Iron complexes of facially capping triphosphorus macrocycles

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Primary and secondary phosphine piano-stool complexes of the type $[\eta^5\text{-CpFeL}_3]^+$ (L = phenylphosphine, **3**, (α-methyl)vinylphosphine, **4**, allylphosphine, **5**, (2-methylpropenyl)phosphine, **5b**, allyl(phenyl)phosphine, **6**) are described. The alkenyl phosphine complexes, **5** and **6**, react by intramolecular hydrophosphination to give the corresponding $[\eta^5\text{-CpFe}]^+$ complexes of 1,5,9-triphosphacyclododecane (12-aneP_3R_3, **2**, R = H), **9** and **10** respectively. Alkylation of the secondary phosphines in **9** is achieved by hydrophosphinations with ethene to give the 12-aneP_3R_3 (R = Et) derivative **11**. These complexes are also obtained by reaction of suitable $[\eta^5\text{-CpFe}]^+$ containing precursor complexes with the corresponding free 12-aneP_3R_3 macrocycle as is the related $[\eta^5\text{-Cp*Fe}]^+$ derivative, **8**. Direct substitution of acetonitrile in $[Fe(CH_3CN)_6][BF_4]_2$ by 12-aneP_3Et_3, leads to the macrocycle piano-stool complex, $[(12\text{-ane}P_3Et_3)Fe(CH_3CN)_3][BF_4]_2$, **7**. The crystal structures of selected primary phosphine, η^5-Cp, η^5-Cp* complexes and **7**, allow a comparison of steric influences upon key macrocycle ring closure reactions and hence an insight into parameters required for the formation of smaller ring sizes by template based methods.

Introduction

Triphosphorus macrocycles provide the opportunity to facially co-ordinate a metal forming a complex where the remaining co-ordination sites will be mutually *cis* to each other as well as *trans* to the good *trans* labilising phosphines. The macrocycle–metal unit may also be expected to be relatively resistant to phosphine dissociation in comparison to analogues with acyclic or monodentate phosphine ligands. These features are of interest in the stabilisation of new classes of complexes of phosphorus ligands as well as in applications such as catalysis. Currently, however, there are only two triphosphorus macrocyclic ligand systems known as the free ligands. The first reported is the 11-membered triphosphine (**1**, Fig. 1) prepared as a mixture of stereoisomers by a high dilution (non-template) method.[1] We have previously reported the other example,[2] which is based upon the 12-membered symmetrical 1,5,9-triphosphacyclododecane (12-aneP_3R_3, **2**, R = H) structure originally prepared on a Group 6 metal tricarbonyl template by Norman.[3] As well as developing synthetic routes to a range of tertiary phosphine derivatives and stereospecific liberations of the free ligands, we have subsequently studied a range of complexes of 12-aneP_3R_3 (R = alkyl, aryl) ligands including functionalised derivatives (at P, R = pendant amine, ether).[4] The $M(CO)_3$ (M = Mo, W) template has more recently been used by Gladysz in the formation of large ring triphosphorus macrocycles by ring closing metathesis of co-ordinated alkenyl phosphines,[5] and by Driess in the synthesis of the 9-membered triphosphacyclononane with –Si–Si– backbone skeletons.[6] The former is not restricted to facially capping co-ordination modes and would be expected to form less stable complexes due to large, flexible ring sizes and the latter is not expected to be stable under a wide range of conditions due to facile protonolysis of the P–Si bonds. Whereas this template method leads to 12-aneP_3R_3 ligands in good yield and stereospecifically, a major disadvantage is that it has not allowed the synthesis of smaller ring sizes, which may be expected to enhance the robustness of the macrocycle–metal interaction.[7] In view of this limitation, we have continued to investigate alternative template systems that may be amenable to the formation of triphosphorus macrocycles with smaller cavities. As part of this study we have investigated iron(II) complexes of primary phosphines in order to assess their suitability for template assisted phosphine cyclisation reactions. Fe(II) readily forms 'piano-stool' complexes in which three mutually *cis* reaction sites are available in a (distorted) *fac*-octahedral structure. Of interest in this context are complexes of the form $[(\eta^5\text{-Cp}^R)FeL_3]^+$ (R = various alkyl/silyl combinations) for which the syntheses and reactivities have been extensively studied and there are numerous examples of analogous complexes containing tertiary mono-phosphines,[8] diphosphines,[9] triphosphines,[10] and phosphite ligands.[11] These complexes appear to offer advantages over previous templates based upon $M(CO)_3$ (M = Cr, Mo, W) units; three features are of particular interest to us. Firstly, variations in cyclopentadienyl ring substituents are readily achieved and introduce the opportunity to vary the solubility of template precursors as well as the steric influence over the *trans* reaction sites (*e.g.* compressing P–Fe–P angles to predispose the phosphines to form smaller ring sizes or alternatively the introduction of chirality). Selective sequential incorporation of precursor phosphines is known to be facile in these complexes

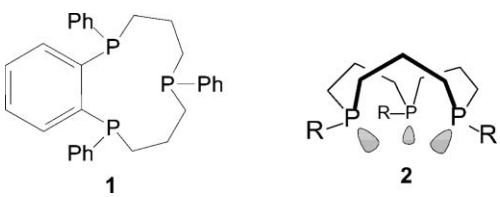

Fig. 1 Previously reported 11-membered (**1**) and 12-membered (**2**, R = H) triphosphorus macrocycles.

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allowing a wide range of precursor complex options including alternative donors, substituents and 'backbone' functions and lastly, the smaller size of Fe(II) (ionic radius 0.76 Å; covalent radius Cr(0) and Mo(0) is 1.17 Å and 1.29 Å respectively) should allow a closer approach of co-ordinated precursor phosphines and a preference for smaller chelate (and hence macrocycle) ring sizes. In addition, the kinetically inert d^6 $[(\eta^5\text{-}Cp^R)Fe]^+$ template should be stable to the conditions of conventional radical or base promoted hydrophosphinations and thus support a range of P–C bond forming reactions. In this context, Wild has demonstrated the deprotonation of co-ordinated phenylphosphine followed by alkylation with bromoethane to give the corresponding co-ordinated ethylphenylphosphine in related $[(\eta^5\text{-}Cp^R)Fe]^+$ complexes.[12]

Further to our report of preliminary results of this study,[13] in this paper, we present and discuss the syntheses of Fe(II) 12-aneP_3R_3 and primary phosphine complexes, their structural properties and their reactivity in template supported intramolecular ring closure reactions, and comparisons with (12-aneP_3R_3)Fe(II) complexes prepared with ligand derived from our previously reported synthesis.

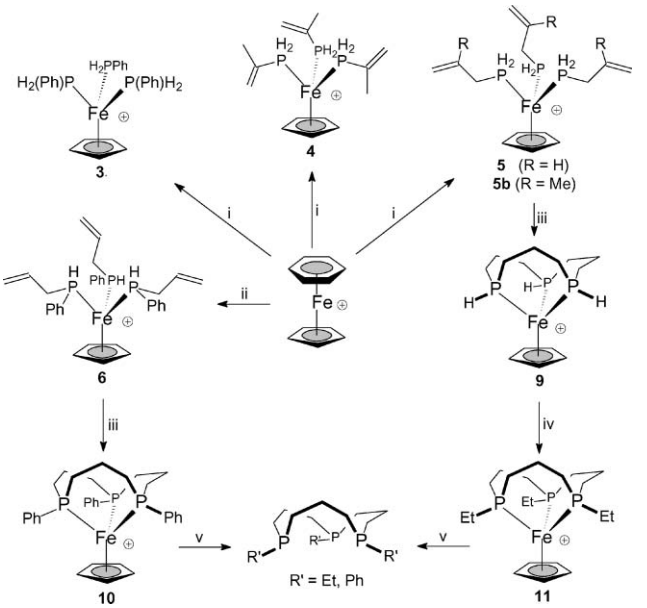
Results and discussion

Primary and secondary phosphine complexes

The photolytic substitution of benzene in (η^5-cyclopentadienyl)-(η^6-benzene)iron(II) hexafluorophosphate by phenylphosphine proceeds smoothly and quantitatively to give the tris-phenylphosphine adduct, $[(\eta^5\text{-}Cp)Fe(PhPH_2)_3]PF_6$, **3**, which was isolated as a light-yellow coloured powder. The ^{31}P NMR spectrum of **3** gives a triplet centred at δ − 10 ppm ($^1J_{P\text{-}H}$ = 344 Hz) corresponding to the co-ordinated phosphines, and the expected septet of the hexafluorophosphate anion centred at δ − 144 ppm ($^1J_{P\text{-}F}$ = 711 Hz). In the ^{1}H NMR spectrum, a quartet assigned to the cyclopentadienyl protons ($^3J_{P\text{-}H}$ = 2 Hz) is observed as well as resonances assigned to phenyl protons and P–H protons (δ 5.69 ppm, d, $^3J_{P\text{-}H}$ = 344 Hz) in the expected area ratios. A strong peak ($\nu_{(P\text{-}H)}$) is observed in the IR spectrum of **3**, at 2314 cm^{-1} and the mass spectrum shows a strong molecular ion $[(M - PF_6)^+$, 451, 100%]. The hexafluorophosphate salt, **3**, has a molar conductivity of 25 Ω cm^2 mol^{-1} in CH_2Cl_2 solution, suggesting a 1 : 1 electrolyte.

