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PAPER

Iron(II) template synthesis of benzannulated triphospha- and triarsamacrocycles†

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Nine-membered 1,4,7-triphospha- and triarsamacrocycles with unsaturated benzo-backbones have been prepared using the $[Cp^R Fe]^+$ unit as a template. The cyclisation involves the attack of a coordinated phosphide (or arsenide) nucleophile at an activated, electrophilic *ortho*-fluorophenyl substituent on a neighbouring pnictide donor. The macrocycle assembly is of the 2 + 1 type where two new chelate rings are formed from appropriately derivatised bidentate and monodentate phosphines/arsines. Both $[(\eta^5\text{-}C_5H_5)Fe]^+$ and $[(\eta^5\text{-}C_5Me_5)Fe]^+$ may be employed for the cyclisation with higher yields generally being observed with the unsubstituted Cp. All new compounds have been characterised by spectroscopic and analytical methods including the single-crystal X-ray structure determination of $[(\eta^5\text{-}C_5H_5)Fe(\text{tribenzo-9ane}P_3\text{-Ph,}Ph^F{}_2)]^+$, **3a**, and $[(\eta^5\text{-}C_5H_5)Fe(\text{tribenzo-9ane}As_3\text{-Ph,}Ph^F{}_2)]^+$, **5**, as the tetraphenylborate salts. The crystal structures are isomorphous and show the unique conformation of these new macrocycles with a 'cup shaped' cavity formed by the rigid benzo-backbones. The $9aneAs_3$ derivative is the first example of a nine-membered triarsamacrocycle.

Introduction

Nitrogen macrocycles having rigid unsaturated conjugated or aromatic hydrocarbon backbones are well known in biological systems. Part of the reason for their presence in living systems derives from the exceptional stability of metal complexes of ligands such as porphyrins, phthalocyanines and corrins. Needless to say the coordination chemistry and properties of these systems have been studied extensively for decades. Rather surprisingly, the chemistry of the related triazamacrocycle, 1,4,7-triaza-tribenzocyclonane, has not been explored; its preparation only recently being reported in patent literature.[1] The absence of studies of 1,4,7-triaza-tribenzocyclonane from the literature contrasts starkly with the large volume of published material on the saturated analogues (*i.e.* TACN and derivatives).

We are interested in phosphorus macrocyclic ligands, particularly those that are suitable for facially capping a metal coordination environment as they should lead to kinetically robust complexes, but with remaining *cis* reactions sites. Both of these features should be of value in developing reactivity in applications such as catalysis. In this context, we have synthesised a series of such ligands by template methods.[2] These have mostly been the direct analogues of TACN or of the larger ring saturated triazamacrocycles, but more recently includes one, or two, unsaturated (benzo) backbones.[3] We have shown that the use of iron cyclopentadienyl piano-stool complexes as templates for the formation of triphosphorus macrocycles is very versatile and it was of interest to see if this approach can be extended to the preparation of macrocycles with fully benzannulated backbones.

Previous macrocyclisation methodology has been based upon pseudo-Michael type additions of co-ordinated primary diphosphines with co-ordinated di- or trialkenyl phosphines[2a,b,d,e] or radical catalysed hydrophosphinations,[2f] neither of which is appropriate for the formation of triphosphamacrocycles with benzannulated backbones. A more amenable route is that based upon an intramolecular nucleophilic attack of a metal-bound phosphide at an electrophilic aromatic carbon.[3b] This synthetic method involves *ortho*-fluorophenyl substituents attached to a mono- or bis-phosphine fragment ligand with the necessary activation of the *ortho* C–F bond being promoted by the inductive effect of the metal centre.[4,5] We have previously established this synthetic approach in the formation of $9aneP_3$ macrocycles with one or two benzo chelates,[3b] and more recently the first carbene-phosphine mixed donor P_2C^{NHC} macrocycle.[6a] Subsequently, Hahn and co-workers have shown this method to work on the same Fe template system.[6b] We report here the extension to the fully benzannulated $9aneP_3$ system to complete the homoleptic series. In addition we have used the same methodology to prepare the triarsenic derivative which represents a unique class as no 9-membered triarsamacrocycle has been reported previously.

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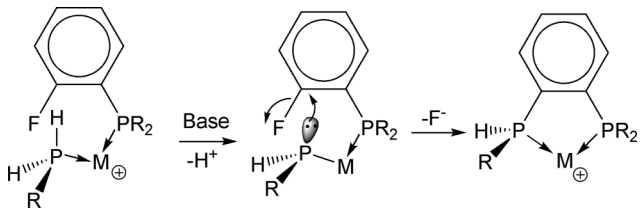
Results and discussion

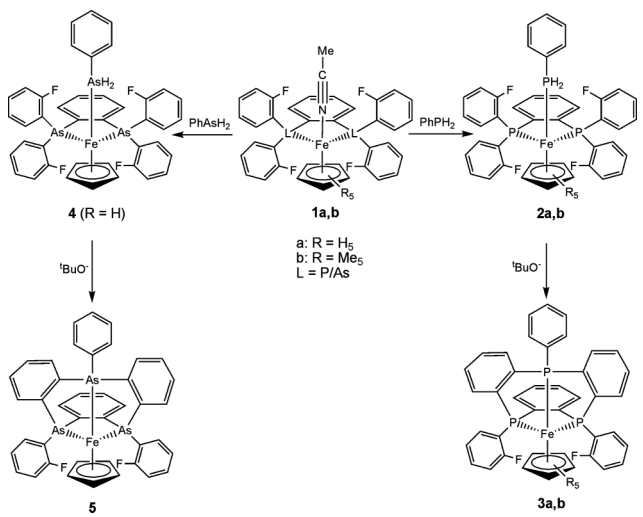
Synthesis of tritertiary tribenzannulated 9aneP$_3$ macrocycles

It is well-known that 2-fluoroaryl groups are susceptible to nucleophilic attack if an electron-withdrawing group is present at the 1-position. In 2-fluoroarylphosphine ligands coordinated to transition metals, the metal is expected to be electron-withdrawing (a property likely to be enhanced in cationic complexes such as the Cp-iron template herein) and so should activate the fluoride-bearing carbons allowing substitution of fluoride by appropriate nucleophiles (Scheme 1).



