[15] X-ray diffraction on a Huber four-circle diffractometer ($\mathrm{Ag}_{\mathrm{K}\alpha}$ radiation): $T = 11(1)$ K, $a = 4.265(1)$, $b = 12.796(1)$, $c = 7.490(1)$ Å, $\beta = 100.77(1)^\circ$, $V = 401.6(1)$ Å^3, monoclinic, space group $P2_1/c$, 12997 reflections measured (4911 independent reflections, $R_{\mathrm{int}} = 0.0169$), absorption correction, $(\sin\theta/\lambda)_{\max} = 1.4$ Å^{-1}; after multipolar refinement (4830 reflections with $I > 0$): $R1 = 0.0202$, $wR2 = 0.0410$, GOF: 1.10. Multipole expansions were extended up to $l = 4$ for C, O, and K, and $l = 2$ for H; isotropic extinction was included; positional and thermal parameters for H were fixed at neutron-diffraction positions. Neutron diffraction at the High Flux Isotope Reactor (Oak Ridge National Laboratory): $T = 15(1)$ K, $a = 4.267(1)$, $b = 12.816(7)$, $c = 7.501(6)$ Å, $\beta = 100.82(6)^\circ$, $V = 402.9(3)$ Å^3; $\lambda = 1.008(2)$ Å. 2991 reflections measured (1436 independent reflections, $R_{\mathrm{int}} = 0.0585$); $(\sin\theta/\lambda)_{\max} = 0.8$ Å^{-1}; absorption correction; agreement indexes (1082 reflections with $I > 2\sigma(\mathrm{I})$): $R1 = 0.0438$, $wR2 = 0.0892$, GOF: 1.03. Positional and anisotropic thermal parameters were refined for all atoms; isotropic extinction was included. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-141183. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[17] Due to strong $\mathrm{O(sp^2)}-\mathrm{O(sp^2)}$ repulsion, the conformation of the isolated anion is nonplanar and the optimized torsion about C1–C2 bond is 90° (in contrast to the observed 13.2(1)°). The $\mathrm{COO^-}$ group is symmetric; therefore, the molecular symmetry is C_s.

[18] $\Phi(\boldsymbol{r}) = \sum_{\mathrm{M}} \frac{Z_{\mathrm{M}}}{|R_{\mathrm{M}} - r|} - \int \frac{\rho(r')}{|r - r'|} \mathrm{d}\boldsymbol{r}'$ ($\boldsymbol{R}_{\mathrm{M}}$ are nuclear positions, and Z_{M} nuclear charges).

[19] Calculated according to Z. Su, P. Coppens, *Acta Crystallogr. Sect. A* **1992**, *48*, 188.

[20] $q(\mathrm{H}) = 0.58$ (QTAM); 0.29 (Mulliken); 0.41 (charge fitting the potential); 0.51 (NBO). Similar charges are found in the dimer. Note that in ref. [1a] Mulliken charges of O(H) and H were given as a single charge ($q(\mathrm{OH}) = -0.19$).

[21] $q(\mathrm{H}) = 0.38(2)$. In addition, a significant population was refined in the 4s orbital of K (0.51(5)e), which implies a partial charge transfer. A model with constrained molecular charges (+1 for K, −1 for $\mathrm{HC_2O_4}$) did not show significant differences in the HB region.

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[23] K$\cdots$O bond paths were found in mainly closed-shell type interactions.

[24] The presence of an H$\cdots$O bond path in the dianionic dimer cannot be defined as a chemical bond within QTAM because the structure is not at equilibrium; however, this means that the instability of the species should not be attributed to an H$\cdots$O repulsion.

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A New Kinetic Template Synthesis of Triphosphacyclodecanes[**]

