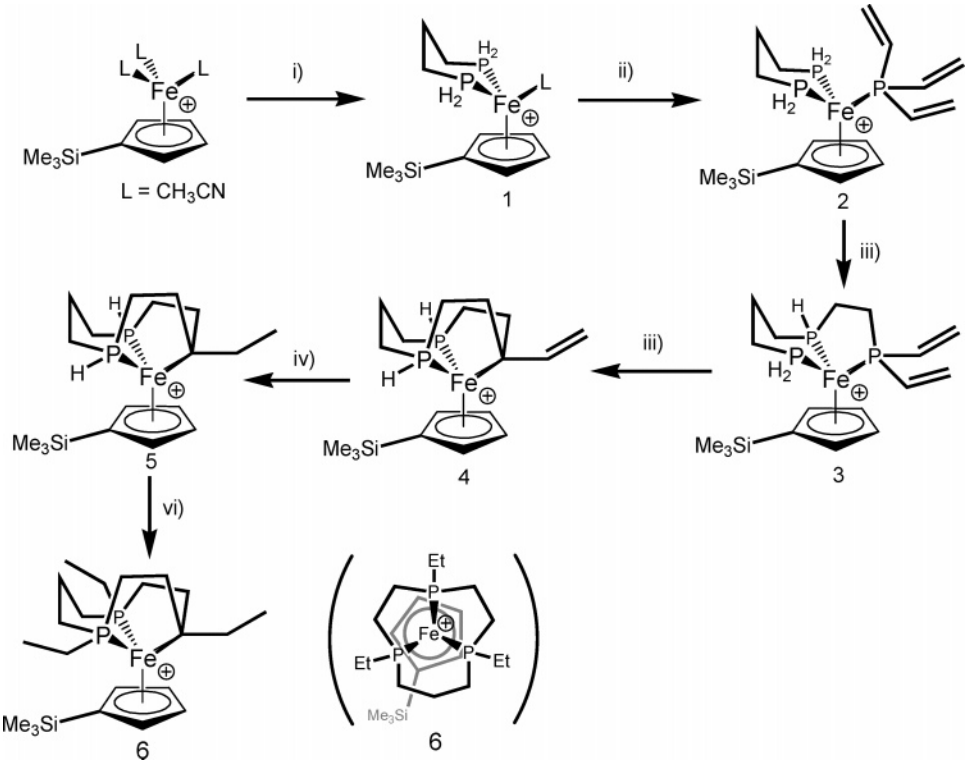
(1) (a) Kyba, E. P.; John, A. M.; Brown, S. B.; Hudson, C. W.; McPhaul, M. J.; Harding, A.; Larsen, K.; Niedzwiecki, S.; Davis, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 139. (b) Kyba, E. P.; Davis, R. E.; Liu, S.-T.; Hassett, K. A.; Brown, S. B. *Inorg. Chem.* **1985**, *24*, 4629. (c) Kyba, E. P.; Brown, S. B. *Inorg. Chem.* **1980**, *19*, 2159.

(2) Diel, B. N.; Brandt, P. F.; Haltiwanger, R. C.; Norman, A. D. *J. Am. Chem. Soc.* **1982**, *104*, 4700.

(3) (a) Edwards, P. G.; Fleming, J. S.; Liyanage, S. S. *Inorg. Chem.* **1996**, *35*, 4563. (b) Edwards, P. G.; Fleming, J. S.; Liyanage, S. S. *J. Chem. Soc., Dalton Trans.* **1996**, 1801.

10.1021/om060798g CCC: $37.00
Publication on Web 12/10/2006

Scheme 1. Synthesis of Symmetrical 10-aneP$_3$ Iron Macrocycle Complexes[a]



[a] Reagents and conditions: (i) 1,3-diphosphinopropane, CH_3CN/PhMe; (ii) trivinylphosphine, 1,2-dichlorobenzene/1,2-dichloroethane; (iii) NEt_3, 1,2-dichlorobenzene/1,2-dichloroethane, 70 °C; (iv) H_2, Pd/C (10%), EtOH; (v) KOBu^t, THF, −78 °C, EtBr.

via a Grubbs' type methathesis coupling of the terminal unsaturated groups at the ends of lengthy alkenyl substituents on coordinated phosphines.[5]

The 2+1 approach has been used by us for the synthesis of a number of triphosphamacrocycles including the elusive 9-aneP$_3$-R$_3$ ligand.[6] These versatile 2+1 methods employ [(η^5-Cp^R)Fe]$^+$ units as templates and are not restricted to hydrophosphination type rections but also include Michael-type additions and S_N2 substitutions at fluoroarylphosphines.[6] This paper establishes this type of approach as a versatile one through the iron-based template synthesis of symmetric and asymmetric 10-aneP$_3$ and symmetric 11-aneP$_3$ derivatives, completing the series from 9- to 12-membered triphosphamacrocycles available using these techniques.

Results and Discussion

Molybdenum(0) and chromium(0) tricarbonyl fragments are effective templates for intramolecular cyclophosphinations of allylphosphine, allowing access to a number of 12-aneP$_3$ macrocycles. However, they have not provided smaller ring triphosphamacrocycles by related templated hydrophosphinations of vinylphosphines. We have speculated that the distance between the reactive centers of the phosphorus-containing precursors in the M(CO)$_3$ templates is too great (as a consequence of the respective metal radii and the long M−P bond lengths) to support the synthesis of 1,4,7-triphosphacyclononanes by such methods.[3b] Structural studies indicate that the distance between adjacent phosphorus atoms, measured by the nonbonded P···P distance, is typically around 3.4 Å for the Mo(CO)$_3$ template and 3.3 Å for the Cr(CO)$_3$ analogues. For a nine-membered ring to form in the preparation of 1,4,7-triphosphacyclononanes, modeling suggests that the nonbonded P···P distance in a tricarbonylchromium complex should be around 3.0 Å. It is not clear what limit this template might have in terms of macrocyclic ring size, although we have been unable to prepare any macrocycle smaller than 12-membered with either Mo(CO)$_3$ or Cr(CO)$_3$ as the supporting unit. The alternative template, [(η^5-RCp)Fe]$^+$, where RCp is a variously substituted cyclopentadienyl group, has features that facilitate the formation of smaller macrocycles. The success of this template relates to the shorter Fe−P bond lengths, the ability to vary the nature of the substituents on the periphery of the Cp unit, and the facility to incorporate a bidentate and monodentate phosphine sequentially without compromising the facial geometry at the metal center. Variation in substituents (R) of the RCp spectator ligand introduces the opportunity to manipulate the steric influence of the spectator ligand and hence the nonbonded distance between precursor coordinated phosphines, a feature absent in the Cr/Mo(CO)$_3$ templates. This template methodology has already provided an alternative synthesis of 12-aneP$_3$-H$_3$, and we have presented some preliminary results of the preparation of asymmetric 10-aneP$_3$ and 9-aneP$_3$ derivatives using such methods.[6] This has been extended to include symmetric 10-aneP$_3$ types and 11-aneP$_3$ macrocycles, full details of which are presented here.

Symmetric 10aneP$_3$ Macrocycle Complexes. The synthesis of the symmetric 1-vinyl-1,4,8-triphosphacyclodecane was achieved by the reaction of 1,3-bis(phosphino)propane with trivinylphosphine on the iron(II) template (Scheme 1). The

(4) Price, A. J.; Edwards, P. G. *J. Chem. Soc., Chem. Commun.* **2000**, 899.

(5) Bauer, E. B.; Ruwwe, J.; Martin-Alvarez, J. M.; Peters, T. B.; Bohling, J. C.; Harnpel, F. A.; Szafert, S.; Lis, T.; Gladysz, J. A. *J. Chem. Soc. Chem. Commun.* **2000**, 2261.

(6) (a) Edwards, P. G.; Whatton, M. L. *Dalton Trans.* **2006**, 442. (b) Edwards, P. G.; Haigh, R.; Li, D.; Newman, P. D. *J. Am. Chem. Soc.* **2006**, *128*, 3818. (c) Edwards, P. G.; Newman, P. D.; Hibbs, D. E. *Angew. Chem., Int. Ed.* **2000**, *39*, 2722. (d) Edwards, P. G.; Newman, P. D.; Malik, K. M. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 2922.

chemistry is related to that used for the preparation of the analogous 9-aneP_3 derivative whereby two new chelate rings are formed in a stepwise fashion by the Michael-type nucleophilic addition of a coordinated primary phosphide to a neighboring vinylic carbon. In contrast to the analogous 1,2-bis(phosphino)ethane (1,2-bpe) system, the 1,3-bis(phosphino)-propane (1,3-bpp) precursor complex, $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(1,3\text{-}bpp)(CH_3CN)]^+$, **1** ($Me_3SiC_5H_4$ is trimethylsilylcyclopentadienyl), cannot be made by irradiating $[\{\eta^5\text{-}Me_3SiC_5H_4\}Fe(CO)_2(CH_3CN)]^+$ in the presence of 1 molar equiv of phosphine, as this leads to intractable product mixtures. Rather, the $[\{\eta^5\text{-}(Me_3Si)C_5H_4\}Fe(CH_3CN)_3]^+$ complex must be generated before addition of the phosphine; $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(1,3\text{-}bpp)(CH_3CN)]^+$, **1**, is then obtained cleanly and in high yield after the addition of 1 molar equiv of 1,3-bpp. The remaining acetonitrile ligand in **1** is replaced by trivinylphosphine upon heating in hydrochlorocarbons, and the subsequent base-catalyzed macrocyclization chemistry proceeds as for the analogous 9-aneP_3-vin complex.[6b] Yields here are generally poorer than those for the synthesis of the related $[(\eta^5\text{-RCp})Fe(9\text{-ane}P_3\text{-}H_2,C_2H_3)]^+$ complexes, and there is a strong preference for the mono- and bis(trimethylsilyl)-cyclopentadienyl, η^5-$Me_3SiC_5H_4$ or η^5-$(Me_3Si)_2C_5H_3$, units in the template. Unsubstituted C_5H_5 and permethylated C_5Me_5 were not suitable for the formation of 10-aneP_3-H_2,C_2H_3. In this case, the lower yields compared to the related $[(\eta^5\text{-RCp})Fe(9\text{-ane}P_3\text{-}H_2,C_2H_3)]^+$ complexes are, in part, a consequence of the increased formation of insoluble precipitates during the reaction. The nature of these solids is undetermined, but they are presumably the products of unwanted intermolecular coupling.