In a similar fashion, photolysis of a dichloromethane suspension of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)][PF_6]$ (Scheme 1) and excess (α-methyl)vinylphosphine gave a deep-orange homogeneous solution from which the product $[(\eta^5\text{-}C_5H_5)Fe(H_2PC_3H_5)_3][PF_6]$, **4**, was isolated. The tris-phosphine complex **4** gives a singlet and a septet in the $^{31}P\{^1H\}$ NMR spectrum, at δ − 4.42 ppm (co-ordinated phosphines) and δ − 144 ppm (PF_6^-, $^1J_{P\text{-}F}$ = 711 Hz) respectively. In the ^{31}P NMR spectrum, the co-ordinated phosphines give rise to a triplet ($^1J_{P\text{-}H}$ = 336 Hz). In the ^{1}H NMR spectrum, cyclopentadienyl and P–H protons give rise to a quartet (δ 4.54 ppm, $^3J_{P\text{-}H}$ = 2 Hz) and a doublet (δ 5.16 ppm, $^1J_{P\text{-}H}$ = 336 Hz) respectively; two further resonances (δ 1.95, δ 5.45 ppm) are in the appropriate area ratio and are assigned to the vinyl-methyl and methylene protons respectively.

The IR spectrum of **4** shows a strong, sharp absorption corresponding to ν(P–H) at 2319 cm^{-1}, and the mass-spectrum shows a decomposition pattern relating to $[(M - PF_6)^+$, 343, 75%], $[(M - H_2PC_3H_5 - PF_6)^+$, 269, 100%] and $[(M - 2\{H_2PC_3H_5\} - PF_6)^+$, 195, 8%], indicating that the cation sequentially loses phosphine ligands. Complex **4** is a conductor in CH_2Cl_2 solution (Λ_M = 14 Ω cm^2 mol^{-1}) based upon a mono-nuclear cation and consistent with a 1 : 1 electrolyte.



Scheme 1 Reagents and conditions: i) H_2PR, CH_2Cl_2, *hv*; ii) $HPRR'$, CH_2Cl_2, *hv*; iii) AIBN, C_6H_5Cl, 90 °C; iv) C_2H_4 (3 atm), AIBN, C_6H_5Cl, 90 °C; v) Na, NH_3(l).

Crystallisation of **4** from an acetonitrile/diethyl ether mixture gave X-ray diffraction quality crystals. The (α-methyl)vinylphosphine complex **4** is the only structurally characterised complex containing three co-ordinated primary phosphines on a $CpFe^+$ fragment; its molecular structure is shown in Fig. 2.

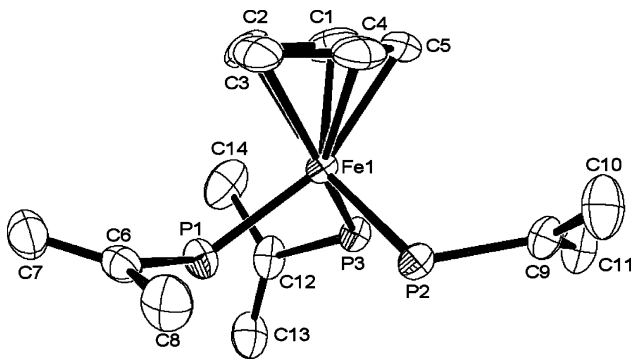


Fig. 2 The molecular structure of the cation in (η^5-cyclopentadienyl)-tris(α-methylvinylphosphine)iron(II) hexafluorophosphate, **4**. Selected bond lengths (Å) and angles (°): Fe(1)–C(4), 2.077(5); Fe(1)–C(3), 2.079(5); Fe(1)–C(1), 2.079(5); Fe(1)–C(2), 2.083(5); Fe(1)–C(5), 2.079(5); Fe(1)–P(2), 2.162(1); Fe(1)–P(3), 2.175(1); Fe(1)–P(1), 2.176(1); C(6)–C(7), 1.329(8); C(6)–C(8), 1.496(8); C(9)–C(10), 1.321(8); C(9)–C(11), 1.492(7); C(12)–C(13), 1.313(8); C(12)–C(14), 1.504(8). P(2)–Fe(1)–P(3), 91.74(5); P(2)–Fe(1)–P(1), 93.61(6); P(3)–Fe(1)–P(1), 90.35(6); C(6)–P(1)–Fe(1), 121.50(2); C(9)–P(2)–Fe(1), 117.20(2); C(12)–P(3)–Fe(1), 117.82(2).

The photolytic substitution of co-ordinated benzene in $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)][PF_6]$ by three equivalents of allylphosphine gives (η^5-cyclopentadienyl)tris(allylphosphine)iron(II) hexafluorophosphate, **5**, as an orange/yellow solid in quantitative yield.

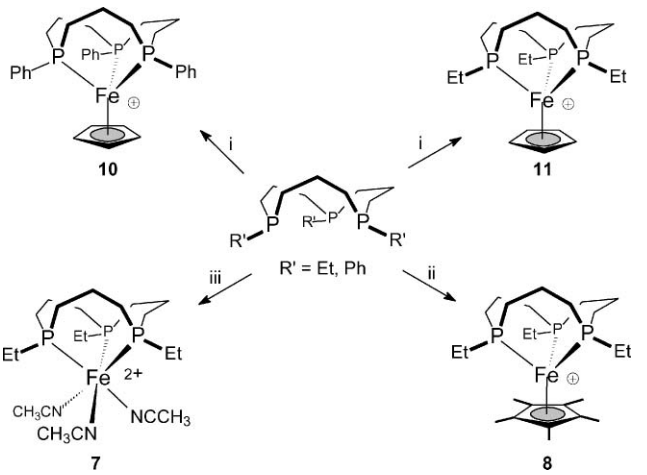
The ^{31}P NMR spectrum shows a triplet (co-ordinated allylphosphine, $^{1}J_{P\text{–}H}$ = 328 Hz) at δ − 9.05 ppm and a septet (PF_6^-, $^{1}J_{P\text{–}F}$ = 711 Hz) at δ − 144 ppm. As with compounds **3** and **4** the ^{1}H NMR spectrum of **5** has a similar quartet, due to the cyclopentadienyl protons ($^{3}J_{P\text{–}H}$ = 2 Hz) and a doublet due to the P–H protons ($^{1}J_{P\text{–}H}$ = 328 Hz); the allyl protons give rise to three poorly resolved resonances at δ 2.54, δ 5.20 and δ 5.82 ppm in a ratio of 2 : 1 : 2. The IR spectrum of **5** shows a sharp, strong peak at 2319 cm^{-1} corresponding to $\nu_{(P\text{–}H)}$, and the mass-spectrum (ES-MS) only shows the cation, with no major degradation products, [(M − PF_6)$^+$, 343, 100%]. **5** is a conductor in CH_2Cl_2 solution with a molar conductivity of 25 Ω cm^2 mol^{-1}. Similarly, [(η^5-C_5H_5)Fe(η^6-C_6H_6)][PF_6] reacts with 2-methylpropenylphosphine (methallylphosphine) to give yellow/orange **5b** for which analytical, spectroscopic and conductivity data indicate a structure directly analogous to **5**. The reaction of allylphosphine with [(η^5-C_5H_5)Fe(CH_3CN)$_3$][PF_6] also gives rise to the tris-allylphosphine adduct **5**, but the substitution was not selective and the product was obtained as a mixture with partially substituted products. More forcing conditions result in degradation of allyl phosphines. It has previously been noted that substitution of the first two acetonitrile ligands in [(η^5-C_5H_5)Fe(CH_3CN)$_3$]$^+$ proceeds more readily than the last and that 'mixed' complexes are readily formed.[14]

In a similar manner to the synthesis of **5**, the reaction of [(η^5-C_5H_5)Fe(η^6-C_6H_6)][PF_6] with *rac*-allyl(phenyl)phosphine also proceeds to give the corresponding tris-phosphine complex **6**, quantitatively. Since racemic secondary phosphine was used, there are a number of possible diasteromers of **6** and NMR spectra were correspondingly complex. In the ^{31}P{^{1}H} NMR spectrum, four broad resonances were observed in the region expected for co-ordinated secondary phosphines and each gave rise to a doublet ($^{1}J_{P\text{–}H}$ = 346 Hz) in the ^{31}P NMR spectrum. The IR spectrum of **6** showed a single, strong, but broad absorption for ν(P–H) at 2303 cm^{-1}. The salt is a 1 : 1 electrolyte in dichloromethane and an intense molecular ion was observed in the mass-spectrum.