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Although the first macrocycles containing solely phosphorus atoms in the ring were reported nearly thirty years ago, there are surprisingly few studies on the coordination chemistry of these potentially very interesting ligands, especially when compared to the intensely studied nitrogen analogues. Early preparations including those of Horner et al.[1] and Kyba et al.[2] were by metal-free solution or high dilution methods, and were nonstereoselective giving a mixture of all possible isomers of the macrocycles. For the smallest triphosphorus macrocyclic ring system ([11]ane$\mathrm{P_3}$) known to date, Kyba et al. achieved the separation and characterization of all isomers; for the *syn,syn,anti* ligand isomer vigorous conditions (boiling xylenes) were required for the inversion of the phosphorus center and formation of facially coordinated complexes.[3] More recently, metal template approaches by Horner and Kunz,[4] Stelzer et al.,[5] Norman et al.,[6] and us[7] have been studied in order to direct the cyclization step. For facially capping triphosphanes, the template allows control of the stereochemistry at the phosphorus centers; however, liberation of the macrocycle is commonly nontrivial and to date, only 12-membered triphosphamacrocycles have been obtained as the free ligands by this method, albeit stereospecifically.[7] Variations in ring size are difficult to achieve by the established $\mathrm{M(CO)_3}$ templates (M = Group 6 metal) which does not allow manipulation and control of steric (or electronic) influences upon the cyclization step; the 12-membered ring is the smallest obtained by this method and attempts to decrease ring size by cyclization of vinyl phosphanes have failed in our hands.[8] We are interested in facially capping triphosphanes in which the phosphorus lone pairs are fixed in the favored all-*syn* orientation forcing remaining coordination sites in their complexes into mutually *cis* orientations.

This has prompted us to seek new template methods for the formation of triphosphamacrocycles to allow access to smaller ring sizes and rational high-yield routes to selectively functionalized ligands. We have chosen to investigate $[\eta^5\text{-CpFe(L)}_3]^+$ (L = monodentate or arene ligand; Cp = $\eta^5\text{-C}_5\mathrm{Me}_5$) complexes as potential templates since they are readily prepared and form facial trisphosphane complexes which tend to have good air-stability.[9] Of particular interest is that substituents on the Cp ring may be widely varied which may allow manipulation of steric influences upon the *trans*-coordinated phosphanes. Herein we report the synthesis of

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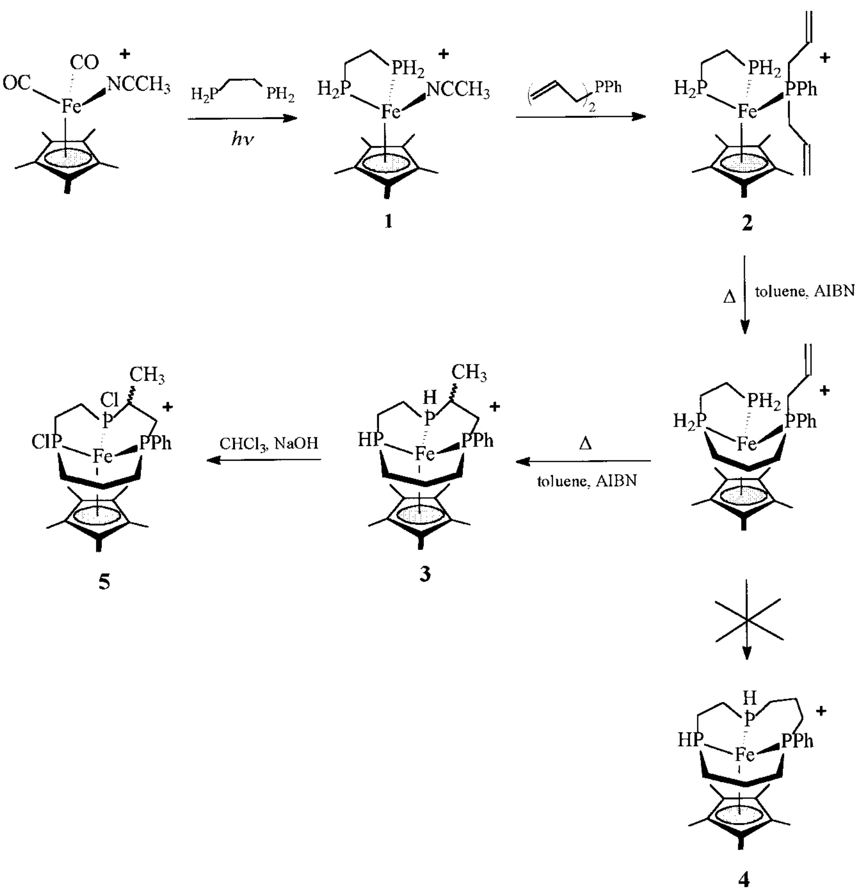

Scheme 1. Kinetic template synthesis of triphosphacyclodecanes.

the first [10]aneP$_3$ macrocycle by the Fe^{II}-template cyclization of a coordinated di-primary phosphane (1,2-diphosphanylethane, 1,2-dpe) and diallylphenylphosphane (Scheme 1).[10]