The macrocyclic product $[\{\eta^5\text{-}Me_3SiC_5H_4\}Fe(10\text{-ane}P_3\text{-}H_2,C_2H_3)]PF_6$, **4**, is a yellow solid that may be crystallized from ethanol. Crystals suitable for single-crystal X-ray analysis were not obtained, as the complex tended to form clusters of very fine, friable needles. The $^{31}P\{^1H\}$ NMR spectrum consists of a low-field triplet at δ 126.9 ppm ($^2J_{P-P}$ 33 Hz) and an upfield doublet with the same coupling constant at δ 56.0 ppm. The former is assigned to the unique tertiary phosphorus and the latter to the two equivalent secondary phosphines; this was confirmed on inspection of the proton-coupled ^{31}P NMR spectrum, which showed a doublet with $^1J_{P-H} = 364$ Hz for the secondary phosphines. The $^2J_{P-P}$ value is sensitive to the ring size of the macrocycle, as will be discussed below.

The vinyl function in $[\{\eta^5\text{-}Me_3SiC_5H_4\}Fe(10\text{-ane}P_3\text{-}H_2,C_2H_3)]^+$, **4**, was reduced cleanly with 10% palladium on carbon in ethanol to give $[\{\eta^5\text{-}Me_3SiC_5H_4\}Fe(10\text{-ane}P_3\text{-}H_2,Et)]^+$, **5**, in quantitative yield. The $^{31}P\{^1H\}$ NMR spectrum of **5** is very similar to that of the vinyl precursor **4**, but the tertiary phosphine in **5** resonates at δ 137.3 ppm, approximately 10 ppm downfield of the precursor; this is typical for dialkylvinylphosphines compared to analogous dialkylethylphosphines. The triethyl system $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(10\text{-ane}P_3\text{-}Et_3)]^+$, **6**, is obtained after the ethylation of the secondary phosphines in **5** with bromoethane in the presence of 2 molar equiv of potassium *tert*-butoxide. As for the synthesis of the related $[(\eta^5\text{-RCp})Fe(9\text{-ane}P_3\text{-}Et_3)]^+$, where R = $Me_3SiC_5H_4$ or $(Me_3Si)_2C_5H_3$, the trimethylsilyl groups are lost if excess KO^{t}Bu is employed.

The $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(10\text{-ane}P_3\text{-}Et_3)]PF_6$, **6**, thus obtained can be crystallized from methanol on cooling. A single-crystal X-ray structure of the complex is shown in Figure 1. The structure shows the $Me_3SiC_5H_4$ and 10-aneP_3 ligands to be facially capping the pseudo-octahedral metal center as expected. The Fe−P bond lengths are 2.1788(10) and 2.1921(10) Å for the two phosphorus donors incorporated in one six- and one five-membered chelate {hereafter defined as P(6,5)}and 2.1784-

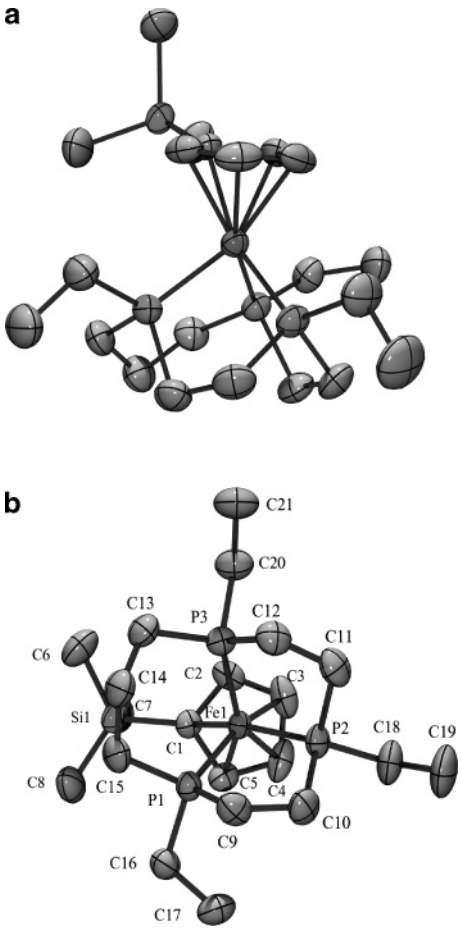
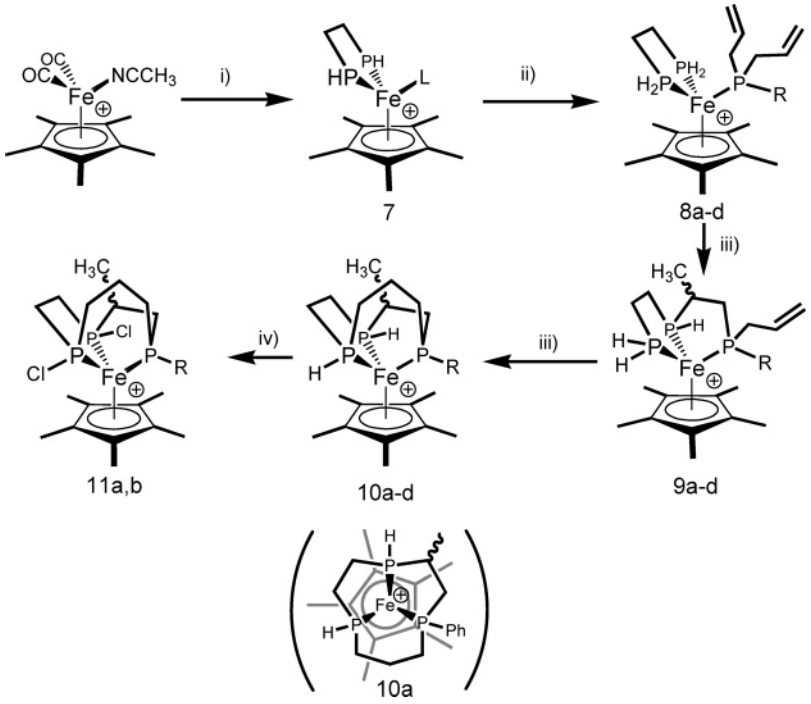


Figure 1. Two views of the crystal structure of the cation of **6**, $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(10\text{-ane}P_3\text{-}Et_3)]^+$: (a) approximately parallel to the $SiMe_3Cp$ plane; (b) approximately perpendicular to the Cp plane with the atom-labeling scheme. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Fe1−$Cp_{(centroid)}$ 1.730-(6), Fe1−P2 2.1784(10). Fe1−P1 2.1788(10), Fe1−P3 2.1921(10), P1−C16 1.826(4), P1−C15 1.827(4), P1−C9 1.847(4), P2−C18 1.822(4), P2−C10 1.833(4), P2−C11 1.840(4), P3−C20 1.836(4), P3−C13 1.840(4), P3−C12 1.847(4), Si1−C6 1.857(5), Si1−C8 1.860(4), Si1−C7 1.865(4), Si1−C1 1.866(4), Selected bond angles (deg): P1−Fe1−$Cp_{(centroid)}$ 129.0, P2−Fe1−$Cp_{(centroid)}$ 125.0, P3−Fe1−$Cp_{(centroid)}$ 126.8, P2−Fe1−P1 86.50(4), P2−Fe1−P3 85.85-(4), P1−Fe1−P3 90.12(4), C16−P1−C15 101.27(19), C16−P1−C9 101.73(19), C15−P1−C9 102.9(2), C16−P1−Fe1 119.36(13), C15−P1−Fe1 117.88(14), C9−P1−Fe1 111.35(13), C18−P2−C10 103.4(2), C18−P2−C11 103.9(2), C10−P2−C11 104.44(19), C18−P2−Fe1 122.29(15), C10−P2−Fe1 111.21(14), C11−P2−Fe1 110.00(15), C20−P3−C13 102.9(2), C20−P3−C12 103.40-(19), C13−P3−C12 103.64(19), C20−P3−Fe1 116.55(13), C13−P3−Fe1 118.82(13), C12−P3−Fe1 109.79(14). Torsion angle (deg): C3−C2−C1−Si1 15.7.

(10) Å for the unique phosphorus that is a component of two five-membered chelates {defined as P(5,5) in subsequent discussion}. These Fe−P bond lengths are comparable to those observed in $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(9aneP_3Et_3)]^+$, where values of 2.153(4), 2.178(4), and 2.196(5) Å are observed.[6b] The P−Fe−P angles are 90.12(4)° for the six-membered ring and 86.50(4)° and 85.85(4)° for the two five-membered chelates. These values are comparable to those observed in the related 9-aneP_3-R_3 complexes.[6b,d] The six-membered ring adopts the expected chair conformation, while the two five-membered rings have an envelope conformation. The $SiMe_3$ moiety is positioned directly over the six-membered ring, which presumably minimizes steric interactions with the nearest hydrogen−hydrogen contacts at

Scheme 2. Synthesis of Unsymmetrical 10-aneP$_3$ Iron Macrocycle Complexes[a]



[a] **a**, R = phenyl; **b**, R = benzyl; **c**, R = allyl; **d**, R = 2-propyl. Reagents and conditions: (i) 1,2-diphosphinoethane, *hν*, CH_3CN; (ii) diallyl(phenyl)phosphine, 1,2-dichloroethane; (iii) AIBN, toluene; (iv) aq NaOH, $CHCl_3$.

2.28 Å. This interaction causes the bond to the silicon atom to be distorted 15.7° from the C_5 plane of the cyclopentadienyl ring. In the analogous 9-aneP$_3$ complex, the distortion is slightly greater at 16.3°.[6b] Of the five Fe−C bond lengths, that to the carbon bearing the silyl group is the longest, at 2.153(3) Å (the distance to the ring centroid is 1.730(6) Å).