Scheme 1

An advantage of the Cp-iron template is that it supports base deprotonation of coordinated primary and secondary phosphines to form coordinated phosphido functions that remain nucleophilic (as the Fe atom is an 18e$^-$ centre, π-base behaviour of the ligand is suppressed). The viability of this approach has been established and we have used such reactions to prepare a dibenzotriphosphamacrocycle.[3b] Extension of this methodology to the preparation of tribenzotriphosphamacrocycles is straightforward requiring only the use of 1,2-bis{di(2-fluorophenyl)phosphino}benzene instead of the ethane derivative (Scheme 2). The cyclisation requires a base to promote initial deprotonation of the primary phosphine and the resulting nucleophilic attack at the *ortho* position of the fluorophenyl ring. This mechanism relates to the work of Saunders[4,5] who observed C–C bond formation following the attack of a nucleophilic methylene carbon derived from one of the peripheral methyls of coordinated Cp* at the *ortho* position of a pentafluorophenyl moiety attached to a co-ordinated diphosphine. Unlike the system of Saunders



Scheme 2

where the reaction is promoted by the addition of catalytic quantities of base, our synthesis of [(η^5-C$_5$H$_5$)Fe(dibenzo-9aneP$_3$-Ph,Ph$^F_2$)]$^+$ required at least a stoichiometric amount of base to quench the released HF and ensure a nearly quantitative yield of the desired compound. This high yield contrasts with the related synthesis of the saturated [(η^5-C$_5$H$_5$)Fe(9aneP$_3$-H$_2$,C$_2$H$_3$)]$^+$ complex where only poor yields were observed with the unmodified Cp unit. The Michael-type ring closure used to prepare the saturated macrocycles was found to be much more efficient when peripheral groups were present on the Cp ligand. The greater efficacy of the unsubstituted Cp template in the current methodology may be attributed to beneficial features of the dehydrofluorinative mechanism including a prior electrostatic attraction between the fluoride and the acidic proton on the primary phosphine leading to increased acidity of the P–H and pre-organising the fragments to favour macrocycle formation.

The precursor complex **1a** was obtained as an air-sensitive red powder in very good yield (94%). The ^{31}P{^{1}H} NMR spectrum consists of a triplet at 92.5 ppm ($^3J_{P\text{-}F}$ = 36.0 Hz) which is shifted downfield with respect to the free di-phosphine ligand (–32.6 ppm) and indicative of co-ordination to the metal ion. In addition to the expected aromatic peaks (7.70–6.90 ppm) in the ^{1}H NMR spectrum, a broadened singlet at 3.96 ppm due to the Cp fragment is observed. The ^{13}C{^{1}H} NMR spectrum shows peaks due to the methyl protons of the acetonitrile ligand at δ_C 2.8 ppm, the Cp group at δ_C 81.5 ppm and resonances for the aromatic carbons amassed between 123.2 and 133.9 ppm. A characteristic doublet is observed at 165.0 ppm ($^1J_{C\text{-}F}$ = 242.9 Hz) in the ^{13}C{^{1}H} NMR spectrum of **1a** which can be assigned to the fluorine-bearing *ortho*-carbon. The ^{19}F NMR spectrum shows a singlet at –98.0 ppm suggesting time-averaged equivalence of all the fluorophenyl groups. The CN stretch for the co-ordinated acetonitrile appears in the infrared spectrum at 2266 cm^{-1}. Addition of phenylphosphine and subsequent heating to 60 °C in ClCH$_2$CH$_2$Cl gave the complex **2a** as a yellow, slightly air-sensitive powder in excellent yield (93%). The ^{31}P{^{1}H} NMR spectrum of **2a** shows an AX$_2$ pattern at 84.6 ($^2J_{P\text{-}P}$ = 51.0 Hz) and 12.1 ppm for the bidentate and monodentate phosphines, respectively. The most distinctive feature of the ^{1}H NMR spectrum is the large doublet at 4.38 ppm with $^1J_{P\text{-}H}$ of 347 Hz for the PH hydrogens of the coordinated phenylphosphine. The ^{19}F NMR spectrum showed a singlet at –98.0 ppm representing the co-ordinated bidentate phosphine.

The addition of base to a solution of the precursor complex **2a** led to the formation of the complete macrocycle and complex **3a** was isolated as an air-stable yellow powder in good yield. The ^{31}P{^{1}H} NMR spectrum of **3a** shows the usual downfield shift in δ_P of ~120 ppm (t, $^2J_{P\text{-}P}$ = 32.8 Hz) for the phenylphosphine P-atom, consistent with its incorporation into the macrocycle ring (this is expected as the phosphorus is a constituent of two chelate rings as opposed to being a simple monodentate donor) and a broadened doublet for the fluorophenylphosphines at 127.5 ppm. Attempts to resolve any fine coupling for the PPh^F phosphines in **3a** by recording the ^{31}P{^{1}H} NMR spectrum at low temperature led instead to more complicated resonance patterns. Inspection of the ^{19}F NMR spectrum, which is a broad singlet at RT, at these low temperatures revealed the presence of four distinct resonances, two of which were of approximately equal intensity. This is likely the result of restricted rotation about the P–Ph^F bond at these lower

temperatures resulting in all possible rotamers being observed and where the rotation is sufficiently fast at ambient temperatures to lead to a time-averaged spectrum. The ^{1}H and ^{13}C NMR spectra are largely uninformative, the only characteristic features being the presence of the doublet of doublets at δ_C 165.3 ($^{1}J_{C-F}$ = 252.9 Hz, $^{2}J_{C-P}$ = 4.8 Hz) ppm.

Fine needle like yellow crystals of **3a** suitable for X-ray diffraction were obtained by anion exchange with $NaB(C_6H_5)_4$ and subsequent recrystallisation from acetonitrile at −37 °C. Two views of the crystal structure are shown in Fig. 1. The upper view illustrates the relatively regular 'piano-stool' arrangement of ligands, whereas the lower view emphasises the distinctive toroidal cavity that is made by the orientation of the three benzo groups and which might be suitable as an anion binding space. The fluorines occupy disordered positions with the two fluorines equally distributed between all three observed positions and the structure was refined with partial ($^{2}/_{3}$) occupancies. The Cp ring is also rotationally disordered, as is common in half-sandwich compounds of this type; only one position of the Cp ring is shown in Fig. 1 for clarity. The value of 2.149(1) Å for the average Fe–P bond length is appreciably smaller than that measured for the dibenzannulated example where the Fe–P bonds averaged 2.164(1) Å. The P–Fe–P bond angles of 86.51(5), 86.49(5) and 86.75(5)° are all compressed from the ideal 90° as a consequence of the rigid nature of the 5-membered rings and, indeed, the macrocycle as a whole, and are comparable with those for the reported dibenzo-9aneP$_3$ example. Slightly smaller angles have been reported for the saturated Fe(II) systems but direct comparison is not possible because these literature examples have bulkier Cp^R ligands that influence the P–Fe–P angles. The distance between the centroid of the Cp ring and the Fe atom is 1.535 Å and the distance between the Fe atom and the centroid of the P_3 ring is 1.313 Å.