The hitherto unknown [(η^5-C$_5$Me$_5$)Fe(1,2-dpe)(CH$_3$CN)]BF$_4$ (**1**) is readily prepared by photolysis of a 1:1 mixture of [(η^5-C$_5$Me$_5$)Fe(CO)$_2$(CH$_3$CN)]BF$_4$ and 1,2-dpe in acetonitrile. The coordinated acetonitrile in **1** is substituted with diallylphenylphosphane on heating in 1,2-dichloroethane to give complex **2** in quantitative yield. The ^{31}P{^{1}H} NMR spectrum of **2** shows the expected triplet ($\delta = 45.4$) and doublet ($\delta = 11.9$, $J_{P,P} = 51$ Hz). Heating **2** in toluene at 80 °C in the presence of azobisisobutyronitrile (AIBN) gives a mixture from which complex **3** can be obtained as air- and moisture-stable yellow needles in 35 % yield after chromatography and anion exchange. The ^{31}P{^{1}H} NMR spectrum of **3** consists of an ABX pattern with a low-field triplet at $\delta = 111.7$ ($J_{P,P} = 25$ Hz), and two doublets of doublets at $\delta = 65.7$ and 61.7 ($J_{P,P} = 54$ and 25 Hz). The resonance signals at $\delta = 111.7$ and 61.7 in the ^{31}P NMR spectrum were attributed to secondary phosphanes ($^1J_{P,H} = 348$ and 340 Hz, respectively). This pattern precludes structure **4** (Scheme 1), as a simple AX$_2$ ^{31}P NMR spectrum would be expected for this complex. The ^{31}P NMR spectrum is compatible with structure **3**; the low-field resonance signal is assigned to the secondary phosphane α to the C-methyl carbon atom as it is a component of two five-membered chelates which are known to cause low-field ^{31}P shifts relative to six-membered chelates;[11] the presence of the exocyclic methyl- and methine-carbon atoms are confirmed in the ^{13}C DEPT NMR spectrum. The ^{1}H NMR spectrum is complex but consistent with the structure, the exocyclic CH$_3$ group is observed as a doublet of doublets at $\delta = 1.46$ ($J = 12$ and 7 Hz).

Attempts to grow crystals of **3** suitable for single-crystal X-ray analysis were unsuccessful. This prompted a search for a derivative of the parent macrocyclic complex that could be crystallized in an appropriate form. Following our recent observation of the halogenation of coordinated secondary phosphane macrocycles by halocarbons in the presence of base,[12] the reaction of **3** with NaOH in chloroform gave rise to a new complex **5** in high yield. The ^{31}P NMR spectrum of **5** showed new resonance signals at $\delta = 222.6$ and 202.5 and the loss of peaks attributable to secondary phosphanes. In addition, the appearance of the resonance signal from the tertiary phosphorus had changed to a doublet of doublets at $\delta = 59.8$ ($J_{P,P} = 13.5$ and 6 Hz). The IR spectrum of **5** showed an absence of bands attributable to ν_{PH} stretches. The structure of **5** was determined by a single-crystal X-ray diffraction study of a sample recrystallized from methanol in air. Orange crystals of the complex were obtained as the hemihydrate of the hexafluorophosphate salt.[13] Two views of the cation **5** are shown in Figure 1.

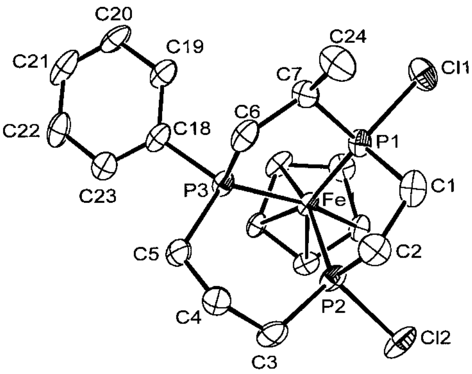

Figure 1. An Ortep[19] representation of the cation **5**. The cyclopentadienyl methyl groups have been removed for clarity. Selected bond lengths [Å] and angles [°]: Fe-P1 2.153(2), Fe-P2 2.148(2), Fe-P3 2.210(2), P1-Cl1 2.061(2), P2-Cl2 2.084(2); P1-Fe-P2 84.51(8), P1-Fe-P3 86.77(7), P2-Fe-P3 89.00(6).