The aforementioned chemistry is also appropriate for the bis(trimethylsilyl)cyclopentadienyliron(II) template, but as noted previously with the 9-aneP$_3$ derivatives, care has to be exercised during the final ethylation, as the presence of excess base leads to C−Si bond cleavage to give product mixtures that are not easily separated. C_5Me_5 proved a less useful ligand for the template chemistry to produce 10-aneP$_3$-R$_3$ derivatives, with greatly reduced yields in macrocyclic products being obtained when this derivative was employed. Likewise, the nonsubstituted Cp templates did not give easily isolable materials when used for the synthesis of the symmetric 10-aneP$_3$ macrocycles.

Asymmetric 10-aneP$_3$ Systems. The synthesis of the asymmetric 10-aneP$_3$ macrocyclic complexes with the preferred 1,2,3,4,5-pentamethylcyclopentadienyl template is summarized in Scheme 2. The coordinated acetonitrile in [(η^5-C_5Me_5)Fe(1,2-dpe)(CH_3CN)]$^+$, **7**, is readily substituted with either triallylphosphine or tertiary diallylphosphines upon heating in 1,2-dichloroethane to give complexes of the type [(η^5-C_5Me_5)Fe(1,2-dpe)(PRR′$_2$)]BF_4, **8**, as yellow or orange solids in quantitative yield. The complexes are characterized by their $^{31}P\{^1H\}$ NMR spectra, which consist of the expected A_2X pattern at δ 41.2t and 10.8d (**8a**), 45.4t and 12.0d (**8b**), 46.1t and 13.2d (**8c**), and 51.9t and 13.0d (**8d**). The doublets are due to the primary phosphines, as confirmed from the proton-coupled ^{31}P spectra, which show a typically large $^1J_{P-H}$ coupling constant of around 350 Hz. Heating the ternary [(η^5-C_5Me_5)Fe(1,2-dpe)(PRR′$_2$)]BF_4 complexes in toluene at 80 °C in the presence of AIBN gave mixtures from which macrocyclic complexes of type **10** can be obtained as yellow, air- and moisture-stable solids in variable yield. The radical-induced cyclization of [(η^5-C_5Me_5)Fe(1,2-bpe){PPh(C_3H_5)$_2$}]BF_4 is known to produce the 10-membered macrocyclic complex **10a** instead of the anticipated species with a symmetric 11-membered ring. This is the result of an internal hydrophosphination of one of the allylic functions generating an exo-methyl group as opposed to inclusion of all carbons in the macrocyclic ring.[6d] The cyclization does occur on heating alone, but this is impractically slow, hence the addition of AIBN as a radical initiator. The radical-promoted cyclization occurs over a 12−24 h period at 80 °C and is conveniently monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After heating **8a** with AIBN for 1 h, aside from the resonances for **8a**, three discreet doublets of doublets correlating to one secondary, one tertiary, and one primary phosphine are observed in the $^{31}P\{^1H\}$ NMR spectrum at δ 109 (28, 26 Hz), 75 (34, 28 Hz), and 22 (34, 26 Hz) ppm, respectively. The chemical shift of the secondary phosphine is entirely consistent with its incorporation in two five-membered chelate rings. Thus, somewhat surprisingly, it is the five-membered ring that is formed first by an initial internal hydrophosphination of one of the allyl functions (a 5-exo-trig ring closure) to give the intermediate **9a** shown in Scheme 2. The subsequent formation of the six-membered chelate (a 6-endo-trig ring closure) completes the macrocycle. After 12−24 h at 80 °C, the only species detected by $^{31}P\{^1H\}$ NMR spectroscopy is **10a**.

The cyclization chemistry using the 1,2,3,4,5-pentamethylcyclopentadienyl template and 1,2-bpe extended to benzyldiallylphosphine (**7b** → **10b**), triallylphosphine (**7c** → **10c**), and 2-propyldiallylphosphine (**7d** → **10d**), although yields were appreciably lower with these tertiary phosphines. Indeed, the presence of significant quantities of intractable byproducts precluded isolation of **10c** and **10d** as pure compounds, and they were characterized solely by $^{31}P\{^1H\}$ NMR spectroscopy and mass spectrometry. Reasons for the relative failure of the cyclization with diallyl(2-propyl)phosphine are unclear, while the reactions with triallylphosphine were frustrated by unwanted intermolecular coupling reactions. The reaction with *tert*-butyldiallylphosphine failed to produce the desired [(η^5-C_5Me_5)-

Fe(1,2-dpe){P(t-C_4H_9)(C_3H_5)$_2$}]BF_4 precursor, and hence no macrocyclic product could be obtained.

Altering the nature of the Cp fragment had a deleterious effect on the yields of the asymmetric 10-aneP_3 derivatives. Substituting C_5Me_5 for the mono- or bis-1,3-(trimethylsilyl)cyclopentadienyl group led to the production of complex mixtures from which we have been unable to isolate pure compounds. Some of the unwanted byproducts were identified by mass spectrometry as dimeric species resulting from intermolecular hydrophosphination. When unsubstituted C_5H_5 was employed with PPh(C_3H_5)$_2$, two major sets of resonances were observed in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixtures on completion of the cyclization. The first set at δ 126.3t (36 Hz), 80.8dd (61, 36 Hz), and 74.7t (61, 36 Hz) ppm may be assigned to the unsymmetrical [(η^5-C_5H_5)Fe(Me-10-aneP_3-H_2,Ph)]$^+$ complex, and the second set, which appear in an approximately 1:2 intensity ratio at δ 77.7d (62 Hz) and 34.1t (62 Hz), are assigned to the symmetrical [(η^5-C_5H_5)Fe(11-aneP_3-H_2,Ph)]$^+$ complex. This was the only case where the 11-membered macrocycle could be detected in solution by ^{31}P NMR spectroscopy. Unfortunately, it was not possible to separate these two isomers by crystallization and/or chromatography, and other characterization data for the complexes are lacking. These observations do, however, suggest that the peripheral bulk on the cyclopentadienyl fragment has an influence on the outcome of the reaction and the ring size of the resultant macrocycle. When bulky, substituted Cp ligands are used, asymmetric 10-aneP_3 macrocycles predominate, but formation of the symmetric 11-aneP_3 competes favorably when unmodified C_5H_5 is employed.

The $^{31}P\{^1H\}$ NMR spectra of the complexes **10a**−**d** are typically of an ABX type with a low-field triplet at δ 110−115 ppm assignable to the secondary phosphine that is a component of two five-membered chelates and two doublets of doublets in the δ 60−70 ppm range for the remaining phosphorus donors. In the case of **10c**, only a single doublet was observed to higher field (δ 65.5) as a consequence of accidental equivalence of the two respective phosphorus nuclei at the operating frequency of the spectrometer (36.23 MHz). Further confirmation of the structural assignments comes from the $^{13}C\{^1H\}$ DEPT NMR spectra, where one methine carbon resonance is observed as a doublet of doublets in addition to a doublet of doublets for the unique methyl carbon (see Experimental Section). The ^1H NMR spectra of the complexes consist of overlapping, heavily coupled multiplets in the aliphatic region; this is not surprising, as every hydrogen in the macrocycle is unique. The CH_3 group exo to the ring is the exception, being observed as a doublet of doublets in the ^1H spectrum at around δ 1.5 ppm (J = 12 and 7 Hz). The presence of three multiplets for the alkenic protons of the allyl group at δ_H 5.64, 5.44, and 5.29 ppm in **10c** and a diastereomeric ABX pattern for the benzyl CH_2 groups α to phosphorus at δ_P 3.16 (dd, J = 14, 5 Hz) and 2.87 (dd, J = 14 and 5 Hz) ppm for **10b** are other distinguishing features in the ^1H NMR spectra of these complexes.

Hydrophosphination at the internal carbon of one of the allyl groups in the synthesis of the [(η^5-RCp)Fe(Me-10-aneP_3-H_2,R′)]$^+$ complexes creates five chiral centers, namely, the methyl-bearing ring carbon, the three phosphorus donors, and the iron center itself. There is no enantiocontrol during the reaction and the complexes are isolated as racemic mixtures, although the reaction is highly stereospecific in the formation of the exo-methyl derivative. There is no evidence of the epimer in the ^1H NMR spectrum; this selectivity may be due to unfavorable steric interactions with the cyclopentadienyl group that destabilize the alternative endo-conformation or the transition state from which it would arise. The structure of the 1*S*, 3*R*, 4*R*, 8*R*, Fe(*R*)-[(η^5-C_5Me_5)Fe(Me-10-aneP_3-H_2,Ph)]$^+$ enantiomer (*S*,*R*,*R*,*R*,*R*-**10a**) is shown in Figure 2. The gross structure resembles closely that of our previously reported P,P-dichloro derivative, [(η^5-C_5Me_5)Fe(Me-10aneP_3-Cl_2,Ph)]$^+$, **11a**,[6c] although the Fe−P bond to the tertiary phosphine is a little longer (2.195(2) Å) than the other two (2.150(2), 2.169(2) Å). The P_1−Fe−P_3 and P_2−Fe−P_3 angles of the two different five-membered chelate rings are almost identical, at 86.00(7)° and 85.97(8)°, respectively, and are both significantly smaller than that of the six-membered chelate (P1−Fe−P2, 90.07°). These values compare to bond lengths of 2.210(2) (Fe−PPh), 2.147(2) (Fe−PCl), and 2.153(2) Å (Fe−PCl) and angles of 84.51(8)°, 86.77(7)°, and 89.00(6)° for the two five-membered and one six-membered chelate in **11a**.[6c] Steric strain is less in *S*,*R*,*R*,*R*,*R*-**10a** compared to the dichlorinated analogue, as indicated by a reduced Fe−P−C_{ipso} bond angle of 121.7(2)°