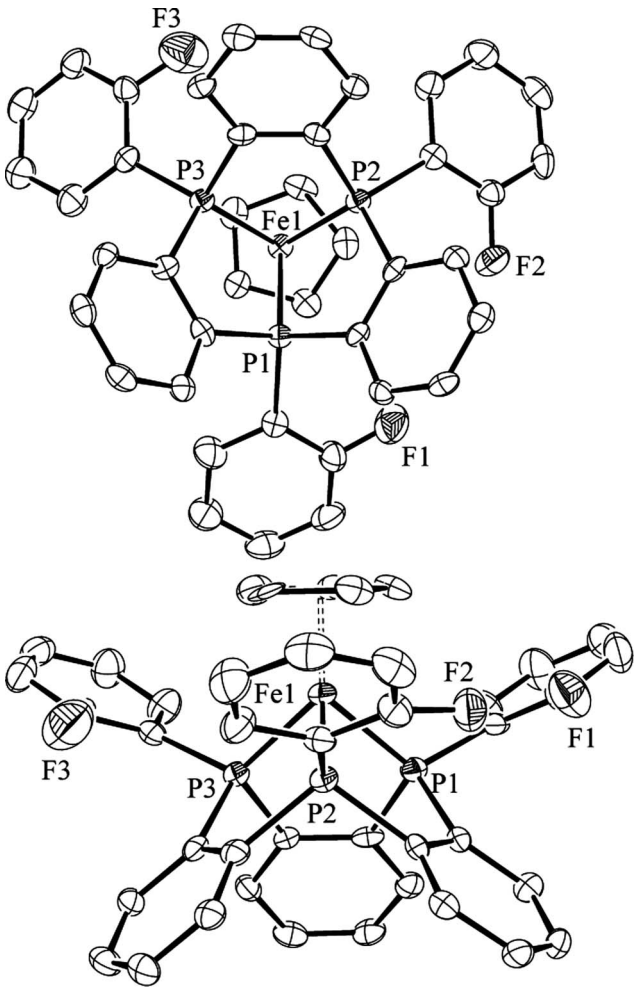


Fig. 1 Two ORTEP views of the cation **3a**. Thermal ellipsoids are drawn at the 30% occupancy level. Selected bond lengths (Å): Fe(1)–P(1) 2.152(1); Fe(1)–P(2) 2.154(1); Fe(1)–P(3) 2.142(1). Selected bond angles (deg): P(1)–Fe(1)–P(2) 86.51(5), P(1)–Fe(1)–P(3) 86.75(5), P(2)–Fe(1)–P(3) 86.49(5). Hydrogen atoms, the Ph_4B^- anion and four molecules of acetonitrile of crystallisation are omitted for clarity.

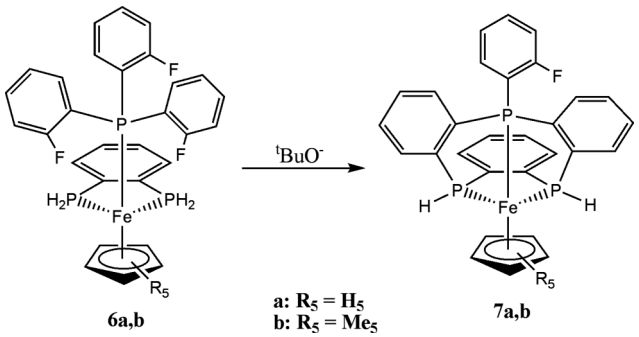
The analogous Cp* tribenzannulated complex can also be synthesised by the same synthetic route. The initial precursor complex $[(\eta^5\text{-}C_5Me_5)Fe\{(Ph^F)_2PC_6H_4P(Ph^F)_2\}(MeCN)]BF_4$, **2b**, was synthesised as a red air-sensitive, THF soluble powder, in very good yield (94%). Characteristic peaks at 1.63 (Cp* methyls) and 2.19 ppm (CH_3CN) are seen in the ^{1}H NMR spectrum along with multiplets in the aromatic region between 6.69 and 7.86 ppm. Otherwise the remaining NMR data reflect closely those observed for the analogous Cp compound. A broad singlet is seen at 90.1 ppm in the $^{31}P\{^{1}H\}$ NMR spectrum and the *ortho*-fluorophenyl groups appear as a singlet at −99.6 ppm in the ^{19}F NMR spectrum. The subsequent cyclisation chemistry proceeds in the same manner as described for the Cp derivative and the resulting complexes **2b** and **3b** show the same general spectroscopic features as those observed for the Cp derivatives above.

The Cp* dibenzannulated triphosphorus macrocycle could not be synthesised as the addition of base resulted in immediate decomposition, possibly as a result of the methyl groups attached to the Cp* attacking the reactive *ortho*-fluorophenyl rings.

Synthesis of disecondary, monotertiary tribenzannulated 9aneP$_3$ macrocycles

Although the synthesis of the tritertiary P_3 macrocycles highlighted above gave good yields of the final products, these products could not be further functionalised readily to allow access to a range of different macrocyclic compounds. In addition, the necessary 1,2-bis{di(2-fluorophenyl)phosphino}benzene precursor was in itself not easy to access on a large scale. Our desire to prepare a number of different derivatives of the tribenzannulated 9aneP$_3$ systems required a synthetic approach that produced complexes with a functionality or functionalities that could be easily converted into other groups by standard synthetic procedures. This flexibility can be realised if one or more P–H groups are present in the initially formed macrocyclic product. Thus, the synthetic procedure highlighted in Scheme 3 was identified as being a more flexible approach to these tribenzannulated systems, this methodology differs from that in Scheme 2 by using the bidentate primary phosphine, 1,2-bis-phosphinobenzene, and a monodentate tertiary phosphine bearing the 2-fluorophenyl substituents. This modification has the synthetic advantage that $P(Ph^F)_3$ is more easily prepared on a multigram scale than the $(Ph^F)_2PC_6H_4P(Ph^F)_2$ species which is itself prepared from 1,2-bis-phosphinobenzene.

The substitution of the acetonitrile in the precursor complex $[(\eta^5\text{-}C_5H_5)Fe(H_2PC_6H_4PH_2)(CH_3CN)]PF_6$ by $P(Ph^F)_3$ is achieved



Scheme 3

by the usual procedure to give **6a** as a yellow, slightly air-sensitive powder in good yield (82%). Coordination of the trifluororarylphosphine is confirmed by the $^{31}P\{^{1}H\}$ NMR spectrum which shows a broad singlet at 22.0 ppm in addition to the singlet at 16.0 ppm for the coordinated bisphosphinobenzene. Although no coupling can be resolved as a consequence of the broad nature of the $^{31}P\{^{1}H\}$ resonance, it is clear that the magnitude of any $^{3}J_{P-F}$ coupling is greatly reduced compared to that seen in the spectrum of the uncoordinated ligand (δ_P –42.1 ppm, $^{3}J_{P-F}$ = 56.6 Hz). This is emphasised in the ^{19}F NMR spectrum of **6a** which shows a singlet at –97.9 ppm. The ^{1}H NMR spectrum shows a broad singlet at 3.61 ppm due to the Cp resonances and complex multiplets from 6.94–7.39 ppm which can be assigned to the aromatic protons. The $^{13}C\{^{1}H\}$ NMR spectrum shows a doublet of doublets at 165.0 ppm ($^{1}J_{C-F}$ = 285.3 Hz, $^{2}J_{C-P}$ = 5.1 Hz) in addition to other aromatic resonances consistent with the formulation. Cyclisation to **7a** was promoted by excess triethylamine and could be conveniently monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy. After 2 h at reflux, a triplet at 89.1 ppm ($^{2}J_{P-P}$ = 35.7 Hz) was observed in the $^{31}P\{^{1}H\}$ NMR spectrum in addition to a complex multiplet at 66.5 ppm; this pattern represents the partially formed macrocycle where one new chelate ring is present. Continued heating led to slow loss of this intermediate and the growth of peaks for complex **7a** as a doublet ($^{2}J_{P-P}$ = 35.7 Hz) and a multiplet at 89.1 and 120.2 ppm respectively. The ^{19}F NMR spectrum showed a singlet at –101.8 ppm and resonances corresponding to aromatic protons (6.95–7.71 ppm) and the Cp hydrogens (3.73 ppm) were the only peaks seen in the ^{1}H NMR spectrum while the $^{13}C\{^{1}H\}$ NMR spectrum shows a slightly broadened doublet at 165.0 ppm ($^{1}J_{C-F}$ = 286.0 Hz), with unresolved $^{2}J_{C-P}$ coupling. The molecular ion was observed in the mass spectrum at 779.6 amu. The Cp* tribenzannulated triphosphorus macrocycle (**7b**) can be synthesised similarly from the $[(\eta^5\text{-}C_5Me_5)Fe(H_2PC_6H_4PH_2)(CH_3CN)]^+$ complex and isolated as a yellow air-stable powder. All spectroscopic features are as expected and are given in the experimental section.