Direct formation of iron(II) 12-aneP_3R_3 complexes

Since the steric properties of the cyclopentadienyliron cationic complexes (and substituted cyclopentadienyl derivatives) may be anticipated to influence subsequent intermolecular cyclisations of primary alkenyl phosphines, it is of interest to compare relevant iron complexes with sterically non-demanding ligands with those bearing more sterically demanding cyclopentadienyl ligands. For this purpose, halogeno and acetonitrile complexes should be readily accessible by reaction of suitable iron precursors with the free macrocycle.

The reaction of 12-aneP_3Et_3 with hexa(acetonitrile)iron(II) bis(tetrafluoroborate) is more straightforward and proceeds rapidly and in high yield at room temperature to give the half-sandwich (piano-stool) compound [*fac*-(12-aneP_3Et_3)-Fe(CH_3CN)$_3$][BF_4]$_2$, **7** (Scheme 2). In the presence of excess macrocycle, there is no evidence of alternative species such as the bis-macrocycle complex in contrast to the behaviour noted for the related trithiacyclononane.[15] **7** may be isolated as a yellow powder, which on crystallisation from acetonitrile/diethyl ether forms deep-orange crystals. **7** has a molar conductivity of 275 Ω cm^2 mol^{-1} in CH_3CN solution, consistent with it being a 2 : 1 electrolyte (based on a mono-nuclear cation); its



Scheme 2 Reagents and conditions: i) [(η^5-C_5Me_5)Fe(CO)$_2$(CH_3CN)]-[BF_4], THF, *hv* or $Cp_2Fe_2(CO)_4$ + [Cp_2Fe][BF_4], THF, *hv*; ii) [(η^5-C_5Me_5)-Fe(CO)$_2$(CH_3CN)][BF_4], THF, *hv*; iii) [Fe(CH_3CN)$_6$][BF_4]$_2$, CH_3CN/CH_2Cl_2.

composition is also confirmed by analytical data. The ^{31}P{^{1}H} NMR spectrum of **7** shows a singlet at δ 36 ppm corresponding to the co-ordinated phosphines. The ^{1}H NMR spectrum of **7** gives rise to broad and complex resonances due to coincident and overlapping multiplets but is consistent with other 12-aneP_3Et_3 complexes. The ^{13}C{^{1}H} NMR spectrum shows resonances due to co-ordinated macrocycle and ethyl groups. **7** is poorly soluble in most solvents with which it does not react, except acetonitrile and nitromethane. The ν(C–N) absorptions in the IR spectrum of **7** are observed at 2290 cm^{-1} and 2330 cm^{-1}, as expected for a complex of this nature with approximate C_{3v} symmetry and in close agreement with an analogous tripodal phosphine complex, [4-$MeOC_6H_4CH_2C(CH_2PPh_2)_3Fe(NCMe)_3$][$BF_4$]$_2$, which has ν(C–N) stretching frequencies at 2288 cm^{-1} and 2324 cm^{-1}.[16] Crystals suitable for X-ray diffraction studies were readily obtained and the molecular structure of **7** is shown in Fig. 3 together with selected bond lengths and angles.

Reaction of the pentamethylcyclopentadienyl precursor [(η^5-C_5Me_5)Fe(CO)$_2$(CH_3CN)][BF_4] with 12-aneP_3Et_3 under UV irradiation gave the mixed sandwich compound [(η^5-C_5Me_5)Fe(12-aneP_3Et_3)][BF_4], **8** as expected, in high yield (80%). Complex **8** is a conductor in CH_2Cl_2 solution with a molar conductivity of 50 Ω cm^2 mol^{-1}, based upon a mono-nuclear cation, confirming that the complex is a 1 : 1 electrolyte. **8** gives a single resonance at δ 32.9 ppm in the ^{31}P NMR spectrum, and has a mass spectrum showing the molecular ion [(M − BF_4)$^+$, 497, 100%]. Crystallisation of **8** from an acetonitrile/diethyl ether mixture afforded crystals suitable for X-ray diffraction studies. The structure of **8** with selected bond angles and lengths is shown in Fig. 4.

Template assisted formation of iron(II) macrocycle complexes

A number of ring-closing methods for the template assisted formation of macrocycles were investigated. Reaction of [(η^5-C_5H_5)Fe($PhPH_2$)$_3$][PF_6], **3** with six equivalents of ^{t}BuOK and three equivalents of 1,3-dibromopropane, either sequentially or simultaneously leads to a large array of products which could not be separated and a complex of the target macrocycle, triphenyltriphosphacyclododecane, could not be identified.

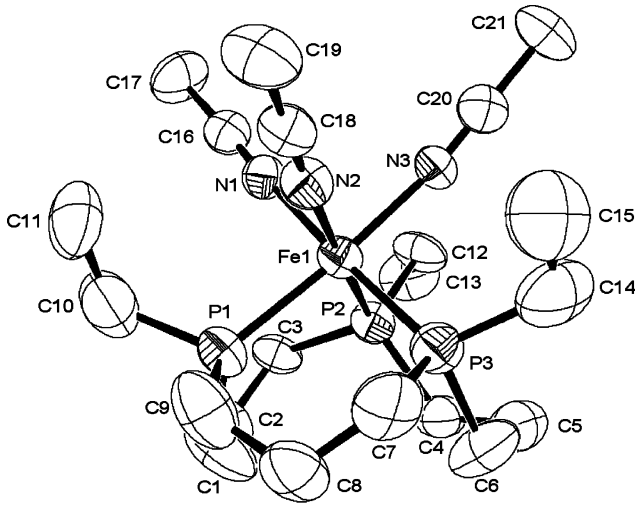


Fig. 3 The molecular structure of the cation in tris(acetonitrile)(η^3-1,5,9-triethyl-1,5,9-triphosphacyclododecane)iron(II) bis(tetrafluoroborate), **7**. Selected bond lengths (Å) and angles (°): Fe(1)–N(2), 1.956(4); Fe(1)–N(3), 1.960(4); Fe(1)–N(1), 1.971(5); Fe(1)–P(1), 2.215(2); Fe(1)–P(3), 2.220(2); Fe(1)–P(2), 2.225(2); N(1)–C(16), 1.117(6); N(2)–C(18), 1.131(6); N(3)–C(20), 1.120(6). N(2)–Fe(1)–N(3), 86.22(18); N(2)–Fe(1)–N(1), 88.33(18); N(3)–Fe(1)–N(1), 86.09(18); N(2)–Fe(1)–P(1), 90.14(14); N(3)–Fe(1)–P(1), 175.43(14); N(1)–Fe(1)–P(1), 91.05(14); N(2)–Fe(1)–P(3), 89.72(14); N(3)–Fe(1)–P(3), 91.33(14); N(1)–Fe(1)–P(3), 176.86(14); P(1)–Fe(1)–P(3), 91.41(7); N(2)–Fe(1)–P(2), 175.82(13); N(3)–Fe(1)–P(2), 91.23(13); N(1)–Fe(1)–P(2), 88.19(13); P(1)–Fe(1)–P(2), 92.24(6); P(3)–Fe(1)–P(2), 93.65(7); C(16)–N(1)–Fe(1), 176.0(5); N(1)–C(16)–C(17), 178.5(7); C(18)–N(2)–Fe(1), 175.4(5); N(2)–C(18)–C(19), 179.0(7); C(20)–N(3)–Fe(1), 171.3(5); N(3)–C(20)–C(21), 177.4(6).