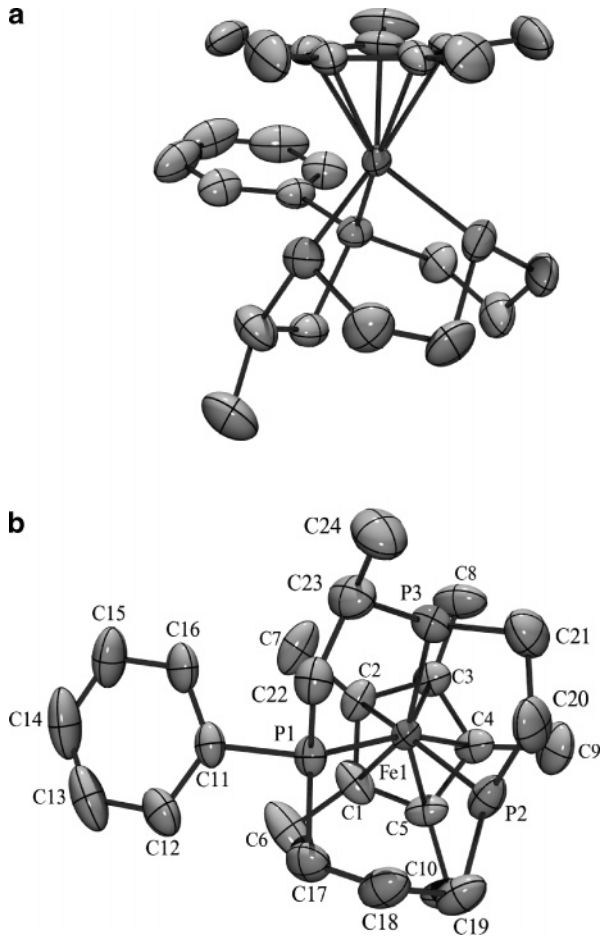
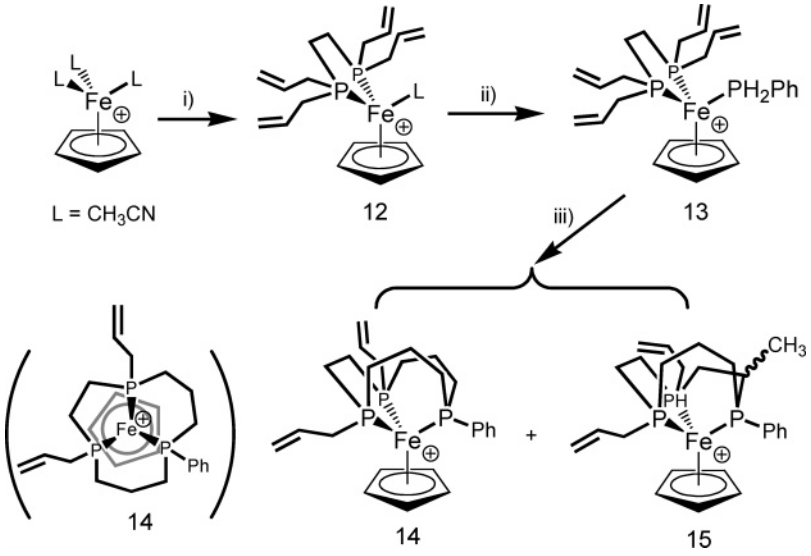


Figure 2. Two views of the crystal structure of the cation of **10a**, 1*S*,3*R*,4*R*,8*R*,Fe-[(η^5-C_5Me_5)Fe(Me-10-aneP_3-H_2,Ph)]$^+$: (a) approximately parallel to the Cp* plane; (b) approximately perpendicular to the Cp plane with the atom labeling scheme. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Fe1−$Cp_{(centroid)}$ 1.728(6), Fe1−P2 2.150(2), Fe1−P3 2.169(2), Fe1−P1 2.195(2), P1−C11 1.833(6), P1−C22 1.841(6), P1−C17 1.853(6), P2−C19 1.821(7), P2−C20 1.853(8), P3−C21 1.812(8), P3−C23 1.864(7), C22−C23 1.505(10), C23−C24 1.514(10). Selected bond angles (deg): P1−Fe1−$Cp_{(centroid)}$ 131.2, P2−Fe1−$Cp_{(centroid)}$ 122.9, P3−Fe1−$Cp_{(centroid)}$ 127.0, P2−Fe1−P3 85.94(8), P2−Fe1−P1 90.06(7), P3−Fe1−P1 85.97(7), C11−P1−C22 101.8(3), C11−P1−C17 102.2(3), C22−P1−C17 102.1(3), C11−P1−Fe1 121.4(2), C22−P1−Fe1 110.6(2), C17−P1−Fe1 116.2(2), C19−P2−C20 104.8(4), C19−P2−Fe1 122.0(3), C20−P2−Fe1 111.6(2), C21−P3−C23 107.9(4), C21 P3 Fe1 110.1(3), C23−P3 Fe1−112.0(2), C22−C23−P3 108.5(5), C24−C23−P3 114.2(6).

Scheme 3. Synthesis of 11-aneP$_3$ Iron Macrocycle Complexes[a]



[a] Reagents and conditions: (i) 1,2-bis(diallylphosphino)ethane, CH_3CN; (ii) $PhPH_2$, CH_2Cl_2; (iii) RT, 14 days.

[cf. 122.4(7)° in **11a**] and smaller deviations from coplanarity for the methyl substituents and the ring carbons of the C_5Me_5 unit; the methyls are bent away from the metal by an average of 7.1° compared to 10.8° in [(η^5-C_5Me_5)Fe(Me-10-aneP$_3$-Cl$_2$,-Ph)]$^+$, **11a**.[6c]

The chiral cyclopentadienyl derivative, neomenthylcyclopentadienyliron(II), [(η^5-neomenthCp)Fe(II)], was employed in an effort to invoke some diastereoselectivity in the synthesis of the unsymmetrical 10-aneP$_3$ complexes. However, the yields of macrocycle were poor with this template, and there was no detectable diastereoselectivity by ^{31}P and ^{1}H NMR spectroscopic analysis of the isolated products. The ^{31}P{^{1}H} NMR spectrum of [(η^5-neomenthCp)Fe(Me-10-aneP$_3$-H$_2$,Ph)]$^+$, **10e**, consisted of two sets of AMX doublets of doublets, one for each diastereoisomer. The intensities of all the peaks were equivalent, suggesting no diastereoselectivity during the synthesis. This was confirmed on inspection of the ^{1}H NMR spectrum, which revealed eight separate peaks of equal intensity for the four unique cyclopentadienyl protons of each diastereomer.

As noted previously, if solutions of the disecondary macrocyclic complexes in chlorinated solvents are exposed to the atmosphere, the secondary phosphines are chlorinated to give complexes of the type [(η^5-RCp)Fe(Me-10-aneP$_3$-Cl$_2$,R′)]$^+$. This is relatively slow in the absence of base, but is rapid when the solutions are left in contact with aqueous sodium hydroxide. The coordinated chlorinated phosphines resonate at $\delta_P > 200$ ppm in the ^{31}P{^{1}H} NMR spectra (see Experimental Section). We have previously commented on similar chlorinations achieved with molybdenum(0) complexes of triphosphacyclododecanes.[7]

11-aneP$_3$ Derivatives. The failure to isolate symmetric 11-membered triphosphamacrocycle complexes from the reaction of 1,2-dpe with triallyphosphine or tertiary diallylphosphines was surprising, and different procedures for their synthesis were required. The next obvious approach was to place the allylic functions on the bidentate phosphine and to use a primary monodentate phosphine as highlighted in Scheme 3. 1,2-Bis(diallylphosphino)ethane, 1,2-tape, was acquired from 1,2-bis(dichlorophosphino)ethane by reaction with 4 molar equiv of allylmagnesium bromide. The diphosphine was coordinated to [(η^5-C_5H_5)Fe]$^+$ by visible light photolyses of a solution of [(η^5-C_5H_5)Fe(η^6-C_6H_6)]$^+$ containing 1 molar equiv of 1,2-tape. The iron(II) precursors highlighted in Schemes 1 and 2 were not appropriate for this synthesis, as the UV conditions needed for labilization of the metal-carbonyls could compromise the P-allyl functions. The complex [(η^5-C_5H_5)Fe(1,2-tape)(MeCN)]$^+$, **12**, was formed in good yield, and the final MeCN ligand was replaced by phenylphosphine on stirring a solution of **12** and $PhPH_2$ at room temperature for several days to give **13**. This latter complex was not isolated because all attempts to purify the compound were frustrated by its ready tendency to undergo ring-closure reactions resulting in contamination by macrocyclic products and their acyclic intermediates (which are readily identified by their ^{31}P NMR spectra). Solutions of **13** were thus left for 14 days at room temperature to allow complete cyclization to give a mixture of the desired 11-membered triphosphamacrocycle complex [(η^5-C_5H_5)Fe{11-aneP$_3$-Ph,-(C_3H_5)$_2$}]$^+$, **14**, and the asymmetric 10-aneP$_3$ derivative, [(η^5-C_5H_5)Fe{Me-10-aneP$_3$-Ph,(C_3H_5)$_2$}]$^+$, **15**. Efforts to acquire the desired complex by UV-initiated coupling were unsuccessful, with complex reaction mixtures resulting even after short-term exposure to UV light. However, the reaction mixtures typically consisted of 1:1 mixtures of the two isomers (**14**, **15**) at all stages of the cyclization, as determined by ^{31}P{^{1}H} NMR spectroscopy (i.e., their rates of formation are similar). Although the 11-aneP$_3$ complex could be isolated from this reaction, because of the competitive formation of the unsymmetric [(η^5-C_5H_5)Fe{Me-10-aneP$_3$-Ph,(C_3H_5)$_2$}]$^+$ complex, **15**, the isolated yield was very poor (5%). Unlike the 11-membered derivative, the 10-membered complex could not be isolated in a pure state.

The complex [(η^5-C_5H_5)Fe{11-aneP$_3$-Ph,(C_3H_5)$_2$}]$^+$, **14**, was crystallized from tetrahydrofuran as its hexafluorophosphate salt and its structure determined by single-crystal X-ray analysis (Figure 3). The average Fe−P bond lengths (2.197 Å) are greater in this complex than in the crystallographically characterized 9-aneP$_3$ and 10-aneP$_3$ complexes, and more significantly, the P−Fe−P bond angles for the two six-membered chelate rings are expanded to 95.0° (average) compared to 90° for the symmetric and unsymmetric 10-aneP$_3$ complexes. This may simply be a consequence of the larger ring size; however, this is not the case for the 12-aneP$_3$ complex [(η^5-C_5Me_5)Fe(12-aneP$_3$-Et$_3$)]$^+$, where the average P···P distance is 3.137(4) Å

(7) Jones, D. J.; Edwards, P. G.; Tooze, R. P.; Albers, T. *J. Chem. Soc., Dalton Trans.* **1999**, 1945.