Dibenzannulated 9aneP_3 macrocycles are also accessible by this second method when the 1,2-bis(phosphino)benzene is replaced with 1,2-bis(phosphino)ethane, albeit in somewhat lower yields than for the tribenzannulated analogue.

Synthesis of tribenzannulated 9anePAs$_2$ and 9aneAs$_3$ macrocycles

Both of the methods developed above should be amenable to extension to the 9anePAs$_2$ and 9aneAs$_3$ macrocycles by simple replacement of the P-containing synthons with the analogous arsenic ligands. Arsenic is not as common a donor type as phosphorus in coordination chemistry and is rare in macrocyclic systems; there are no reports of homoleptic 9aneAs$_3$ species. The necessary $(Ph^F)_2AsC_6H_4As(Ph^F)_2$ and $As(Ph^F)_3$ precursor ligands are readily prepared in the same fashion as for the phosphorus analogues. Following method 1, the complex $[(\eta^5\text{-}C_5H_5)Fe\{(Ph^F)_2AsC_6H_4As(Ph^F)_2\}(CH_3CN)]^+$ (**1c**) is prepared by the same procedure that provided the P-analogue and was isolated as a purple solid. The complex is somewhat unstable in solution especially when exposed to air but appears indefinitely stable in the solid-state in the absence of air. The ^{19}F NMR spectrum showed a characteristic singlet at –99.8 ppm. The $^{13}C\{^{1}H\}$ NMR spectrum showed a singlet at 2.6 ppm representing the co-ordinated acetonitrile, a broad singlet for the Cp carbons at 76.4 ppm and a characteristic doublet for the *ortho*-fluoro carbon at 165.0 ppm ($^{1}J_{C-F}$ = 241.9 Hz). A characteristic peak at 2262 cm^{-1} is seen for the co-ordinated acetonitrile in the infrared spectrum. Substitution of the MeCN ligand with phenylphosphine is straightforward with complex **3c** being obtained as an orange powder in good yield. The nature of the complex is confirmed by NMR spectroscopy with singlets being observed in the $^{31}P\{^{1}H\}$ and ^{19}F NMR spectra at –3.0 and –101.4 ppm, respectively. All other spectroscopic features are very similar to the related phosphorus systems which have already been discussed.

Use of phenylarsine instead of phenylphosphine with the $[(\eta^5\text{-}C_5H_5)Fe\{(Ph^F)_2AsC_6H_4As(Ph^F)_2\}(CH_3CN)]^+$ precursor gave the complex $[(\eta^5\text{-}C_5H_5)Fe\{(Ph^F)_2AsC_6H_4As(Ph^F)_2\}(PhAsH_2)]^+$ (**4**) and ultimately the novel triarsamacrocycle complex **5**, following reaction with base, as an orange solid. Complex **4** was characterised by an upfield shift in the ^{19}F NMR spectrum to –101.5 ppm upon replacement of the coordinated acetonitrile by phenylarsine. The $^{13}C\{^{1}H\}$ NMR spectrum showed the characteristic doublet (assigned to the carbon bearing the fluorine) at 164.9 ppm ($^{1}J_{C-F}$ = 239.8 Hz). The ^{19}F NMR spectrum of the macrocycle complex **5** shows a singlet at –100.1 ppm at room temperature which splits into 3 separate resonances when the sample is cooled to –80 °C. This reflects the presence of rotamers at low temperature as proposed for the 9aneP_3 analogue above. As stated, the triarsenic macrocycle is unique. The only other example of a triarsenic macrocycle was synthesised by Kyba under high dilution conditions where he was able to obtain the non-templated macrocycle as a mixture of isomers.[7] Our synthesis occurs in good yield (73%) but efforts to liberate the free macrocycle has thus far proved unsuccessful.

Fine needle like yellow crystals of **5** suitable for X-ray diffraction were obtained after anion exchange with $NaBPh_4$ and subsequent recrystallisation from acetonitrile at –37 °C. Two views of the cation (Fig. 2) are shown to illustrate the similarity between the triphosphorus and triarsenic analogues of this type of macrocycle; the structures are isomorphous. Again, the two fluorine atoms are disordered between three positions and the Cp ring is rotationally disordered, as was observed for the phosphine analogue. Again, for clarity, only one position of the Cp ring is shown in Fig. 2. The fluorines were again successfully refined with partial occupancies ($^{2}/_{3}$). The gross structure resembles closely that of the triphosphorus macrocycle with the only significant differences being the increased average Fe–As bond length of 2.223(1) Å compared to the Fe–P lengths in the P_3 analogue (average 2.149(1)); and the average As–Fe–As angle in **5** (86.97(5)°) is also slightly larger than the average P–Fe–P angle in **3a** (86.53(5)°). The