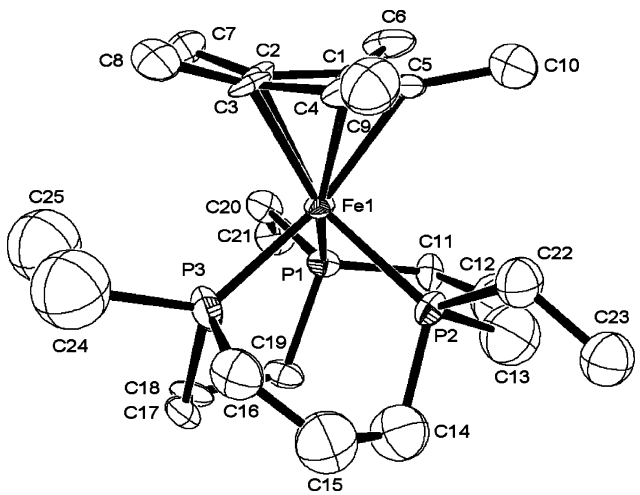


Fig. 4 The molecular structure of the cation in (η^5-pentamethylcyclopentadienyl)(η^3-1,5,9-triethyl-1,5,9-triphosphacyclododecane)iron(II) tetrafluoroborate, **8**. Selected bond lengths (Å) and angles (°): Fe(1)–C(2), 2.135(10); Fe(1)–C(1), 2.150(10); Fe(1)–C(5), 2.121(11); Fe(1)–C(4), 2.147(11); Fe(1)–C(3), 2.165(10); Fe(1)–P(2), 2.204(3); Fe(1)–P(3), 2.213(3); Fe(1)–P(1), 2.214(3). P(2)–Fe(1)–P(3), 89.67(12); P(2)–Fe(1)–P(1), 89.78(12); P(3)–Fe(1)–P(1), 91.78(11).

In an attempt to cyclotrimerise the co-ordinated α-methyl-(vinyl)phosphine ligands in **4**, to give the respective triphosphacyclononane complex, several experimental methods were attempted. Although the non-bonded P–P distances in **4** appear to be similar to those expected for a co-ordinated triphosphacyclononane macrocycle, the tri-primary phosphine complex failed to cyclise in a range of different solvents, radical initiators or photolysis, reaction times and temperatures (*e.g.* 120 °C for 7 days); these attempts led to recovery of **4** or decomposition.

Intramolecular hydrophosphinations of the tris-allylphosphine derivative **5** proceed differently however. Heating **5** in a suitable solvent in the presence of a radical initiator gives rise to the cyclised tri-secondary phosphine macrocycle complex **9**, which was isolated as a yellow powder. A sharp singlet is observed in the $^{31}P\{^1H\}$ NMR spectrum at δ 12.7 ppm; the ^{31}P NMR spectrum is a doublet ($^1J_{P\text{–}H} = 336$ Hz) confirming this peak to be due to secondary phosphines. There is also the expected septet attributed to the hexafluorophosphate anion. The ^1H NMR spectrum shows two resonances for the backbone methylene protons as complex and broadened multiplets at δ 1.60 and 1.90 ppm in a ratio of 2 : 1 respectively and a doublet assigned to the P–H proton at δ 4.80 ($^1J_{P\text{–}H} = 336$ Hz); as before, the cyclopentadienyl protons give rise to a quartet (δ 4.64 ppm, $^3J_{P\text{–}H} = 2$ Hz). The ν(P–H) absorption in the IR spectrum is readily identified (2303 cm^{-1}). The mass spectrum of **9** also shows the cation, with no major degradation products, [$(M - PF_6)^+$, 343, 100%]. The molar conductivity of **9** is 32 Ω cm^2 mol^{-1}, consistent with a 1 : 1 electrolyte.

Cyclisation reactions of **5** were shown to be solvent dependent. In THF, the intermediates and final product have low solubilities and precipitated during the reaction giving rise to correspondingly poor yields. In anisole, reasonable yields were obtained, although the reaction was relatively slow and intermediates predominated after extended reaction times. Chlorobenzene was found to be the most successful, and yields of 40% for the final macrocyclic product were recorded.

The cyclisation was monitored by ^{31}P and $^{31}P\{^1H\}$ NMR spectroscopy, and if stopped prior to completion, the starting material, intermediates, and final product were all observed. These NMR spectra are remarkably similar to those obtained from the analogous partially completed Cr(0) and Mo(0) template cyclisations. For Mo and Cr, this behaviour has been explained by stepwise P–C bond formation as the reaction proceeds, giving rise to acyclic phosphine intermediate complexes bearing both secondary and primary phosphine ligands (clearly two intermediates are feasible).[3,4d] The spectra obtained from the reaction of **5** (under similar conditions to that of Mo or Cr) also indicate that the iron template behaves similarly.

In a similar fashion and despite the mixture of diastereomers, the radical (AIBN) promoted intramolecular hydrophosphination of the allyl functions in **6**, gave rise to a number of products from which the desired 1,5,9-triphenyl-1,5,9-triphosphacyclododecane macrocycle complex, [(η^5-C_5H_5)Fe(12-aneP_3Ph_3)][PF_6] **10**, can be isolated in moderate (30%) yield as a yellow/orange powder. The identity of **10** is also confirmed by its alternative preparation directly from the free triphenyl macrocycle;[17] reaction of *syn*,*syn*-1,5,9-triphenyl-1,5,9-triphosphacyclododecane with [(η^5-C_5H_5)-Fe(η^6-C_6H_6)][PF_6] under photolytic conditions allowed the isolation of **10** in high yield. The ^{31} P NMR spectrum of **10** shows a singlet at δ 35 ppm assigned to the tertiary phosphines of the co-ordinated triphenyl-macrocycle and the expected resonance due to the PF_6^- counter-ion (δ − 144 ppm, septet, $^1J_{P\text{–}F} = 711$ Hz). Again, there is a characteristic quartet ($^3J_{P\text{–}H} = 2$ Hz) due to the cyclopentadienyl protons in the ^1H NMR spectrum of **10**

and there are two broad resonances in both the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra attributable to the backbone methylenes indicating the equivalence of the P-bonded carbons and their protons. The IR spectrum of the material obtained by either method shows the absence of ν(P–H) absorptions, as expected. The macrocycle complex **10** is a 1 : 1 electrolyte in CH_2Cl_2 and shows an intense molecular ion in the mass-spectrum (ES-MS) with no identifiable degradation products, [$(M - PF_6)^+$, 571, 100%].

In a manner similar to the synthesis of the tritertiary phosphine macrocycle on either the Cr or Mo templates,[2] the reaction of **9** with excess ethene, in the presence of a radical initiator (AIBN), proceeds smoothly to give the co-ordinated 1,5,9-triethyl-1,5,9-triphosphacyclododecane ligand complex, [(η^5-C_5H_5)Fe(12-aneP_3Et_3)][BF_4], **11**. Alternatively, **11** may be prepared by reaction of the free tritertiary phosphine macrocycle ligand with a number of mono-cyclopentadienyl precursor complexes in yields up to 80%. In either case, **11** is isolated as an orange crystalline solid with identical spectroscopic and analytical properties. The ^{31}P NMR spectrum consists of a temperature-invariant singlet at δ 38 ppm indicating magnetically equivalent phosphines and the absence of secondary phosphines. The cyclopentadienyl protons appear as a quartet in the ^{1}H NMR spectrum, centred at δ 4.26 ppm ($^{3}J_{P-H}$ = 2 Hz). The molar conductivity of **11** in CH_2Cl_2 was 40 Ω cm^2 mol^{-1}, again consistent with a 1 : 1 electrolyte and the mass spectrum of **11** shows the molecular cation as the main peak, *i.e.* [$(M - BF_4)^+$, 427, 100%]. **11** is soluble in most polar solvents, and is readily crystallised from such solvents. The molecular structure of **11** is shown in Fig. 5.