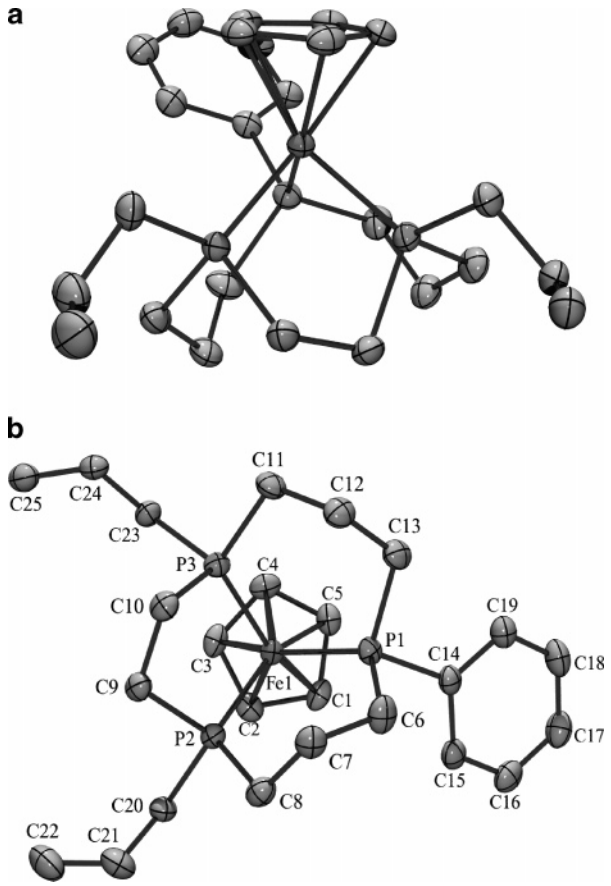


Figure 3. Two views of the crystal structure of the cation of **14**, $[(\eta^5\text{-}C_5H_5)Fe\{11\text{-}aneP_3\text{-}Ph,(C_3H_5)_2\}]^+$: (a) approximately parallel to the Cp plane; (b) approximately perpendicular to the Cp plane with the atom-labeling scheme. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Fe1−C5 2.092(3), Fe1−C3 2.094(4), Fe1−C4 2.100(3), Fe1−C1 2.109(3), Fe1−C2 2.110(3), Fe1−$Cp_{(centroid)}$ 1.722(4), Fe1−P1 2.1943(9), Fe1−P3 2.1954(10), Fe1−P2 2.2026(9), P1−C13 1.835(4), P1−C14 1.849(3), P1−C6 1.857(4), P2−C8 1.834(3), P2−C9 1.844(3), P2−C20 1.844(4), P3−C11 1.833(4), P3−C10 1.840(3), P3−C23 1.848(3), C20−C21 1.498(5), C21−C22 1.309(5), C23−C24 1.499(5), C24−C25 1.309(5). Selected bond angles (deg): P1−Fe1−$Cp_{(centroid)}$ 121.8, P2−Fe1−$Cp_{(centroid)}$ 126.8, P3−Fe1−$Cp_{(centroid)}$ 123.1, P1−Fe1−P3 93.98(4), P1−Fe1−P2 95.93(4), P3−Fe1−P2 85.68(3), C13−P1−Fe1 114.31(12), C14−P1−Fe1 115.71(11), C6−P1−Fe1 121.25(13), C8−P2−Fe1 119.15(12), C9−P2−Fe1 109.28(12), C20−P2−Fe1 119.44(12), C11−P3−Fe1 118.79(12), C10−P3−Fe1 111.50(12), C23−P3−Fe1 115.69(12), C13−P1−C14 101.59(17), C13−P1−C6 102.63(19), C14−P1−C6 98.38(16) C8−P2−C9 102.10(16), C8−P2−C20 102.93(17), C9−P2−C20 101.25(16), C11−P3−C10 104.01(17), C11−P3−C23 102.46(17), C10−P3−C23 102.50(16), C22−C21−C20 125.0(4), C25−C24−C23 124.2(4).

and the P−Fe−P angles average 90°.[8] This distortion may also be described by the nonbonded P···P distances; in **14**, those between the phosphorus atom of the six-membered chelates are substantially larger (3.266 and 3.210 Å) than the corresponding distances in **6** (3.094 Å) and **10a** (3.073 Å). In all cases, the P···P distances between the phosphorus atoms in the five-membered chelates are similar (2.976, 2.985 Å in **6**; 2.944, 2.975 Å in **10a**; and 2.911 Å in **14**). A distinction between all these complexes is in the nature of the Cp unit, being unsubstituted in the case of the current 11-$aneP_3$ (**14**) as opposed to C_5Me_5 for the asymmetric 10-$aneP_3$ and 12-$aneP_3$ complexes and $(Me_3Si)C_5H_4$ for the symmetric 10-$aneP_3$ complex. Observations from the formation of the asymmetric 10-$aneP_3$ and the 9-$aneP_3$ macrocycles show that the nature of the Cp group has a direct influence on the kinetics and efficiency of macrocycle formation, with greater peripheral bulk generating higher yields of products in shorter times. We have recently shown that increasing the steric bulk of the Cp spectator ligand has a significant influence on compressing P−Fe−P angles in related triphosphine and 12-$aneP_3$-R_3 complexes with a consequent decrease in P···P distances.[8] Although the electronic differences between the dissimilar Cp donors may play a part, it is steric influences that appear to control the cyclizations. Thus, the Cp ligands are not simply spectator ligands in these systems but have a direct influence on the cyclization and the nature of the resultant products. This is presumably due to the bulkier $(Me_3Si)C_5H_4$, $(Me_3Si)_2C_5H_3$, and C_5Me_5 donors forcing the reactive centers (phosphide lone pair and/or radical and alkenyl carbon) closer together, enhancing the rate of macrocyclization. This steric effect is observed in the crystal structures of the various complexes by the Fe−P−C_{exo} angles, where C_{exo} is the α-carbon of the nonring substituent(s) at P (ethyl, phenyl, allyl). The values for these angles range from >125° in $[(\eta^5\text{-}C_5Me_5)Fe(9\text{-}aneP_3\text{-}Et_3)]^+$ [6d] to an average of 122.1° in $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(9\text{-}aneP_3\text{-}Et_3)]^+$ [6b] and are 122.9°, 122.5°, and 121.4° for the unique Fe−P−C_{exo} angles in $[\{\eta^5\text{-}(Me_3Si)_2C_5H_3\}Fe(9\text{-}aneP_3\text{-}H_2,C_2H_3)]^+$,[6b] $[(\eta^5\text{-}C_5Me_5)Fe(Me\text{-}10aneP_3\text{-}Cl_2,Ph)]^+$,[6c] and $[(\eta^5\text{-}C_5Me_5)Fe(Me\text{-}10aneP_3\text{-}H_2,Et)]^+$, respectively, and average 119.4° in $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(10\text{-}aneP_3\text{-}Et_3)]^+$. These values are all appreciably greater than the Fe−P−C_{exo} angles in the $[(\eta^5\text{-}C_5H_5)Fe\{11\text{-}aneP_3\text{-}Ph,(C_3H_5)_2\}]^+$, **14**, complex, where values of 115.7°, 115.29°, and 119.23° are observed. The comparable angles in the $[(\eta^5\text{-}C_5Me_5)Fe(12\text{-}aneP_3\text{-}Et_3)]^+$ complex are only slightly larger at 117.2° (average).[8] Although this data must be treated with caution because of the differences within the complexes (notably differences in the number of five- and six-membered chelates for each macrocycle), the observation of increased cyclization rates and improved yields coupled with the structural features do support the notion that the nature of the Cp ligand does influence the cyclization, and, in this case, they are not strictly simple spectator ligands.

The ^{31}P NMR spectrum of **14** consists of a doublet at δ 81.0 ppm ($^2J_{P-P}$, 63 Hz) assigned to the allyl-bearing tertiary phosphines and a triplet at δ 37.9 ppm ($^2J_{P-P}$, 63 Hz) for the unique tertiary phenylphosphine of the macrocycle. These shifts are determined by the nature of the phosphorus donors and tend toward lower fields when the phosphorus is part of one or more five-membered chelate rings.[9] Trends within the ^{31}P NMR spectra can be identified that are characteristic of a given ring size. The chemical shift of a given P donor becomes increasingly positive along the series 12-$aneP_3$ < 11-$aneP_3$ < 10-$aneP_3$ < 9-$aneP_3$, consistent with the change from three six-membered chelates through mixed six- and five-membered chelates to three five-membered chelate rings.[9] In addition, it appears that the value of $^2J_{P-P}$ is also influenced by the ring size, being 63 Hz for the symmetric $[(\eta^5\text{-}C_5H_5)Fe\{11\text{-}aneP_3\text{-}Ph,(C_3H_5)_2\}]^+$, 33 Hz for $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(10\text{-}aneP_3\text{-}H_2,C_2H_3)]^+$, and 21 Hz for $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(9\text{-}aneP_3\text{-}H_2,C_2H_3)]^+$ (the value for the 9-$aneP_3$ derivatives is sensitive to the nature of the Cp group, but there is little difference between unsubstituted Cp and the silylated derivatives, and the trend is a genuine one).[6b] This again relates to the individual chelate ring size or, more specifically, the

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

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

relevant P−Fe−P bond angle, with the largest values of $^2J_{P-P}$ being associated with the larger intermetal bond angles and vice versa. These observations are in accord with those for related noncyclic species.

Liberation Studies. To date, none of the tertiary or secondary triphosphine macrocycles have been successfully liberated from the metal and the d^6 octahedral Fe(II) template appears kinetically remarkably inert and resistant to disruption by conventional agents such as CN^-. The nine-membered triphosphacyclononane has been liberated as its trioxide by exhaustive oxidation,[6b] but the ligands described here remain unknown in the free uncoordinated state. The iron center does undergo reversible one-electron oxidation in most cases, although attempts to scavenge the iron from the oxidized Fe(III) complexes with various agents (CN^-, EDTA, OH^-) have not been successful. These studies continue.