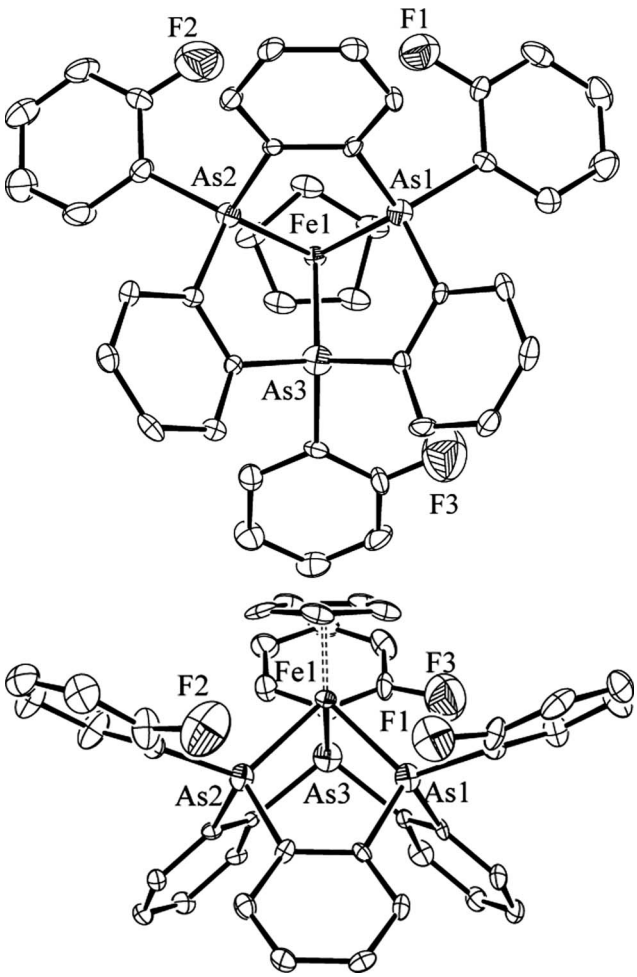


Fig. 2 Two ORTEP views of the cation **5**. Thermal ellipsoids are drawn at the 30% occupancy level. Selected bond lengths (Å): Fe(1)–As(1) 2.2340(14); Fe(1)–As(2) 2.2252(14); Fe(1)–As(3) 2.2100(14). Selected bond angles (deg): As(1)–Fe(1)–As(2) 86.81(5), As(2)–Fe(1)–As(3) 86.88(5), As(1)–Fe(1)–As(3) 87.23(5). Hydrogen atoms, the Ph_4B^- anion and four molecules of acetonitrile of crystallisation are omitted for clarity.

Fe–As bonds in **5** are shorter than those observed in a number of iron(II) systems containing monodentate and bidentate arsines, for example the Fe–As bond lengths are 2.235(1), 2.326(2), and 2.3380(5) Å in the complexes $[(\eta^5\text{-}C_5H_5)Fe(diphos)(PhMeAsF)]^+$,[8] $[(\eta^5\text{-}C_5H_5)Fe(diphos)(cyc\text{-}C_3AsPh)]^+$,[9] and $Fe(diars)_2I_2$[10] respectively. The Fe–As distance is most closely similar to the example with the more π-acidic fluoroarsine, rather than the more σ-basic alkyl arsines; the aryl and fluoro-aryl substituents in **5** are likely to render the ligand more similar in π-acidity to the former rather than the latter and thus the bond distances in **5** are unexceptional. The slightly longer Fe–pnictide bond length in **5** in comparison to **3a** is also likely to be limited by the rigid structure of the ligand which may compress these values in comparison to monodentate and less rigid bidentate ligands. The average Fe–As bond length of all known crystallographic structures of complexes of Fe(II) with tertiary arsines is 2.366 Å.[11] The cavity size is illustrated by the non-bonding distances between the individual arsenic atoms; the average As–As distance is 3.060 Å which is again a little longer than the average P–P distance (2.948 Å) in **3a**. These distances suggest the presence of a cavity that may be able to accommodate various anions.

For reasons unknown, the analogous bulkier Cp*Fe^+ system was a poor template for the formation of the $9aneAs_3$ macrocycle. In addition, application of the second methodology for the synthesis of disecondary monotertiary $9aneAs_3$ macrocycles was also unsuccessful; attempts to coordinate 1,2-bis(arsino)benzene to either the Cp or Cp* iron templates lead to decomposition under the reaction conditions; although initial colour changes were observed, the solutions rapidly decomposed to intractable brown materials that were not amenable to further reaction.

Experimental

Methods and materials

All synthetic procedures and manipulations were performed under dry argon or nitrogen using standard Schlenk line techniques. All solvents were freshly distilled from sodium (toluene), sodium/benzophenone (THF) or calcium hydride (acetonitrile, methanol and dichloromethane) under nitrogen before use. All other chemicals were obtained commercially and used as received. The ^{31}P NMR spectra were recorded on a JEOL Eclipse 300 MHz spectrometer operating at 121.7 MHz, and referenced to 85% H_3PO_4 (δ = 0 ppm). ^1H and ^{13}C NMR spectra were obtained using a Bruker 500 MHz spectrometer, operating at 500.0 and 125.8 MHz, respectively, and referenced to tetramethylsilane (δ = 0 ppm). Unless stated otherwise, infrared spectra were recorded as nujol mulls on a Jasco FTIR spectrometer. Mass spectra were obtained using a Waters LCT Premier XE mass spectrometer. Elemental analyses were performed by Medac Ltd, UK.[12] 1,2-Bis{di(2-fluorophenyl)phosphino}benzene, 1,2-bis{di(2-fluorophenyl)phosphino}ethane, and 1,2-bis{di(2-fluorophenyl)arsino}benzene were prepared using literature methods.[13] Other starting materials that had previously been prepared which are utilised in the experimental procedure include $[(\eta^5\text{-}C_5H_5)Fe(H_2PC_6H_4PH_2)CH_3CN]PF_6$, and $[(\eta^5\text{-}C_5Me_5)Fe(H_2PC_6H_4PH_2)CH_3CN]PF_6$.[2a]

Syntheses

$[(\eta^5\text{-}C_5H_5)Fe\{(Ph^F)_2PC_6H_4P(Ph^F)_2\}CH_3CN]PF_6$, 1a. To a solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_3CN)]PF_6$ (0.36 g, 1 mmol) in THF (15 ml) was added a solution of 1,2-bis[di(2-fluorophenyl)phosphino]benzene (0.47 g, 1 mmol) in THF (30 ml) at room temperature. The solution was photolysed with a 100 W table top lamp for 24 h resulting in a colour change from yellow to red. The reaction mixture was filtered through celite and the solvent removed *in vacuo*. Trituration with ether gave a red powder. Yield = 0.78 g (94%). ^1H NMR ($CDCl_3$, 400 MHz) δ 6.9–7.7 (20H, m, Ar*H*), 3.96 (5H, s, C_5H_5), 2.29 (3H, s, CH_3CN) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 165.02 (d, $^1J_{C-F}$ = 242.9 Hz), 123.2–133.9 (m), 115.67 (d, $^1J_{C-P}$ = 23.5 Hz), 81.41 (s, CH), 2.80 (s, CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): 92.5 (s br), –143.7 (septet, $^1J_{P-F}$ = 714 Hz, PF_6^-) ppm. ^{19}F NMR ($CDCl_3$): –98.0 (s), –73.5 (d, $^1J_{F-P}$ = 714 Hz, PF_6^-) ppm. MS: 680 (M^+, 60%). Anal. Calc. for $C_{37}H_{28}NP_3F_{10}Fe$: C, 53.84; H, 3.43; N, 1.70%. Found: C, 53.2; H, 3.2; N, 1.6%.