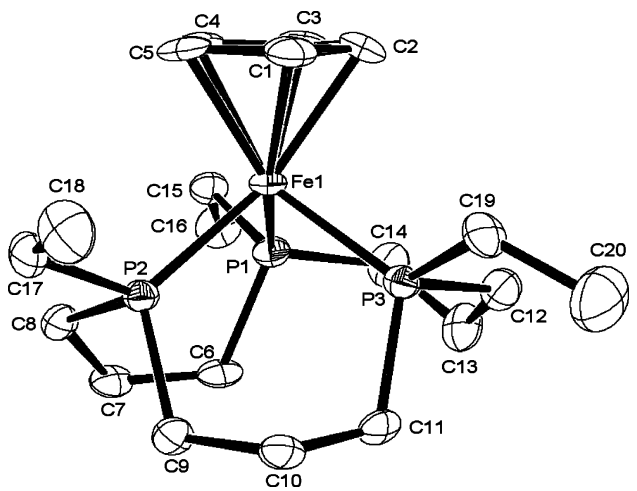


Fig. 5 The molecular structure of the cation in (η^5-cyclopentadienyl)-(η^3-1,5,9-triethyl-1,5,9-triphosphacyclododecane)iron(II) hexafluorophosphate, **11**. Selected bond lengths (Å) and angles (°): Fe(1)–C(3), 2.088(5); Fe(1)–C(2), 2.098(5); Fe(1)–C(1), 2.102(5); Fe(1)–C(5), 2.109(5); Fe(1)–C(4), 2.103(5); Fe(1)–P(3), 2.183(2); Fe(1)–P(1), 2.188(2); Fe(1)–P(2), 2.211(2). P(3)–Fe(1)–P(1), 92.06(6); P(3)–Fe(1)–P(2), 95.43(6); P(1)–Fe(1)–P(2), 90.34(6).

Structural studies

The crystal structures of complexes (**4**), (**7**), (**8**) and (**11**) confirm the distorted *fac*-octahedral co-ordination environment around the iron centre in each case.

For complex **4**, the average P–P non-bonded distance (3.120(2) Å) is significantly shorter than in the Cr(0) and Mo(0) analogues (3.30 Å and 3.49 Å respectively). The metal–phosphorus distances in **4** are shorter (average 2.171(1) Å) than those in the Cr(0) and Mo(0) analogues (averages: 2.326(2) and 2.501(1) Å respectively), although, the average P–M–P bond angle in the Fe complex (91.90(6)°) is slightly larger than for Cr(0) (91.09(5)°) and significantly larger than that for Mo(0) (88.47(4)°).[7] The structure confirms that the $CpFe^+$ fragment does indeed enable closer P–P approaches than in the $Cr/Mo(CO)_3$ analogues. The non-bonded P···P distances in **4** are also very close to the observed S···S non-bonded distances in the related (η^5-cyclopentadienyl)(1,4,7-trithiacyclononane)iron(II) cation (average 3.14 Å).[18] Other parameters in the structure of **4** are unremarkable and a relatively regular piano-stool arrangement is observed in which the planes containing the three phosphines and the five carbons of the cyclopentadienyl ligand are close to parallel with a dihedral angle of 1.7° (1.6° for Fe(1) and 1.8° for Fe(2)).

The two cyclopentadienyl macrocycle complexes **8** and **11** clearly have closely related 'sandwich' structures. Comparisons of structural parameters are of interest however since these two examples allow an analysis of the significance of steric influences of substituted cyclopentadienyl ligands. In the 'parent' cyclopentadienyl derivative **11**, the average Fe–P distances (2.194(2) Å) are only marginally shorter than in the pentamethylcyclopentadienyl analogue **8** (2.210(3) Å). The average Fe–C distances are a little longer in **8** (2.144(11) Å) than they are in **11** (2.100(5) Å). This slight expansion of Fe–ligand distances in **8** with respect to **11** is consistent with a higher steric demand in the former Cp* complex. Perhaps of more significance however are the P–Fe–P angles which in **8** are significantly compressed with respect to those in **11** (averages: 90.41(12)° and 92.61(6)° respectively). These differences lead to a small but significant decrease in the average non-bonded P···P distances (3.171(3) Å in **11** and 3.137(4) Å in **8**) as the steric bulk of the ancillary cyclopentadienyl ligand increases. In addition, the non-bonded P···P distances in **11** are similar to those in **4** indicating that the constraints of the macrocycle backbone do not have a major influence in restricting the freedom of the phosphorus atoms to adopt a favourable bonding position.

This relative trend in steric influence upon the phosphines appears to be further supported by comparisons with the structure of the tris-acetonitrile compound **7**. In **7**, the *trans* acetonitrile ligands will have about as little a steric influence upon the phosphines as is possible, however the average Fe–P distance (2.220(2) Å) is slightly longer than in **11** although the average P–Fe–P angle (92.43(7)°) is similar. A steric origin of this relative bond lengthening in **7** appears unsupportable and is more likely due to electronic factors; acetonitrile is probably a better σ-donor in these systems than is cyclopentadienyl which might be expected to lead to a higher *trans* influence as observed. This leads to an increase in the average non-bonded P···P distance in **7** (3.206(3) Å) in comparison to **11**. In other respects, the structure of **7** is unremarkable. The trends in structural data discussed above do indicate that not only does reducing the size of the metal ion/atom decrease the non-bonded P···P distances, but so does the steric influence of the ancillary 'spectator' ligands. The ability to manipulate steric properties to useful effect is absent in the metal–tricarbonyl templates previously reported and the use of cyclopentadienyl–metal templates introduces another potentially

very useful control over template supported ring closure reactions of these types.

Experimental

Techniques and instruments

All reactions were carried out in an atmosphere of dry nitrogen. All solvents were dried by refluxing over conventional drying agents. The compounds $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)][PF_6]$,[19] α-methyl(vinyl)phosphine,[20] (2-methylpropenyl)phosphine and allylphosphine,[21] phenylphosphine,[22] allyl(phenyl)phosphine,[23] *syn*,*syn*-1,5,9-triethyl-1,5,9-triphosphacyclododecane,[2] *syn*,*syn*-1,5,9-triphenyl-1,5,9-triphosphacyclododecane,[17] were prepared by literature methods. $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)][PF_6]$ was purified by extraction into acetone, filtration through Celite® and evaporation *in vacuo* followed by recrystallisation from an acetone/diethyl ether mixture in order to remove aluminium containing impurities. All other reagents were obtained from the Aldrich Chemical Company and, where appropriate, were degassed before use. NMR spectra were recorded on a Bruker WM360 instrument operating at 360.13 (^{1}H), 90.53 (^{13}C) MHz or a JEOL FX-90 instrument operating at 36.23 (^{31}P) MHz. All NMR spectra were recorded in $CDCl_3$ solution except where noted, with the ^{1}H and ^{13}C NMR chemical shifts quoted in ppm relative to solvent and ^{31}P NMR chemical shifts quoted in ppm relative to 85% external H_3PO_4. The infrared spectra were recorded in Nujol, or as KBr discs on a Perkin-Elmer 783-IR spectrometer. Mass spectra and microanalyses were obtained within this department. Conductivities were measured at 25 °C using 5×10^{-5} mol dm^{-3} solutions. UV photolyses were performed with a Hanovia 125 W mercury discharge lamp at room temperature under a N_2 stream.

Preparation of complexes 3, 4, 5, 5b and 6

The syntheses of these complexes were very similar and so a general method is described. To a frozen solution of phosphine [1.20×10^{-3} mol, phenylphosphine (**3**), (α-methyl)vinylphosphine (**4**), allylphosphine (**5**), (2-methyl)propenylphosphine (**5b**), and (allyl)phenylphosphine (**6**)] in CH_2Cl_2 (50 ml) was added (η^5-cyclopentadienyl)(η^6-benzene)iron(II) hexafluorophosphate (2.91×10^{-4} mol, 0.10 g). The mixture was allowed to warm to room temperature and was photolysed, with stirring for 8 hours at ambient temperature using an incandescent tungsten lamp (white light, 150 W). Following removal of solvent and unreacted phosphine *in vacuo*, the product remained as a powder (varying from light-yellow to deep-orange depending upon the phosphine) in almost quantitative yields (>90% yield in all cases). Purification was by recrystallisation from acetonitrile/diethyl ether mixtures, except **6**, where the crude product was purified by column chromatography (silica gel, 2% MeOH in CH_2Cl_2).