Conclusions

The cationic cyclopentadienyliron(II) template is very versatile and allows incorporation of a range of different bidentate and monodentate phosphines that are suitable precursors for triphosphine macrocycle syntheses by intramolecular hydrophosphinations. The ability to selectively introduce di-primary phosphines with a mono-tertiary phosphine, or alternatively a di-tertiary phosphine with a mono-primary phosphine, allows the formation of triphosphine macrocycles that bear either secondary or tertiary phosphines and the subsequent opportunity to functionalize these donors with a range of substituents. This template also allows the manipulation of the steric bulk of the spectator cyclopentadienyl group (and consequential influences) by variation of its substituents. Increasing steric bulk has a significant influence upon both the rates of ring closure reactions and yields of products. In circumstances where the ring closure reaction has a choice of P−C bonds it may form (e.g., in the intramolecular hydrophosphination of P-allyl substituents), increasing the steric bulk of the Cp ligand increases the selectivity for the formation of the smaller ring alternative. In the cyclopentadienyliron template system, control of both of these variables (choice of precursor phosphines, choice of Cp derivatives) is facile and appropriate combinations lead to a wide range of triphosphine macrocycles from 9- to 12-membered rings and with a range of secondary and tertiary alkyl or aryl phosphine donors.

Experimental Section

The syntheses of the complexes were performed under nitrogen using standard Schlenk line techniques. All solvents were freshly distilled from sodium (toluene), sodium/benzophenone (THF), or calcium hydride (acetonitrile and 1,2-dichloroethane) under nitrogen before use. The ^{31}P NMR spectra were recorded on Jeol FX90Q, Jeol Eclipse 300, and Bruker AMX360 spectrometers operating at 36.23, 121.7, and 145.8 MHz, respectively, and referenced to 85% H_3PO_4 ($\delta = 0$ ppm). ^{1}H (400.13 MHz) and ^{13}C{^{1}H} (100 MHz) NMR spectra were obtained using a Bruker DPX400 spectrometer and referenced to tetramethylsilane ($\delta = 0$ 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. [(η^5-Me_3SiCp)Fe(CO)$_2$(MeCN)]PF_6 and related precursor complexes were prepared as detailed previously.[6c]

(Acetonitrile)(η^5-trimethylsilylcyclopentadienyl){1,3-bis(phosphino)propane}iron(II) Hexafluorophosphate, 1. A solution of [(η^5-Me_3SiCp)Fe(CO)$_2$(MeCN)]PF_6 (1.0 g, 2.3 mmol) in acetonitrile (100 mL) was irradiated for 24 h using a 125 W Hanovia UV lamp. The dark brown solution was filtered and a 10% w/v solution of 1,3-bis(phosphino)propane in toluene (2.7 mL, 2.3 mmol) added thereto. After stirring overnight, the solvent was removed in vacuo and the orange residue washed with diethyl ether and recrystallized from acetonitrile. Yield: 0.92 g (82%). ^{31}P{^{1}H} NMR {145.8 MHz, $(CD_3)_2CO$, 20 °C }: δ −30.4 (s) ppm. ^{1}H NMR {400 MHz, $(CD_3)_2$-CO, 20 °C}: δ 5.06 (d br, $^1J_{H,P} = 330$ Hz, 4H, PH_2), 4.83 (br, 2H, Cp-H), 4.29 (br, 2H, Cp-H), 2.43 (s, 3H, CH_3CN), 1.12 (t br, 4H, CH_2PH_2), 0.32 (s, 9H, $SiCH_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 20 °C): δ 134.9 (s, C), 92.6 (s, C), 81.7 (s, C), 75.5 (s, C), 22.9 (s, CH_3) 13.9 (t, $^2J_{C,P} = 18.5$ Hz, CH_2), 4.5 (d, $^1J_{C,P} = 31.5$ Hz, CH_2), 0.03 (s, CH_3) ppm. The compound failed to give acceptable mass spectroscopic and analytical data and was used in subsequent reactions as isolated.

(η^5-Trimethylsilylcyclopentadienyl)(1-vinyl-1,4,8-triphosphacyclodecane)iron(II) Hexafluorophosphate, 4. A solution of **1** (1.0 g, 2.05 mmol) in a 1:1 mixture of chlorobenzene and 1,2-dichloroethane (100 mL) was added to 2.3 mL (1 molar equiv) of a 10% w/v solution of trivinylphosphine in toluene followed by triethylamine (2 mL). The solution was heated to 70 °C and held at this temperature for 48 h. The yellow solution was filtered, the solvent removed in vacuo, and the residue extracted with ethanol (2 × 50 mL). Removal of the ethanol gave the desired compound as a bright yellow solid. Yield: 550 mg (51%). ^{31}P{^{1}H} NMR {36.23 MHz, $(CD_3)_2CO$, 20 °C}: δ 126.9 (t, $^2J_{P,P} = 33$ Hz), 56.0 (d, $^2J_{P,P} = 33$ Hz) ppm. ^{1}H NMR {400 MHz, $(CD_3)_2CO$, 20 °C}: δ 6.81 (m, 1H, CH:CH_2), 6.15 (dd, $^3J_{H,P} = 34.7$ Hz, $^3J_{H,H} = 12.7$ Hz, 1H, CH:CH_2), 5.98 (t, $^3J_{H,P}$, $^3J_{H,H} = 18.5$ Hz, 1H, CH:CH_2), 5.98 (d br, 364 Hz, 2H, PH), 4.76 (br, 2H, Cp-H), 4.61 (br, 2H, Cp-H), 2.6−2.4 (m, 8H, CH_2), 2.2−2.0 (m, 4H, CH_2), 1.48 (t, 2H, CH_2), 0.11 (s, 9H, $SiCH_3$) ppm. ^{13}C{^{1}H} NMR {100 MHz, $(CD_3)_2$-CO, 20 °C}: δ 135.8 (d, $^1J_{C,P} = 36.0$ Hz, CH:CH_2), 127.9 (s, CH:CH_2), 97.6 (d, $^2J_{C,P} = 5.0$ Hz, CH), 86.8 (d, $^2J_{C,P} = 5.0$ Hz, CH), 82.5 (s, CH), 31.2 (d, $^1J_{C,P} = 27.7$ Hz, CH_2), 21.0 (t, $^{1,2}J_{C,P} = 15.0$ Hz, CH_2), 19.4 (m, CH_2), 16.8 (s, CH_2), 0.05 (s, CH_3Si) ppm. MS (APCI), *m*/*z*: 413 (100) [{η^5-(Me_3Si)Cp}FeL]$^+$. Anal. Calcd for $C_{17}H_{32}P_4F_6SiFe$ (%): C, 36.57; H, 5.79. Found: C, 36.6; H, 5.8. IR (KBr): 2325 m (ν_{PH}).

(η^5-Trimethylsilylcyclopentadienyl)(1-ethyl-1,4,8-triphosphacyclodecane)iron(II) Hexafluorophosphate, 5. To a solution of **4** (0.556 g, 1.0 mmol) in ethanol (150 mL) was added 50 mg of palladium on carbon (10%) catalyst, and the mixture was stirred vigorously at room temperature. A stream of hydrogen gas was bubbled at a low rate through the solution. The progress of the reaction was monitored using ^{31}P{^{1}H} NMR spectroscopy. After completion of the reaction (determined by complete loss of the ^{31}P resonance at δ_P 126.9 ppm and concomitant appearance of a peak at δ_P 137.1 ppm), the solution was filtered to remove the catalyst, and the solvent was removed under reduced pressure. Yield of **3**: 0.55 g, 1.0 mmol. ^{31}P{^{1}H} NMR {36.23 MHz, $(CD_3)_2CO$, 20 °C}: δ 137.3 (t, $^2J_{P,P} = 32$ Hz), 56.4, (d, $^2J_{P,P} = 32$ Hz), ^{1}H NMR {400 MHz, $(CD_3)_2CO$, 20 °C}: δ 5.94 (d, br, $^1J_{H,P} = 352$ Hz), 4.82 (d, $^3J_{H,P} = 1.9$ Hz, 2H, CpH), 4.65 (d, $^3J_{H,P} = 1.9$ Hz, 2H, CpH), 2.49−2.23 (m, CH_2, 8H), 1.91, (m, CH_2CH_3), 1.76−1.63 (m, CH_2, 4H), 1.33 (m, CH_3), 0.30 (s, CH_3, 9H). ^{13}C{^{1}H} NMR {100 MHz, $(CD_3)_2$-CO, 20 °C}: δ 88.1 (s, CH), 78.6 (s, CH), 24.2 (d, $^1J_{C,P} = 24.2$ Hz, CH_2), 21.1 (t, $^{1,2}J_{C,P} = 14.1$ Hz, CH_2), 19.6 (m, CH_2), 16.9 (s, CH_2), 8.7 (d, $^1J_{C,P} = 8.0$ Hz, CH_2), 7.0 (s, CH_3), 0.02 (s, CH_3Si) ppm. MS (APCI), *m*/*z*: 415 (20) [{η^5-(Me_3Si)Cp}FeL]$^+$. Anal. Calcd for $C_{17}H_{34}P_4F_6SiFe$ (%): C, 36.44; H, 6.13. Found: C, 36.1; H, 6.0. IR (KBr): 2319 m (ν_{PH}).