[(η⁵-C_5Me_5)Fe{$(Ph^F)_2PC_6H_4P(Ph^F)_2$}CH_3CN]BF_4, 1b. To a solution of [(η⁵-C_5Me_5)Fe(CO)$_2$(CH_3CN)]BF_4 (1.13 g, 3 mmol) in THF (10 ml) was added a solution of 1,2-bis[di(2-fluorophenyl)phosphino]benzene (1.56 g, 3 mmol) in THF (15 ml) at room temperature. The solution was photolysed with a 100 W table top lamp for 24 h resulting in a colour change from yellow to red. The reaction mixture was filtered through celite, the solvent removed *in vacuo* and the solid triturated with ether to give a red powder. Yield = 2.53 g (94%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.7–7.9 (20H, m, Ar*H*), 2.19 (3H, s, CH_3CN), 1.63 (15H, s, C_5Me_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 165.02 ($^1J_{C-F}$ = 242.9, $^3J_{C-P}$ = 7.0 Hz), 123.2–133.9 (m), 118.10 (s, C), 115.67 (d, $^1J_{C-P}$ = 23.5 Hz), 87.31 (C), 9.54 (s, CH_3), 3.92 (s, CH_3) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz): 90.1 (s br) ppm. ^{19}F NMR ($CDCl_3$): –99.6 (s) ppm. MS: 751 (M^+, 80%). Anal. Calc. for $C_{42}H_{38}NBP_2F_8Fe$: C, 60.24; H, 4.58; N, 1.67%. Found: C, 59.9; H, 4.4; N, 1.5%.

[(η⁵-C_5H_5)Fe{$(Ph^F)_2AsC_6H_4As(Ph^F)_2$}$CH_3CN$]$PF_6$, 1c. To a solution of [(η⁵-C_5H_5)Fe(*p*-xylene)]PF_6 (0.37 g, 1 mmol) in acetonitrile (15 ml) was added a solution of 1,2-bis[di(2-fluorophenyl)arsino]benzene (1 mmol) in acetonitrile (15 ml). This was photolysed with a 100 W table top lamp for 24 h resulting in a colour change from yellow to dark blue. The reaction mixture was filtered through celite, the solvent removed *in vacuo* and the solid triturated with ether to give a purple-blue powder Yield = 0.87 g (95%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.7–7.5 (20H, m, Ar*H*), 3.95 (5H, s, C_5H_5), 2.29 (3H, s, CH_3CN) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 164.99 (d, $^1J_{C-F}$ = 241.9 Hz), 125.5–136.4 (m), 121.60 (s), 115.52 (d, $^1J_{C-P}$ = 24.1 Hz), 76.4 (s, CH), 2.60 (s, CH_3) ppm. ^{19}F NMR ($CDCl_3$): –99.8 (s), –73.5 (d, $^1J_{F-P}$ = 714 Hz, PF_6^-) ppm. MS: 768 (M^+, 100%). Anal. Calc. for $C_{37}H_{28}NPAs_2F_{10}Fe$: C, 48.66; H, 3.10; N, 1.53%. Found: C, 48.2; H, 3.0; N, 1.6%.

[(η⁵-C_5H_5)Fe{$(Ph^F)_2PC_6H_4P(Ph^F)_2$}$(PhPH_2)$]PF_6, 2a. [(η⁵-C_5H_5)Fe{$(Ph^F)_2PC_6H_4P(Ph^F)_2$}CH_3CN]PF_6, **1a** (0.75 g, 0.96 mmol) was dissolved in 1,2-dichloroethane (40 ml). Phenylphosphine (0.5 ml) was added and the reaction mixture heated to 60 °C for 6 h until the colour changed from red to orange. The solvent was removed *in vacuo* and the solid residue triturated with ether to give a yellow powder. Yield = 0.80 g (93%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.8–7.6 (25H, m, Ar*H*), 4.38 (2H, d, $^1J_{H-P}$ = 331 Hz, P*H*), 3.81 (5H, s, C_5H_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 163.29 (d, $^1J_{C-F}$ = 252.7 Hz), 125.2–135.0 (m), 117.60 (d, $^1J_{C-P}$ = 23.0 Hz), 82.88 (s, CH) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz): 84.6 (d, $^2J_{P-P}$ = 51 Hz), 12.1 (t, $^2J_{P-P}$ = 51 Hz), –143.7 (septet, $^1J_{P-F}$ = 714 Hz, PF_6^-) ppm. ^{19}F NMR ($CDCl_3$): –98.0 (s), –73.5 (d, $^1J_{F-P}$ = 714 Hz, PF_6^-) ppm. MS: 749 (M^+, 100%). Anal. Calc. for $C_{41}H_{32}P_4F_{10}Fe$: C, 55.05; H, 3.61%. Found: C, 55.2; H, 3.2%.

[(η⁵-C_5Me_5)Fe{$(Ph^F)_2PC_6H_4P(Ph^F)_2$}$(PhPH_2)$]BF_4, 2b. Phenylphosphine (0.4 ml, 3.6 mmol) was added to a solution of **1b** (0.80 g, 0.96 mmol) in THF (30 ml). The reaction mixture was heated to 60 °C for 24 h until the colour changed from red to orange. The solvent was removed *in vacuo* and the residue triturated with ether to give a yellow powder. Yield = 0.80 g (92%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.9–7.5 (25H, m, Ar*H*), 4.45 (2H, d, $^1J_{H-P}$ = 343 Hz, P*H*), 1.63 (15H, s, C_5Me_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 165.85 (d, $^1J_{C-F}$ = 325.7 Hz), 124.9–135.1 (m), 87.70 (s, C), 9.70 (s, CH_3) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz): 81.7 (s), 10.1 (s) ppm. ^{19}F NMR ($CDCl_3$): –98.2 (s) ppm. MS: 820 (M^+, 100%). Anal. Calc. for $C_{46}H_{42}P_3F_8BFe$: C, 60.95; H, 4.68%. Found: C, 60.5; H, 4.7%.

[(η⁵-C_5H_5)Fe{$(Ph^F)_2AsC_6H_4As(Ph^F)_2$}$(PhPH_2)$]$PF_6$, 2c. **1c** (0.88 g, 0.96 mmol) was dissolved in 1,2-dichlorobenzene (30 ml). Phenylphosphine (0.5 ml, 4.5 mmol) was added and the reaction mixture heated to 60 °C for 16 h until the colour changed from dark blue to orange. The solvent was removed *in vacuo* and the residue triturated with ether to give a yellow powder. Yield = 0.86 g, (91%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.7–7.5 (25H, m, Ar*H*), 4.63 (2H, d, $^1J_{H-P}$ = 338 Hz, P*H*), 3.98 (5H, s, C_5H_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 164.32 (d, $^1J_{C-F}$ = 243.2 Hz), 124.0–136.0 (m), 115.61 (d, $^1J_{C-P}$ = 23.2 Hz) 80.9 (s, CH) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz): 11.8 (s), –143.7 (septet, $^1J_{P-F}$ = 714 Hz, PF_6^-) ppm. ^{19}F NMR ($CDCl_3$): –101.4 (s), –73.5 (d, $^1J_{F-P}$ = 714 Hz, PF_6^-) ppm. MS: 837 (M^+, 100%). Anal. Calc. for $C_{41}H_{32}P_2As_2F_{10}Fe$: C, 50.13; H, 3.29%. Found: C, 49.8; H, 3.2%.