(η^5-Cyclopentadienyl)tris(phenylphosphine)iron(II) hexafluorophosphate, 3. Analysis found (calculated): C, 46.2 (46.34); H, 4.6 (4.40%). MS(ES), *m*/*z*: $[(M - PF_6)^+$, 451, 100%]. IR: ν(P–H) = 2314 cm^{-1}/KBr disc. $\Lambda_M = 24.90\ \Omega\ cm^2\ mol^{-1}$. ^{31}P NMR, δ (ppm): −9.91 (t, $^1J_{P\text{-}H} = 344$ Hz, cation); −144.00 (septet, $^1J_{P\text{-}F} = 711$ Hz, anion). ^{1}H NMR, δ (ppm): 4.48 (q, $^3J_{P\text{-}H} = 2$ Hz, Cp–*H*); 5.69 (d br m, $^1J_{P\text{-}H} = 344$ Hz, P–*H*); 7.35 (c m, phenyl *H*'s). ^{13}C{^{1}H} NMR, δ (ppm): 81.1 (s, cyclopentadienyl *C*'s); 126.5, 129.9, 131.4, 132.8 (all s, phenyl *C*'s).

(η^5-Cyclopentadienyl)tris(α-methylvinylphosphine)iron(II) hexafluorophosphate, 4. Analysis found (calculated): C, 34.6 (34.45); H, 5.5 (5.37%). MS(ES), *m*/*z*: $[(M - PF_6)^+$, 343, 75%], $[(M - PF_6 - H_2PC_3H_5)^+$, 269, 100%], and $[(M - PF_6 - 2H_2PC_3H_5)^+$, 195, 8%]. IR: ν(P–H) = 2319 cm^{-1} (KBr disc). $\Lambda_M = 14\ \Omega\ cm^2\ mol^{-1}$. ^{31}P NMR, δ (ppm): −4.42 (t, $^1J_{P\text{-}H} = 336$ Hz, cation); −144.44 (septet, $^1J_{P\text{-}F} = 711$ Hz, anion). ^{1}H NMR, δ (ppm): 1.95 (d, $^2J_{H\text{-}H} = 40$ Hz, $H_2PC(CH_3)CH_2$); 4.54 (q, $^3J_{P\text{-}H} = 2$ Hz, Cp–*H*); 5.16 (d br m, $^1J_{P\text{-}H} = 336$ Hz, P–*H*); 5.45 (c m, $H_2PC(CH_3)CH_2$). ^{13}C{^{1}H} NMR, δ (ppm): 22.8 (s, $H_2PC(CH_3)CH_2$); 79.1 (s, cyclopentadienyl *C*); 124.9 (s, $H_2PC(CH_3)CH_2$); 128.0 (d, $^1J_{P\text{-}C} \approx 56$ Hz, $H_2PC(CH_3)CH_2$).

(η^5-Cyclopentadienyl)tris(allylphosphine)iron(II) hexafluorophosphate, 5. Analysis found (calculated): C, 34.5 (34.45); H, 5.3 (5.37%). MS(ES), *m*/*z*: $[(M - PF_6)^+$, 343, 100%]. IR: ν(P–H) = 2319 cm^{-1}/KBr disc. $\Lambda_M = 25\ \Omega\ cm^2\ mol^{-1}$. ^{31}P NMR, δ (ppm): −9.05 (t, $^1J_{P\text{-}H} = 328$ Hz, cation); −144 (septet, $^1J_{P\text{-}F} = 711$ Hz, anion). ^{1}H NMR, δ (ppm): 2.54 (m, $H_2PCH_2CHCH_2$); 4.56 (br d, $^1J_{P\text{-}H} = 328$ Hz, $H_2PCH_2CHCH_2$); 4.55 (q, $^3J_{P\text{-}H} = 2$ Hz, Cp–*H*); 5.20 (m, $H_2PCH_2CHCH_2$); 5.82 (m, $H_2PCH_2CHCH_2$). ^{13}C{^{1}H} NMR, δ (ppm): 28.2 (d, $^1J_{P\text{-}C} = 40$ Hz, $H_2PCH_2CHCH_2$); 80.1 (s, cyclopentadienyl *C*'s); 119.7 (s, $H_2PCH_2CHCH_2$); 133.9 (s, $H_2PCH_2CHCH_2$).

(η^5-Cyclopentadienyl)tris(2-methylpropenylphosphine)iron(II) hexafluorophosphate, 5b. Analysis found (calculated): C, 38.4 (38.51); H, 6.2 (6.08%). MS(ES), *m*/*z*: $[(M - PF_6)^+$, 385, 40%]. IR: ν(P–H) = 2306 cm^{-1}/KBr disc. $\Lambda_M = 25\ \Omega\ cm^2\ mol^{-1}$. ^{31}P NMR, δ (ppm): −13.35 (t, $^1J_{P\text{-}H} = 332$ Hz, cation); −143.80 (septet, $^1J_{P\text{-}F} = 711$ Hz, anion). ^{1}H NMR, δ (ppm): 1.80 (br s, $H_2PCH_2C(CH_3)CH_2$); 2.52 (br s, $H_2PCH_2C(CH_3)CH_2$); 4.63 (br q, $^3J_{P\text{-}H} = 2$ Hz, Cp–*H*); 4.74 (d br m, $^1J_{P\text{-}H} = 332$ Hz, P–*H*); 4.93 (d m, $^2J_{H\text{-}H} = 11$ Hz, $H_2PCH_2C(CH_3)CH_2$). ^{13}C{^{1}H} NMR, δ (ppm): 22.2 (s, $H_2PCH_2C(CH_3)CH_2$); 31.7 (d, $^1J_{P\text{-}C} \approx 50$ Hz, $H_2PCH_2C(CH_3)CH_2$); 79.3 (s, cyclopentadienyl *C*); 114.7 (s, $H_2PCH_2C(CH_3)CH_2$); 141.3 (s, $H_2PCH_2C(CH_3)CH_2$).

***rac*-(η^5-Cyclopentadienyl)tris(allylphenylphosphine)iron(II) hexafluorophosphate, 6.** Analysis found (calculated): C, 53.9 (53.67); H, 5.4 (5.31%). MS(ES), *m*/*z*: $[\{(\eta5\text{-}C_5H_5)Fe(PhPHC_3H_5)_3\}^+$, 571, 100%]. IR: ν(P–H) = 2303 cm^{-1} (KBr disc). $\Lambda_M = 39\ \Omega\ cm^2\ mol^{-1}$. ^{31}P{^{1}H} NMR, δ (ppm): 55.79, 57.19, 61.28, 63.11 (all br d, all $^1J_{P\text{-}H} = 346$ Hz, P–H); −144 (septet, $^1J_{P\text{-}F} = 711$ Hz, anion). ^{1}H NMR, δ (ppm): 2.5 (br m, $PhHPCH_2CHCH_2$); 4.42 (q, $^3J_{P\text{-}H} = 2$ Hz, Cp–*H*'s); 4.64 (br d, $^1J_{P\text{-}H} = 346$ Hz, P–H); 5.25 (br m, $PhHPCH_2CHCH_2$); 5.6 (br m, $PhHPCH_2CHCH_2$); 7.3 (*m*, phenyl *H*'s). ^{13}C{^{1}H} NMR, δ (ppm): 27.9 (br d, $^1J_{P\text{-}C} \approx 40$ Hz), $PhHPCH_2CHCH_2$); 79.7 (br s, cyclopentadienyl *C*'s); 120.5 (br s, $PhHPCH_2CHCH_2$); 135.2 (br s, $PhHPCH_2CHCH_2$) [127.4 (s), 130.4 (d), 131.7 (s), 132.8 (s), phenyl *C*'s, doublet is the *ipso C*.]

Preparation of tris(acetonitrile)(η^3-1,5,9-triethyl-1,5,9-triphosphacyclododecane)iron(II) bis(tetrafluoroborate), 7

$[Fe(CH_3CN)_6][BF_4]_2$ (0.233 g, 4.90×10^{-4} mol) was dissolved in a mixture of acetonitrile (20 ml) and dichloromethane (20 ml). To this was added 1,5,9-triethyl-1,5,9-triphosphacyclododecane

(0.150 g, 4.90 × 10^{-4}mol) as a solution in CH_2Cl_2 (10 ml), the colour of the solution immediately became orange. The solution was stirred for 1 hour, and the solvent removed *in vacuo* leaving an oily residue of **7**, which was washed with diethyl ether (2 × 20 ml). The resultant powder was recrystallised from a mixture of acetonitrile with diethyl ether to give X-ray quality crystals (0.134 g, 63% yield). Analysis found (calculated): C, 38.3 (38.49); H, 6.4 (6.27%). MS(ES), *m/z*: no assignable peaks. IR: ν(C–N) = 2290 cm^{-1} and 2330 cm^{-1} (KBr disc). Λ_M = 275 Ω cm^2 mol^{-1}. ^{31}P NMR, δ (ppm): 36.21 (s, cation). ^{1}H NMR, δ (ppm): 1.06 (m, PCH_2CH_3); 1.65 (br m, PCH_2CH_3 and $PCH_2CH_3CH_2P$); 1.83 (br m, $PCH_2CH_2CH_2P$); 1.93 (s, CH_3CN). $^{13}C\{^1H\}$ NMR, δ (ppm): 3.8 (s, CH_3CN) 16.2 (s, PCH_2CH_3); 22.8 (br s, $PCH_2CH_2CH_2P$); 23.4 (d, $^1J_{P\text{-}C} \approx 50$ Hz); 26.4 (d, $^1J_{P\text{-}C} \approx 50$ Hz, $PCH_2CH_2CH_2P$); 129.8 (s, CH_3CN).