(η^5-Trimethylsilylcyclopentadienyl)(1,4,8-triethyl-1,4,8-triphosphacyclodecane)iron(II) Hexafluorophosphate, 6. A solution of **5** (0.5 g, 8.9×10^{-4} mol) in 20 mL of THF was cooled to −78 °C and stirred. To this yellow solution was added potassium *tert*-butoxide (0.2 g, 1.78 mmol) and stirred at this temperature for 10 min until the solution had deepened to a red color. The solution was then allowed to warm to room temperature while stirring, after

which time it was cooled again to −78 °C, and bromoethane (0.2 mL, 2.68 mmol) was added. The mixture was allowed to warm to room temperature and stirred overnight. The yellow-brown solution was filtered and washed with THF, and the solvent was removed in vacuo. The brown solid was redissolved in dichloromethane and column chromatographed on neutral alumina, the yellow fraction being collected and the solvent removed in vacuo. Crystals suitable for X-ray crystallography were grown from cooling a solution of the complex in methanol. Yield: 66 mg (12%). $^{31}P\{^1H\}$ NMR {36.23 MHz, $(CD_3)_2CO$, 20 °C}: δ 134.7 (t, $^2J_{P,P} = 36$ Hz), 84.7 (d, $^2J_{P,P} = 36$ Hz) ppm. ^1H NMR (300 MHz, $CDCl_3$, 20 °C): δ 4.39 (br, 2H, CpH), 4.24 (br, 2H, CpH), 2.6−2.0 (m, 8H), 2.0−1.5 (m, 7H), 1.4−0.9 (m, 12H), 0.24 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$, 20 °C): δ 91.0 (s, CH), 74.9 (s, CH), 30.4 (dd, $^1J_{C,P} = 30$ Hz, $^2J_{C,P} = 3.7$ Hz, CH_2), 27.5 (t, $^{1,2}J_{C,P} = 13.9$ Hz, CH_2), 26.7 (t, $^{1,2}J_{C,P} = 13.9$ Hz, CH_2), 25.1 (d, $^1J_{C,P} = 27.8$ Hz, CH_2), 22.6 (q, $^{1,2}J_{C,P} = 13.9$ Hz, CH_2), 18.8 (s, CH_2), 9.4 (d, $^2J_{C,P} = 8.3$ Hz, CH_3), 8.39 (s, CH_3), 0.94 (s, CH_3) ppm. MS (APCI), *m*/*z*: 471 (100) [{η^5-(Me_3Si)Cp}FeL]$^+$. Anal. Calcd for $C_{21}H_{42}P_4F_6SiFe$ (%): C, 40.91; H, 6.88. Found: C, 40.9; H, 6.8. IR (KBr): 2316 m (ν_{PH}).

(η^5-Pentamethylcyclopentadienyl)(diallylphenylphosphine)-(1,2-diphosphino-ethane)iron(II) Tetrafluoroborate, 8a. To a solution of **7**[6b] (1.0 g, 2.42 mmol) in 1,2-dichloroethane (50 mL) was added diallylphenylphosphine (0.5 mL, 2.55 mmol), and the mixture was heated at 80 °C for 2 h. After cooling, the solvent was evaporated in vacuo to give a dark yellow oil, which was used without further purification in the synthesis of **10a**. Yield: 1.35 g (99%). $^{31}P\{^1H\}$ NMR (36.23 MHz, CH_2Cl_2): δ 45.4 (t, $^2J_{P,P} = 51$ Hz), 11.9 (d, $^2J_{P,P} = 51$ Hz) ppm.

***rac*-(η^5-Pentamethylcyclopentadienyl)(1-phenyl-3-methyl-1,4,7-triphospha-cyclodecane)iron(II) Hexafluorophosphate, 10a.** A solution of **8a** (1.35 g, 2.41 mmol) in toluene (200 mL) containing azoisobutyronitrile (∼0.2 g) was heated at 90 °C for 8 h. After cooling, volatile materials were removed in vacuo, and the dark residue was dissolved in a small quantity of dichloromethane and applied to a basic alumina column (5 × 3.5 cm). The desired compound was eluted as a yellow band with 0.5% methanol in CH_2Cl_2 as eluant. The solution was dried over $MgSO_4$ and filtered, and the volatiles were removed to give an orange solid. This was dissolved in methanol (5 mL) and solid ammonium hexafluorophosphate (300 mg) added thereto. After leaving at 4 °C overnight yellow acicular crystals of **10a** had precipitated. These were filtered off, washed sparingly with cold methanol, and dried in vacuo. Yield: 500 mg (33%). $^{31}P\{^1H\}$ NMR {36.23 MHz, $CDCl_3$, 20 °C}: δ 111.7 (t, $^2J_{P,P} = 25$ Hz), 65.7 (dd, $^2J_{P,P} = 54$, 25 Hz), 61.7 (dd, $^2J_{P,P} = 54$, 25 Hz) ppm. ^1H NMR {400 MHz, $CDCl_3$, 20 °C}: δ 7.38 (m, 3H, Ph), 7.22 (t, $^3J_{H,H} = 6.1$ Hz, 2H, Ph), 5.32 (d br, $^1J_{H,P} = 342$ Hz, 1H, PH), 5.15 (d br, $^1J_{H,P} = 339$ Hz, 1H, PH), 2.8−1.6 (m, 10H), 1.46 (dd, $^3J_{H,P} = 12.2$ Hz, $^3J_{H,H} = 7.2$ Hz, 3H, CH_3), 1.39 (s, 15H, $CpCH_3$), 1.3−0.8 (m, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 20 °C): δ 138.0 (d, $^1J_{C,P} = 27.3$ Hz, C), 130.6 (d, $^2J_{C,P} = 7.8$ Hz, CH), 130.3 (s, CH), 129.2 (d, $^3J_{C,P} = 8.0$ Hz, CH), 89.0 (s, C), 38.4 (dd, $^1J_{C,P} = 20.3$ Hz, $^2J_{C,P} = 15.4$ Hz, CH_2), 36.4 (dd, $^1J_{C,P} = 26.9$ Hz, $^2J_{C,P} = 14.4$ Hz, CH), 25.0 (dd, $^1J_{C,P} = 28.0$ Hz, $^2J_{C,P} = 6.9$ Hz, CH_2), 22.5 (dd, $^1J_{C,P} = 26.8$ Hz, $^2J_{C,P} = 17.1$ Hz, CH_2), 19.6 (t, $^{1,2}J_{C,P} = 13.7$ Hz, CH_2), 19.4 (t, $^{1,2}J_{C,P} = 14.0$ Hz, CH_2), 18.4 (dd, $^3J_{C,P} = 15.9$ Hz, $^2J_{C,P} = 7.1$ Hz, CH_3), 18.1 (s, CH_2), 10.1 (s, CH_3). MS (APCI), *m*/*z*: 475 (100) [(η^5-C_5Me_5)FeL]$^+$. Anal. Calcd for $C_{24}H_{38}P_4F_6Fe$ (%): C, 46.46; H, 6.19. Found: C, 46.0; H, 6.3. IR (KBr): 2316 m (ν_{PH}).

***rac*-(η^5-Pentamethylcyclopentadienyl)(1-benzyl-3-methyl-1,4,7-triphospha-cyclodecane)iron(II) Hexafluorophosphate, 10c.** To a solution of **7** (600 mg, 1.47 mmol) in 1,2-dichloroethane (10 mL) was added benzyldiallylphosphine (0.35 mL, 1.71 mmol), and the solution was heated at 70 °C for 3 h. After cooling, the mixture was filtered and the solvents were removed in vacuo to give **8b** as a dark yellow solid. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 36.23 MHz): δ 46.1 (t, 53 Hz)), 13.2 (d, 53 Hz) ppm. The dry solid was dissolved in toluene (200 mL) containing AIBN (50 mg), and the mixture was heated at 80 °C for 72 h. The volatile materials were removed in vacuo, and the dark residue was dissolved in a small quantity of dichloromethane and applied to a basic alumina column (1 × 10 cm). After washing the column with dichloromethane (100 mL), a mixture of the desired compound and some minor unknowns was eluted as a yellow band with 0.2% methanol in CH_2Cl_2 as eluant. The resultant yellow solid was rechromatographed as above to give the pure complex, which was converted to the hexfluorophosphate salt by dissolution in methanol (2 mL) and addition of solid ammonium hexafluorophosphate (300 mg). After adding 0.2 mL of water, the solution was left at 4 °C overnight to give yellow **10b** as a microcystalline solid, which was filtered, washed sparingly with cold aqueous methanol, and dried in vacuo. Yield: 200 mg (33%). $^{31}P\{^1H\}$ NMR (145.8 MHz, $CDCl_3$, 20 °C): δ 114.8 (t, $^2J_{P,P} = 30$ Hz), 68.1 (dd, $^2J_{P,P} = 54$, 26 Hz), 66.8 (dd, $^2J_{P,P} = 54$, 30 Hz) ppm. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.32 (t, $^3J_{H,H} = 7.1$ Hz, 2H, Ph), 7.27 (d, $^3J_{H,H} = 7.1$ Hz, 1H, Ph), 6.92 (d, $^3J_{H,H} = 7.1$ Hz, 2H, Ph), 5.17 (d br, $^1J_{H,P} = 340$ Hz, 1H, PH), 5.15 (d br, $^1J_{H,P} = 350$ Hz, 1H, PH), 3.16 (dd, $^2J_{H,H} = 14.2$ Hz, $^2J_{H,P} = 5.4$ Hz, 1H, $PhCH_2$), 2.87 (dd, $^2J_{H,H} = 14.2$ Hz, $^2J_{H,P} = 5.4$ Hz, 1H, $PhCH_2$), 2.7−0.2 (m, 13H), 1.73 (s, 15H, $CpCH_3$), 1.36 (dd, $^3J_{H,P} = 12.2$ Hz, $^3J_{H,H} = 5.0$ Hz, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 20 °C): δ 134.3 (d, $^2J_{C,P} = 7.0$ Hz, C), 130.6 (s, CH), 129.7 (s, CH), 127.8 (s, CH), 127.8 (s, CH), 89.4 (s, C), 37.0 (dd, $^1J_{C,P} = 8.9$ Hz, $^2J_{C,P} = 6.3$ Hz, CH_2), 34.5 (dd, $^1J_{C,P} = 27.9$ Hz, $^2J_{C,P} = 16.2$ Hz, CH), 30.0 (dd, $^1J_{C,P} = 28.3$ Hz, $^2J_{C,P} = 14.3$ Hz, CH_2), 22.7 (dd, $^1J_{C,P} = 25.7$ Hz, $^2J_{C,P} = 7.0$ Hz, CH_2), 22.3 (dd, $^1J_{C,P} = 22.9$ Hz, $^2J_{C,P} = 6.4$ Hz, CH_2), 20.0 (dd, $^1J_{C,P} = 30.1$ Hz, $^2J_{C,P} = 17.0$ Hz, CH_2), 19.6 (dd, $^1J_{C,P} = 26.9$ Hz, $^2J_{C,P} = 7.2$ Hz, CH_2), 18.7 (s, CH_2), 18.1 (dd, $^3J_{C,P} = 16.9$ Hz, $^2J_{C,P} = 6.9$ Hz, CH_3), 10.4 (s, CH_3) ppm. MS (APCI), *m*/*z*: 475 (100) [(η^5-C_5Me_5)FeL]$^+$. Anal. Calcd for $C_{24}H_{38}P_4F_6Fe$ (%): C, 46.46; H, 6.19. Found: C, 46.0; H, 6.3. IR (KBr): 2316 m (ν_{PH}).