It is clear from Figure 1 that both secondary phosphane groups in **3** have been converted to P–Cl functions as indicated by the spectroscopic data for **5**. In addition, the original characterization of **3** is confirmed by analogy with that of **5**, in which a ten-membered macrocycle containing two five-membered chelates (one with a methyl substituent) are present. The six-membered chelate adopts a chair conformation and both five-membered chelates have an envelope conformation. The methyl group projects equatorially from its chelate but is orientated almost perpendicular to the P_3 plane. The crystal is racemic, with both enantiomers Fe(*R*), P1(*R*), P2(*R*), P3(*S*), C1(*R*) and Fe(*S*), P1(*S*), P2(*S*), P3(*R*), C1(*S*)[17] being present in the asymmetric unit; only the former is shown in Figure 1. The Fe−P(Cl) bonds (av 2.151(2) Å) are both shorter than the Fe−P(Ph) bond length (2.210(2) Å) which is comparable to that in other related systems.[18] In addition, the P1-Fe-P3 and P1-Fe-P2 angles (84.51(8)°and 86.77(7)°, respectively) are significantly less than that of P2-Fe-P3 (89.00(6)°) or corresponding angles in related 12-aneP_3 complexes (e.g. P-Cr-P av 91.09(5)° in [(12aneP_3H_3)Cr(CO)$_3$]).[8] It is noteworthy that the nonbonded P$\cdots$P distances in **5** are significantly shorter (P1−P2 2.892(2), P1−P3 2.997(2), P2−P3 3.054(2) Å) than those observed in [(12-aneP_3H_3)Cr(CO)$_3$] (3.321(4) Å). The methyl groups of the cyclopentadienyl ring in **5** are bent slightly out of the Cp plane, suggesting some steric congestion about the metal center which may be responsible for the formation of the 10-membered as opposed to the 11-membered macrocycle (**4**) as a result of the compression of the P-Fe-P angles and corresponding reduction of the nonbonded P−P distances. These data support the view that introduction of steric control over these types of template cyclization may indeed be very valuable in enabling the formation of smaller ring systems than has previously been achieved.

The formation of **3** presumably involves coupling of the terminal carbon atom of the first allyl group with one of the primary phosphanes in **2** to produce a three-carbon bridge in the intermediate (Scheme 1). The second hydrophosphination, however, occurs at the internal carbon atom of the remaining allyl function to give **3**. As the precursor complex **2** is achiral, there is no control of the stereochemistry and complex **3** is formed as a racemate.

Thus this pentamethylcyclopentadienyliron template provides, as well as a new template system for the synthesis of triphosphorus macrocycles, the first complexes to contain a ten-membered triphosphamacrocycle and a novel example of a metal-templated internal hydrophosphination of an allyl function. Preliminary attempts to liberate the macrocycle from the metal center by reduction are encouraging. We are also investigating the influences of variations of the Cp substituents upon the outcome of the cyclization step and with alternative di-primary phosphane and alkenyl phosphane precursor ligands.

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[13] Crystal data for complex **5**, $C_{24}H_{37}Cl_2F_6O_{0.5}P_4Fe$, $M_r = 698.16$, $T = 150(2)$ K, monoclinic, space group *C*2/c, $a = 30.071(2)$, $b = 9.947(3)$, $c = 20.199(10)$ Å, $\beta = 104.13(2)°$, (by least-squares refinement of the setting angles for 25 reflections within $\theta = 3.05-26.29°$), $V = 5859(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.585\,g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 0.971\,cm^{-1}$, $F(000) = 2880$, crystal size $= 0.2 \times 0.2 \times 0.15$ mm. All crystallographic measurements were made on an Enraf Nonius CAD4 diffractometer. The structure was solved by direct methods[14] and refined on F_o^2 by full-matrix least-squares[14] using all unique data corrected for Lorentz and polarization factors. All non-hydrogen atoms were anisotropic. The hydrogen atoms were inserted in idealized positions with U_{iso} set at 1.5 times the value of U_{eq} of the parent. The weighting scheme used was $w = 1/[\sigma^2(F_o)^2 + (0.0999\,P)^2]$, where $P = [\mathrm{Max}F_o^2 + 2\,F_c^2]/3$; this gave satisfactory agreement analyses. Final R_1 (on *F*) and wR_2 (on F_o^2) values were 0.1410 and 0.2010 for all 5935 data and 345 parameters. The corresponding *R* values were 0.0777 and 0.1803 for 3545 data with $I > 2\sigma(I)$. Sources of scattering factors as in ref. [15]. Empirical absorption corrections were carried out by the DIFABS method.[16] The numbering of the atoms is shown in Figure 1. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133102. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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