[(η⁵-C_5H_5)Fe(tribenzo-9aneP_3-Ph,Ph^F_2)]PF_6, 3a. Potassium *tert*-butoxide (2 mole equivalents, 0.09 g, 0.78 mmol) was added to a solution of **2a** (0.33 g, 0.39 mmol) in THF (40 ml) and the reaction mixture left to stir overnight. After filtering, the solvent was removed *in vacuo* to give a yellow solid. Yield = 0.26 g (78%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.3–7.6 (25H, m, Ar*H*), 3.81 (5H, s, C_5H_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 163.29 (d, $^1J_{C-F}$ = 252.7 Hz), 129.9–134.7 (m), 115.34 (d, $^1J_{C-P}$ = 23.1 Hz), 82.13 (s, CH) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz): 127.5 (d, $^2J_{P-P}$ = 32.8 Hz), 119.6 (t, $^2J_{P-P}$ = 32.8 Hz), –143.7 (septet, $^1J_{P-F}$ = 714 Hz, PF_6^-) ppm. ^{19}F NMR ($CDCl_3$): –98.4 (s), –73.5 (d, $^1J_{F-P}$ = 714 Hz, PF_6^-) ppm. MS: 709 (M^+, 100%). Anal. Calc. for $C_{41}H_{30}P_4F_8Fe$: C, 57.63; H, 3.55%. Found: C, 57.5; H, 3.2%.

[(η⁵-C_5Me_5)Fe(tribenzo-9aneP_3-Ph,Ph^F_2)]BF_4, 3b. **2b** (0.35 g, 0.39 mmol) was dissolved in THF (30 ml), and potassium *tert*-butoxide (catalytic quantity) was added to the solution. The reaction was heated to 60 °C for 16 h. After filtration, the solvent was removed *in vacuo* to give a yellow solid. Yield = 0.23 g (78%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.9–7.3 (25H, m, Ar*H*), 1.67 (15H, s, C_5Me_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 165.80 (d, $^1J_{C-F}$ = 324.3 Hz), 123.9–134.9 (m), 80.1 (s), 10.1 (s) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz): 117.3 (t, $^2J_{P-P}$ = 35.3 Hz), 111.9 (m) ppm. ^{19}F NMR ($CDCl_3$): –100.9 (s) ppm. MS: 780 (M^+, 100%). Anal. Calc. for $C_{46}H_{40}P_3F_6BFe$: C, 63.76; H, 4.66%. Found: C, 63.2; H, 4.4%.

[(η⁵-C_5H_5)Fe(tribenzo-9aneAs_2P-Ph,Ph^F_2)]PF_6, 3c. **2c** (0.22 g, 0.22 mmol) was dissolved in THF (40 ml) and potassium *tert*-butoxide (0.5 g) was added as a solid to the solution. The reaction was left to stir overnight, filtered and the solvent removed *in vacuo* to give a yellow solid. Yield = 0.15 g (73%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.9–7.7 (25H, m, Ar*H*), 3.98 (5H, s, C_5H_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 128.9–135.1 (m), 82.0 (s) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz): 134.6 (s), –143.7 (septet, $^1J_{P-F}$ = 714 Hz, PF_6^-) ppm. ^{19}F NMR ($CDCl_3$): –100.1 (s), –73.5 (d, $^1J_{F-P}$ = 714 Hz, PF_6^-) ppm. MS: 797 (M^+, 100%). Anal. Calc. for $C_{41}H_{30}P_2As_2F_8Fe$: C, 52.26; H, 3.22%. Found: C, 49.8; H, 3.2%.

[(η⁵-C_5H_5)Fe{$(Ph^F)_2AsC_6H_4As(Ph^F)_2$}($PhAsH_2$)]$PF_6$, 4. Phenylarsine (0.8 ml, 0.96 mmol) was added to a solution of **1c** (0.88 g, 0.96 mmol) in 1,2-dichloroethane (30 ml) and the reaction mixture heated to 60 °C for 6 h until the colour changed from red to orange. The solvent was removed *in vacuo* and the residue triturated with ether to give an orange powder. Yield = 0.86 g (86%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.8–7.6 (25H, m, Ar*H*), 4.01 (5H, s, C_5H_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 164.91 (d, $^1J_{C-F}$ = 239.8 Hz), 128.9–135.1 (m), 83.4 (s) ppm. ^{19}F NMR ($CDCl_3$): –101.5 (s) ppm. MS: 881 (M^+, 100%). Anal. Calc. for $C_{41}H_{32}PAs_3F_{10}Fe$: C, 47.98; H, 3.15%. Found: C, 47.8; H, 2.9%.

[(η⁵-C_5H_5)Fe(tribenzo-9aneAs_3-Ph,Ph^F_2)]PF_6, 5. **4** (0.22 g, 0.22 mmol) was dissolved in THF (40 ml), and potassium *tert*-butoxide (0.50 g) was added to the solution. The reaction was left to stir overnight and filtered. The solvent was removed *in vacuo* to give a yellow solid. Yield = 0.16 g (73%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.9–7.8 (25H, m, Ar*H*), 3.98 (5H, s, C_5H_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 164.92 (d, $^1J_{C-F}$ = 240.0 Hz), 130.1–132.4 (m), 78.1 (s) ppm. ^{19}F NMR ($CDCl_3$): –101.5 (s), –73.5 (d, $^1J_{F-P}$ = 714 Hz, PF_6^-) ppm. MS: 822 (M^+ – F, 100%). Anal. Calc. for $C_{41}H_{30}PAs_3F_8Fe$: C, 49.93; H, 3.07%. Found: C, 49.2; H, 2.9%.

[(η⁵-C_5H_5)Fe($H_2PC_6H_4PH_2$){$P(Ph^F)_3$}]PF_6, 6a. To a solution of [(η⁵-C_5H_5)Fe($H_2PC_2H_4PH_2$)(CH_3CN)]PF_6 (0.43 g, 0.96 mmol) in acetonitrile (35 ml) was added tris(*ortho*-fluorophenyl)phosphine (0.32 g, 1 mmol) and the reaction mixture heated to 60 °C for 18 h whereupon a colour change from red to yellow was observed. The solvent was removed *in vacuo* and the resultant solid triturated with ether to give a yellow powder. Yield = 0.31 g (46%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.9–7.4 (16H, m, Ar*H*), 4.35 (5H, s, C_5H_5), 3.44 (4H, d, $^1J_{H-P}$ = 379 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 165.18 (d, $^1J_{C-F}$ = 285.3 Hz), 120–135 (m), 80.6 ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): 60.8 (t, $^2J_{P-P}$ = 57 Hz), 11.5 (dq, $^2J_{P-P}$ = 57 Hz, $^5J_{P-F}$ = 16 Hz) ppm. ^{19}F NMR ($CDCl_3$): –97.9 (s), –73.5 (d, $^1J_{F-P}$ = 714 Hz, PF_6^-) ppm. MS: 579 (M^+, 100%). Anal. Calc. for $C_{29}H_{25}P_4F_9Fe$: C, 48.09; H, 3.49%. Found: C, 47.5; H, 3.4%.