Preparation of (η^5-pentamethylcyclopentadienyl)(η^3-1,5,9-triethyl-1,5,9-triphosphacyclododecane)iron(II) tetrafluoroborate, 8

[(η^5-C_5Me_5)Fe(CO)$_2$(CH_3CN)][BF_4] (0.123 g, 3.27 × 10^{-4} mol) and 1,5,9-triethyl-1,5,9-triphosphacyclododecane (0.110 g, 3.59 × 10^{-4} mol, in 10 ml of THF) were dissolved in THF (100 ml), and the solution irradiated (UV, 3 hours). The orange solution was filtered through Celite® and the solvent removed *in vacuo* to leave **9** as a dark orange powder. Recrystallisation from an acetonitrile/diethyl ether mixture yielded crystals of X-ray diffraction quality (0.150 g, 80% yield). Analysis found (calculated): C, 51.2 (51.40); H, 8.1 (8.28%). MS(ES), *m/z*: [(M − BF_4)$^+$, 497, 100%]. Λ_M = 50 Ω cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR, δ (ppm): 32.86 (s). ^{1}H NMR, δ (ppm): 1.15 (br m, PCH_2CH_3), 1.50 (br m, PCH_2CH_3), 1.65 (s, Cp–CH_3), 1.68 (br m, $PCH_2CH_2CH_2P$), and 1.92 (br m, $PCH_2CH_2CH_2P$). $^{13}C\{^1H\}$ NMR, δ (ppm): 9.0 (s, Cp–CH_3); 14.8 (s, PCH_2CH_3); 22.9 (br s, $PCH_2CH_2CH_2P$); 27.8 (d, $^1J_{P\text{-}C} \approx 40$ Hz, $PCH_2CH_2CH_2P$); 78.4 (br s, cyclopentadienyl *C*'s).

Preparation of (η^5-cyclopentadienyl)(η^3-1,5,9-triphosphacyclododecane)iron(II) hexafluorophosphate, 9

5 (0.100 g, 2.05 × 10^{-4} mol) and AIBN (~1–2% molar equivalent) were dissolved in chlorobenzene (~70 ml), giving a yellow homogeneous solution which was stirred at 90 °C for 8 hours. After cooling to ambient temperature and removal of the solvent under reduced pressure. the residue was extracted into CH_2Cl_2, filtered and the solvent again removed to yield **9** as a light yellow powder (0.040 g, 40% yield). Analysis found (calculated): C, 34.1 (34.45); H, 5.1 (5.37%). MS(ES), *m/z*: [(M − PF_6)$^+$, 343, 100%]. IR: ν(P–H) = 2303 cm^{-1} (KBr disc). Λ_M = 32 Ω cm^2 mol^{-1}. ^{31}P NMR, δ (ppm): 12.71 (d, $^1J_{P\text{-}H}$ = 336 Hz, cation); −145 (septet, $^1J_{P\text{-}F}$ = 711 Hz, anion). ^{1}H NMR, δ (ppm): 1.60 (m, $PCH_2CH_2CH_2P$); 1.90 (m, $PCH_2CH_2CH_2P$); 4.40 (q, $^3J_{P\text{-}H}$ = 2 Hz, Cp–*H*'s); 4.80 (br d, $^1J_{P\text{-}H}$ = 336 Hz, P–H). $^{13}C\{^1H\}$ NMR, δ (ppm): 22.0 (br s, $PCH_2CH_2CH_2P$); 25.2 (d, $^1J_{P\text{-}C} \approx 40$ Hz, $PCH_2CH_2CH_2P$); 79.5 (br s, cyclopentadienyl *C*'s).

Preparation of (η^5-cyclopentadienyl)(η^3-1,5,9-triphenyl-1,5,9-triphosphacyclododecane)iron(II) hexafluorophosphate, 10

6 (0.100 g, 1.39 × 10^{-4} mol) was dissolved in chlorobenzene (~50 ml), and AIBN (~1–2% molar equivalent) was added. The mixture was heated at 90 °C for 48 hours giving crude **10**. The crude product was isolated as an orange powder following removal of solvent and washing with diethyl ether (2 × 20 ml). Column chromatography using basic alumina with CH_2Cl_2 and methanol (0.2% by volume) as eluant yielded the desired product (0.030 g, 30% yield). The cyclo-trimerisation may also be carried out in other polar solvents including chlorobenzene or anisole but the reaction is less efficient. Analysis found (calculated): C, 53.7 (53.60); H, 5.4 (5.31%). MS(ES), *m/z*: [(M − PF_6)$^+$, 571, 100%]. Λ_M, 36 Ω cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR, δ (ppm): 35.00 (s). ^{1}H NMR, δ (ppm): 1.85 (br m, $PCH_2CH_3CH_2P$); 2.05 (br m, $PCH_2CH_2CH_2P$); 4.20 (q, $^3J_{P\text{-}H}$ = 2 Hz, Cp–*H*'s); 7.34 (c m, phenyl H's). $^{13}C\{^1H\}$ NMR, δ (ppm): 24.0 (br s, $PCH_2CH_2CH_2P$); 29.1 (d, $^1J_{P\text{-}C} \approx 40$ Hz, $PCH_2CH_2CH_2P$); 79.7 (s, cyclopentadienyl *C*'s) [127.1 (s), 130.2 (d), 131.4 (s), 132.9 (s); phenyl *C*'s, doublet is the substituted *C*.]

Alternative preparation of (η^5-cyclopentadienyl)(η^3-1,5,9-triphenyl-1,5,9-triphosphacyclododecane)iron(II) hexafluorophosphate, 10

A solution of 1,5,9-triphenyl-1,5,9-triphosphacyclododecane (0.100 g, 2.2 × 10^{-4} mol, in 10 ml of THF) was added to a solution of [(η^5-C_5H_5)(η^5-C_6H_6)Fe][PF_6] (0.076 g, 2.2 × 10^{-4} mol), and the mixture irradiated (UV, 8 hours). Removal of solvent *in vacuo* and recrystallisation from an acetonitrile/diethyl ether mixture gave **10** as an orange powder (0.158 g, 80% yield). Analytical data matched that found for the product obtained from **6** described above.

Preparation of (η^5-cyclopentadienyl)(η^3-1,5,9-triethyl-1,5,9-triphosphacyclododecane)-iron(II) hexafluorophosphate, 11

Complex **9** (0.100 g, 2.05 × 10^{-4} mol) was dissolved in chlorobenzene (~50 ml) and transferred to a 500 ml steel autoclave, containing AIBN (~1–2% molar equivalent). The vessel was pressurised with ethene (3 atm), and the sealed autoclave was heated at 90 °C for 8 hours. Following cooling and venting the solvent was removed *in vacuo* and the residue crystallised from acetonitrile/diethyl ether to give **11** as a deep-orange microcrystalline solid (0.111 g, 95% yield). Analysis found (calculated): C, 47.0 (46.74); H, 7.6 (7.45%). MS(ES), *m/z*: [(M − PF_6)$^+$, 427, 100%]. Λ_M, 40 Ω cm^2 mol^{-1}. ^{31}P: 38.09 (s, cation); −145 (septet, $^1J_{P\text{-}F}$ = 711 Hz, anion). ^{1}H NMR, δ (ppm): 1.28 (br m, PCH_2CH_3); 1.61 (br m, PCH_2CH_3 and $PCH_2CH_3CH_2P$); 1.87 (br m, $PCH_2CH_2CH_2P$); 4.26 (q, $^3J_{P\text{-}H}$ = 2 Hz, Cp–*H*). $^{13}C\{^1H\}$ NMR, δ (ppm): 14.6 (s, PCH_2CH_3); 23.1 (br s, $PCH_2CH_2CH_2P$); 28.2 (d, $^1J_{P\text{-}C} \approx 40$ Hz, $PCH_2CH_2CH_2P$); 78.9 (br s, cyclopentadienyl *C*'s).