***rac*-(η^5-Pentamethylcyclopentadienyl)(4,7-dichloro-1-phenyl-3-methyl-1,4,7-triphosphacyclodecane)iron(II) Hexafluorophosphate, 11a.** A solution of **10a** (50 mg, 8.1 × 10^{-5} mol) in dichloromethane (5 mL) was stirred with a 10% aqueous solution of sodium hydroxide for 1 h. The organic phase was isolated, washed with water (3 × 2 mL), and dried over $MgSO_4$. After filtering, the solvent was removed to yield an orange solid. Yield: 95%. $^{31}P\{^1H\}$ NMR (145.8 MHz, $CDCl_3$, 20 °C): δ 222.6 (dd, $^2J_{P,P} = 8.2$, 6.0 Hz), 202.5 (dd, $^2J_{P,P} = 13.8$, 8.2 Hz), 59.8 (dd, $^2J_{P,P} = 13.8$, 6.0 Hz) ppm. ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ 7.41 (t, $^3J_{H,H} = 7.1$ Hz, 2H, Ph), 7.21 (d, $^3J_{H,H} = 7.1$ Hz, 2H, Ph), 7.10 (d, $^3J_{H,H} = 7.1$ Hz, 1H, Ph), 3.3−1.2 (m, 13H), 1.54 (dd obs, $^3J_{H,P} = 14.0$ Hz, $^3J_{H,H} = 6.8$ Hz, 3H, CH_3), 1.46 (s, 15H, $CpCH_3$) ppm. MS (APCI), *m*/*z*: 509 (75) [(η^5-C_5Me_5)FeL − Cl]$^+$. Anal. Calcd for $C_{24}H_{36}P_4Cl_2F_6Fe$ (%): C, 41.82; H, 5.28. Found: C, 42.0; H, 5.3.

***rac*-(η^5-Pentamethylcyclopentadienyl)(4,7-dichloro-1-benzyl-3-methyl-1,4,7-triphosphacyclodecane)iron(II) Hexafluorophosphate, 11b.** A solution of **10b** (50 mg, 8.1 × 10^{-5} mol) in dichloromethane (5 mL) was stirred with a 10% aqueous solution of sodium hydroxide for 1 h. The organic phase was isolated, washed with water (3 × 2 mL), and dried over $MgSO_4$. After filtering, the solvent was removed to yield an orange solid. Yield: 92%. $^{31}P\{^1H\}$ NMR (145.8, $CDCl_3$, 20 °C): δ 220.3 (dd, $^2J_{P,P} = 15.8$, 8.1 Hz), 203.5 (dd, $^2J_{P,P} = 19.0$, 8.1 Hz), 57.0 (dd, $^2J_{P,P} = 19.0$, 15.8 Hz) ppm. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.30 (t, $^3J_{H,H} = 7.1$ Hz, 2H, Ph), 7.25 (d, $^3J_{H,H} = 7.1$ Hz, 1H, Ph), 6.94 (d, $^3J_{H,H} = 7.1$ Hz, 2H, Ph), 3.29 (dd, $^2J_{H,H} = 14.4$ Hz, $^2J_{H,P} = 6.2$ Hz, 1H, $PhCH_2$), 2.93 (dd, $^2J_{H,H} = 14.4$ Hz, $^2J_{H,P} = 6.2$ Hz, 1H, $PhCH_2$), 2.7−0.2 (m, 13H), 1.82 (s, 15H, $CpCH_3$), 1.47 (dd, $^3J_{H,P} = 14.0$ Hz, $^3J_{H,H} = 7.1$ Hz, 3H, CH_3). MS (APCI), *m*/*z*: 524 (80) [(η^5-

Table 1. X-ray Data Collection and Refinement Parameters.

	6	10a	14
empirical formula	$C_{21}H_{42}P_4F_6SiFe$	$C_{24}H_{38}F_6P_4Fe$	$C_{25}H_{36}P_4F_6Fe$
fw	616.37	620.27	630.27
temp, K	293	293	150
cryst syst	monoclinic	hexagonal	orthorhombic
space group	$P2(1)/n$	$R\bar{3}$	$P2(1)2(1)2(1)$
a/Å	10.9946(5)	42.467(6)	9.0310(2)
b/Å	16.3024(7)	42.467(6)	15.2330(3)
c/Å	16.0530(7)	9.690(2)	19.7330(4)
β/deg	102.311(2)		
γ/deg		120	
U/Å^3	2811.1(2)	15134(4)	2714.65(10)
Z	4	18	4
D_c/Mg m^{-3}	1.456	1.225	1.542
F(000)	1288	5796	1304
cryst size/mm	0.15 × 0.15 × 0.10	0.25 × 0.20 × 0.16	0.05 × 0.10 × 0.15
θ range/deg	3.13 to 25.45	2.17 to 27.50	3.65 to 27.48
index ranges	$-13 \le h \le 13$, $-19 \le k \le 19$, $-18 \le l \le 19$	$-54 \le h \le 52$, $-54 \le k \le 48$, $-12 \le l \le 12$	$-11 \le h \le 11$, $-19 \le k \le 19$, $-25 \le l \le 25$
no. of reflns collected	17 383	28 355	27 972
no. of indep reflns	5143	7692	6202
R_{int}	0.1584	0.0939	0.0826
no. of data/restraints/params	5143/0/304	7692/71/363	6202/0/326
absorp corr, μ	0.856	0.683	0.847
goodness of fit on F^2	1.061	1.080	1.065
final R1, wR2 [$I > 2\sigma(I)$]	0.0591, 0.1183	0.0771, 0.2155	0.0403, 0.0875
(all data)	0.0814, 0.1290	0.1045, 0.2286	0.0602, 0.0955
largest diff peak and hole/e Å^{-3}	0.754 and −0.522	1.404 and −0.757	0.427 and −0.338

C_5Me_5)FeL − Cl]$^+$. Anal. Calcd for $C_{25}H_{38}P_4Cl_2F_6Fe$ (%): C, 42.69; H, 5.46. Found: C, 42.2; H, 5.3.

(Acetonitrile)(η^5-cyclopentadienyl){1,2-bis(diallylphosphino)-ethane}iron(II) Hexafluorophosphate, 12. To a solution of [(η^5-C_5H_5)Fe(η^6-C_6H_6)]PF_6 (1 g, 2.92 mmol) in acetonitrile (100 mL) was added 1,2-bis(diallylphosphino)ethane (0.74 g, 2.92 mmol), and the solution was irradiated for 12 h using a 100 W visible lamp. The solvent was removed in vacuo to give the desired compound as a red solid. Yield: 1.99 g (82%). $^{31}P\{^1H\}$ NMR (145.8 MHz, CD_3CN, 20 °C): δ 89.3 (s) ppm. ^1H NMR (400 MHz, CD_3CN, 20 °C): δ 5.90 (m, 4H, CH:CH_2), 5.20 (m, 8H, CH:CH_2), 4.39 (s br, CpH), 2.30 (s, CH_3CN), 2.80 (m, 4H, CH_2), 1.70 (m, 8H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, 20 °C): δ 130.2 (m, CH:CH_2), 118.4 (d, CH:CH_2), 32.7 (m, CH_2), 30.4 (m, CH_2), 22.4 (m, CH_2) ppm. MS (APCI), m/z: 375 (50) [(η^5-Cp)FeL − MeCN]$^+$. IR (KBr): 2278 cm^{-1} (ν_{CN}).

(η^5-Cyclopentadienyl)(1-phenyl-5,8-diallyl-1,5,8-triphosphacycloundecane)-iron(II) Hexafluorophosphate, 14. To a solution of **12** (0.60 g, 1.07 mmol) in dichloromethane (50 mL) was added phenylphosphine (0.12 g, 1.07 mmol), and the red solution was stirred at room temperature for 2 weeks. The yellow solution was evaporated to dryness in vacuo to give a yellow solid, which was recrystallized from THF. Yield: 35 mg (5%). $^{31}P\{^1H\}$ NMR (121.7 MHz, CD_3CN, 20 °C): δ 81.0 (d, $^2J_{P,P}$ = 63 Hz), 37.9 (t, $^2J_{P,P}$ = 63 Hz) ppm. ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ 7.58 (m, 3H, Ph), 7.46 (m, 2H, Ph), 5.90 (m, 2H, CH:CH_2), 5.21 (m, 4H, CH:CH_2), 4.20 (s br, 5H, Cp-H), 2.8 (m, 8H, CH_2), 2.7 (m, 4H, CH_2), 2.2 (m, 4H, CH_2), 1.8 (m, 4H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, 20 °C): δ 143.4 (d, C), 130.5 (s, CH), 129.5 (s, CH), 128.6 (s, CH), 128.0 (m, CH:CH_2), 118.0 (m, CH:CH_2), 81.0 (s, C), 37.4 (m, CH_2), 27.3 (m, CH_2), 25.9 (m, CH_2), 24.4 (m, CH_2), 18.8 (m, CH_2) ppm. MS (APCI), m/z: 485 (100) [(η^5-Cp)FeL]$^+$.

X-ray Crystallography. Crystallographic measurements were performed on a Bruker Nonius kappa CCD area detector using monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-96)[10] and refined on F_o^2 by full-matrix least-squares (SHELXL-97)[11] using all the unique data. Empirical absorption corrections were carried out by the XABS[12] and DIFABS[13] methods. The non-hydrogen atoms were refined anisotropically. Figures were produced using ORTEP-3 for Windows version 1.08[14] and PovRay for Windows version 3.5.[15] The crystal data and refinement details are summarized in Table 1.

Acknowledgment. We thank the EPSRC for funding (GR/N06076/01, A.R.B.) and studentship support (R.H., S.M.L.).

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

OM060798G

(10) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
(11) Sheldrick, G. M. *SHELX-97*, program for crystal structure refinement; University of Gottingen: Germany, 1997.
(12) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.
(13) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.
(14) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.
(15) *Persistence of Vision Raytracer*; Pty Ltd; Williamstown, Victoria, Australia, HTTP://www.povray.org.