[(η⁵-C_5Me_5)Fe($H_2PC_6H_4PH_2$){$P(Ph^F)_3$}]BF_4, 6b. [(η⁵-C_5Me_5)-Fe($H_2PC_6H_4PH_2$)(CH_3CN)]BF_4 (0.45 g, 0.98 mmol) was dissolved in acetonitrile (30 ml) and tris(*ortho*-fluorophenyl)phosphine (1.6 g, 5 mmol) added thereto. The reaction mixture was heated to 60 °C for 10 h whereupon the colour changed from red to yellow. The solvent was removed *in vacuo* to give a yellow powder. Yield = 0.59 g (82%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.7–7.4 (16H, m, Ar*H*), 1.72 (15H, s, C_5Me_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 164.00 (dd, $^1J_{C-F}$ = 234.3 Hz, $^2J_{C-P}$ = 6.4 Hz), 121.5–133.8 (m), 115.24 (d, $^1J_{C-P}$ = 24.0 Hz), 87.24 (s), 9.91 (s) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): 63.2 (m), 18.0 (d, $^2J_{P-P}$ = 42 Hz) ppm. ^{19}F NMR ($CDCl_3$): –100.8 (s) ppm. MS: 649 (M^+, 100%). Anal. Calc. for $C_{34}H_{35}P_3F_7BFe$: C, 55.46; H, 4.80%. Found: C, 55.5; H, 4.7%.

[(η⁵-C_5H_5)Fe(tribenzo-9aneP_3-H_2,Ph^F)]PF_6, 7a. Triethylamine (0.5 ml, 5 mmol) was added to a solution of **6a** (0.57 g, 0.78 mmol) in THF (30 ml) and the reaction mixture heated to 60 °C for 8 h. After cooling, the solvent was removed *in vacuo* to give a yellow powder. Yield = 0.20 g (74%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.8–8.2 (16H, m, Ar*H*), 4.35 (5H, s, C_5H_5), 3.44 (d, $^1J_{H-P}$ = 379 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 165.03 (d, $^1J_{C-F}$ = 286.0 Hz), 131–135 (m) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): 123.9 (t, $^2J_{P-P}$ = 27 Hz), 92.3 (t, $^2J_{P-P}$ = 27 Hz) ppm. ^{19}F NMR ($CDCl_3$): –101.8 (s), –73.5 (d, $^1J_{F-P}$ = 714 Hz, PF_6^-) ppm. MS: 539 (M^+, 100%). Anal. Calc. for $C_{29}H_{23}P_4F_7Fe$: C, 50.90; H, 3.39%. Found: C, 50.4; H, 3.4%.

[(η⁵-C_5Me_5)Fe(tribenzo-9aneP_3-H_2,Ph^F)]BF_4, 7b. Triethylamine (0.5 ml, 5 mmol) was added to a solution of **6b** (0.59 g, 0.80 mmol) in THF (30 ml) and the reaction mixture heated to 60 °C for 8 h. The solvent was removed *in vacuo* to give a yellow powder. Yield = 0.50 g (90%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.8–7.4 (16H, m, Ar*H*), 1.70 (15H, s, C_5Me_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 164.71 (d, $^1J_{C-F}$ = 234.3 Hz), 121.5–133.8 (m), 115.54 (d, $^1J_{C-P}$ = 23.0 Hz) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): 115.1 (s), 108.0 (m) ppm. ^{19}F NMR ($CDCl_3$): –103.4 (s) ppm. MS: 609 (M^+, 100%). Anal. Calc. for $C_{34}H_{33}P_3F_5BFe$: C, 58.65; H, 4.79%. Found: C, 58.5; H, 4.5%.

Crystallography

The crystal structures reported herein were obtained on the tetraphenylborate salts of the complexes after anion exchange of the PF_6^- salts with $NaBPh_4$ in acetonitrile from which both compounds crystallise with four molecules of acetonitrile of crystallisation in the unit cell. Anions and solvent molecules are omitted from the figures for clarity; there are no chemically significant intermolecular interactions. Data collection was carried out on a Bruker-Nonius Kappa CCD diffractometer using graphite monochromated Mo-Kα radiation (λ(Mo-Kα) = 0.71073 Å). The instrument was equipped with an Oxford Cryosystems cooling apparatus. Data collection and cell refinement were carried out using COLLECT[14] and HKL SCALEPACK.[15] Data reduction was applied using HKL DENZO and SCALEPACK.[16] The structures were solved using direct methods (Sir92)[16] and refined with SHELX-97.[17] Absorption corrections were performed using SORTAV.[18] All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were inserted in idealised positions with *U*iso set at 1.2 or 1.5 times the *U*eq of the parent atom. In the final cycles of refinement, a weighting scheme that gave a relatively flat analysis of variance was introduced and refinement continued until convergence was reached. In both structures, the carbon positions in the cyclopentadienyl rings and the fluorine positions are disordered. For both **3a** and **5**, the cyclopentadienyl rings were modeled over two positions related by an ~36° rotation, each with 50% occupancy. The two F atoms are distributed over three sites in both structures. For **3a**, an occupancy of $^2/_3$ was used for all sites whereas for **5**, the occupancies refined to 0.61(2), 0.76(2) and 0.63(2). Pertinent data are collected in Table 1.

Conclusions

Nine-membered triphospha- and triarsamacrocycles with unsaturated benzo-backbones have been prepared by a template method based on [Cp^RFe]$^+$ systems. The cyclisation involves the attack of a coordinated phosphide (or arsenide) nucleophile at an electrophilic *ortho*-fluorophenyl carbon suitably activated by virtue of its disposition with regard to a coordinated phosphine. The macrocycle assembly is of the '2 + 1' type where two new chelate rings are formed from appropriately derivatised bidentate and monodentate phosphines/arsines. Both unsubstituted cyclopentadienyl and 1,2,3,4,5-pentamethylcyclopentadienyliron(II)

Table 1 Details of X-ray crystallographic data collection for the complexes

	3a	**5**
Empirical formula	$C_{73}H_{62}BF_2FeN_4P_3$	$C_{73}H_{62}As_3BF_2FeN_4$
Formula weight	1192.84	1324.69
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	15.6204(3)	15.6500(3)
b/Å	14.7050(3)	14.7771(4)
c/Å	27.0880(6)	27.3245(5)
α (°)		
β (°)	102.6900(10)	102.417(2)
γ (°)		
U/Å^3	6070.1(2)	6171.3(2)
Z	4	4
D_c/Mg m^{-3}	1.305	1.426
Reflections collected	37 113	21 135
Independent reflections	11 801	13 900
R_{int}	0.1505	0.0460
Final $R1$, w$R2$ [$I > 2\sigma(I)$]	0.0784, 0.1615	0.0834, 0.2585
(all data)	0.1707, 0.1946	0.1251, 0.3029

templates can be employed for the cyclisation although the former is preferred. The 9aneAs$_3$ is the first example of a nine-membered triarsamacrocycle. Crystal structures of the 9aneP$_3$ and 9aneAs$_3$ complexes show the unique conformation of these original macrocycles with a 'cup shaped' cavity formed by the rigid benzo-backbones.

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Notes and references

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