Alternative preparations of (η^5-cyclopentadienyl)(η^3-1,5,9-triethyl-1,5,9-triphosphacyclododecane)iron(II) hexafluorophosphate, 11

Route 1. $Cp_2Fe_2(CO)_4$ (0.058 g, 1.64 × 10^{-4} mol) and [Cp_2Fe][BF_4] (0.089 g, 3.27 × 10^{-4} mol) were suspended in THF (50 ml). A solution of 1,5,9-triethyl-1,5,9-triphosphacyclododecane (0.100 g, 3.27 × 10^{-4} mol) in THF (10 ml), was added dropwise, and the mixture allowed to stir for 2 hours, during which time the colour changed from brown/blue to a dark brown. The mixture was then irradiated (UV, 3 hours), during which time the colour changed to give a homogeneous yellow solution. The solvent was removed under reduced pressure, and the residue washed with diethyl ether (2 × 20 ml). Recrystallisation

from acetonitrile/diethyl ether gave orange crystals of X-ray crystallographic quality (0.138 g, 82% yield).

Route 2. $CpFe(CO)_2I$ (0.099 g, 3.27×10^{-4} mol) and $AgBF_4$ (64 mg, 3.27×10^{-4} mol) were dissolved in CH_2Cl_2 (50 ml), and 1,5,9-triethyl-1,5,9-triphosphacyclododecane (0.100 g, 3.27×10^{-4} mol, in CH_2Cl_2 (10 ml) was added by syringe. The mixture was refluxed for 8 hours, and after cooling, the solution was filtered to remove AgI leaving a homogeneous yellow solution. The solvent was then removed *in vacuo*, and the residue recrystallised from acetonitrile/diethyl ether (0.146 g, 87% yield).

Route 3. A solution of 1,5,9-triethyl-1,5,9-triphosphacyclododecane (0.100 g, 3.27×10^{-4} mol, in 10 ml of THF) was added to a solution of $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_6H_6)Fe][BF_4]$ (3.27×10^{-4} mol), and the mixture irradiated (UV, 8 hours). After removal of solvent *in vacuo* and recrystallisation, **6** was obtained as an orange, microcrystalline solid (84% yield).

Routes 1, 2, and 3 gave analytical and spectroscopic data identical to that found for the product prepared *via* the new template, as described above.

Liberation of *syn,syn*-1,5,9-triethyl-1,5,9-triphosphacyclododecane and *syn,syn*-1,5,9-triphenyl-1,5,9-triphosphacyclododecane from the '$(\eta^5\text{-}C_5H_5)$Fe' and '$(\eta^5\text{-}C_5Me_5)$Fe' based templates

The liberation reactions where complexes **9**, **10**, and **11** were degraded to their constituent ligands were very similar, and so a general method is described. The cyclopentadienyl macrocycle complex **9** (0.100 g, 1.75×10^{-4} mol) along with sodium metal (1 g, large excess, Li can also be used) were dissolved in liquid ammonia (approximately 50 ml) and the mixture stirred at −78 °C for 8 hours following which the ammonia was allowed to evaporate of its own accord. Methanolic digestion of the excess sodium, followed by removal of solvent *in vacuo* yielded a grey powder. Addition of water (50 ml), followed by extraction into diethyl ether (3×40 ml) gave rise to a yellow organic phase which was washed with water (2×40 ml) to remove residual salts. The organic phase was dried ($MgSO_4$) and the solvent removed *in vacuo* to give the crude macrocycle as a mixture with cyclopentadiene. The triphosphine ligand was obtained as white crystals by recrystallisation from a saturated solution in diethyl ether (0.014 g, 30% yield). Spectroscopic and analytical data were identical to those previously reported.[4]

Crystallography

$[(\eta^5\text{-}C_5H_5)Fe(H_2PC_3H_5)_3][PF_6]$ (4), $[fac\text{-}(12\text{-}aneP_3Et_3)Fe(CH_3CN)_3][BF_4]_2$ (7), $[(\eta^5\text{-}C_5Me_5)Fe(12\text{-}aneP_3Et_3)][BF_4]$ (8) and $[(\eta^5\text{-}C_5Me_5)Fe(12\text{-}aneP_3Et_3)][BF_4]$ (11). Crystallographic data for compounds **4**, **7**, **8** and **11** were recorded on a fast area detector diffractometer using monochromatic Mo-Kα radiation in a manner described previously.[24] The unit-cell parameters for each compound were determined by least-squares refinement of the setting angles for 250 reflections. The structures of all four compounds were solved by direct methods (SHELXS-96)[25] and refined on F^2 by full-matrix least-squares methods (SHELXL-97)[26] using all unique data (following absorption correction using DIFABS[27]). The F atoms of the PF_6^- (**2**) and BF_4^- (**7**, **8** and **11**) anions are extensively disordered, and these were refined with partial site occupancies. The C(3), C(4) and C(12) atoms in **4**, the O atom of the diethyl ether solvate in **11**, and C(12)–C(15) and C(25) atoms in **8** were also disordered, and similarly treated. All non-hydrogen atoms were refined anisotropically, with ISOR restraints being used for some of the atoms belonging to the disordered groups in compounds **7**, **8** and **11**. The hydrogen atoms in all structures were included in calculated positions (riding model), except those on the disordered carbon atoms in **8**. Diagrams were drawn with ORTEP3 for Windows.[28] The crystal data and refinement results are summarised in Table 1.

Table 1 Data collection and refinement parameters for compounds **4**, **7**, **8** and **11**

	Compound **4**	Compound **7**	Compound **8**	Compound **11**
Empirical formula	$C_{28}H_{52}F_{12}Fe_2P_8$	$C_{21}H_{42}B_2F_8FeN_3P_3$	$C_{25}H_{48}BF_4FeP_3$	$C_{24}H_{48}BF_4FeOP_3$
Formula weight	976.16	658.96	584.20	588.19
Temperature/K	293(2)	293(2)	150(2)	150(2)
Wavelength/Å	0.71069	0.71069	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	*P*21/*n*	*P*21/*n*	*Pbca*	*P*2(1)/*c*
a/Å	17.011(3)	10.296(2)	15.3920(10)	8.0750(10)
b/Å	10.913(2)	15.901(3)	13.1650(10)	19.277(2)
c/Å	22.793(5)	18.784(4)	27.211(3)	17.8520(10)
α/°	90	90	90	90
β/°	90.65(3)	92.23(3)	90	92.190(10)
γ/°	90	90	90	90
V/Å^3	4231.0(14)	3072.9(11)	5513.9(8)	2776.8(5)
Z	4	4	8	4
ρ_{calc}/Mg m^{-3}	1.532	1.424	1.407	1.407
μ/mm^{-1}	1.062	0.712	0.762	0.759
F(000)	2000	1368	2480	1248
Crystal size/mm	0.35 × 0.20 × 0.20	0.35 × 0.20 × 0.20	0.40 × 0.15 × 0.05	0.35 × 0.20 × 0.20
Reflections collected	68181	9317	17175	9165
Independent reflections	7394 [*R*(int) = 0.1094]	4358 [*R*(int) = 0.0649]	4244 [*R*(int) = 0.1618]	3964 [*R*(int) = 0.0978]
Goodness-of-fit on F^2	1.057	0.955	1.270	0.898
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0642$, $wR2 = 0.1697$	$R1 = 0.0521$, $wR2 = 0.1032$	$R1 = 0.0756$, $wR2 = 0.1539$	$R1 = 0.0534$, $wR2 = 0.1247$
R indices (all data)	$R1 = 0.0755$, $wR2 = 0.1792$	$R1 = 0.0909$, $wR2 = 0.1089$	$R1 = 0.2197$, $wR2 = 0.1805$	$R1 = 0.0842$, $wR2 = 0.1309$
Largest diff. peak and hole/e Å^{-3}	1.625 and −1.120	0.517 and −0.297	0.756 and −0.503	0.580 and −0.507

CCDC reference numbers 277603–277606.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b509627h

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