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Manganese(I) Templates for the Construction of Benzannulated Triphosphamacrocycles

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Nine-membered 1,4,7-triphosphamacrocycles with unsaturated benzo-backbones have been prepared using the $[(CO)_3Mn]^+$ unit as a template. Two synthetic methods have been employed for the macrocyclisation both of which involve the attack of a coordinated phosphide at an activated, electrophilic *ortho*-fluorophenyl substituent on a neighbouring pnictide donor. Addition of base to the precursor complex *fac*-$[(CO)_3Mn(dfppb)(PhPH_2)]^+$, **1**, where dfppb = 1,2-*bis*[di(2-fluorophenyl)phosphino]benzene, results in the direct formation of the macrocyclic compound *fac*-$[Mn(CO)_3(tribenzo\text{-}9aneP_3\text{-}Ph,Ph^F{}_2)]^+$, **3**. A second precursor, namely *fac*-$[(CO)_3Mn(1,2\text{-}bpb)\{P(Ph^F)_3\}]^+$, **5**, where 1,2-bpb = 1,2-*bis*(phosphino)benzene, undergoes spontaneous partial macrocyclisation when dissolved in THF to give the intermediate complex *fac*-$[(CO)_3Mn\{H_2PC_6H_4P(H)C_6H_4P(Ph^F)_2\}]^+$, **6**, which contains a linear tridentate phosphine with the unusual combination of a primary, secondary and tertiary phosphine donor. Addition of base to **6** gives the desired macrocyclic complex *fac*-$[Mn(CO)_3(tribenzo\text{-}9aneP_3\text{-}H_2,Ph^F)]^+$, **7**, which is converted in *situ* to the more stable dimethylated *fac*-$[Mn(CO)_3(tribenzo\text{-}9aneP_3\text{-}Me_2,Ph^F)]^+$, **8**. The new complexes have been fully characterised by spectroscopic and analytical methods including single crystal X-ray structure determinations for **1**, **3**, **5**, **6** and **8**.

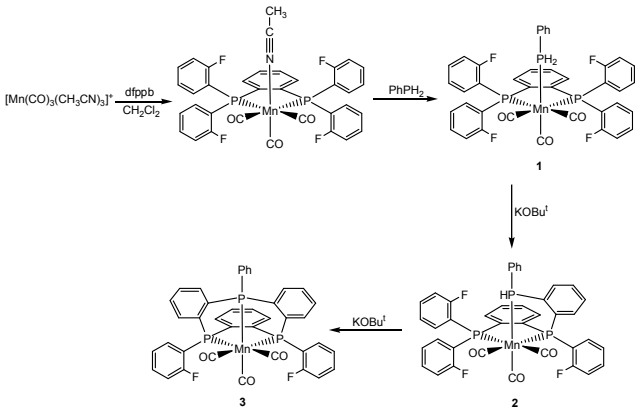
Introduction

Following Norman's elegant synthesis of 1,5,9-triphosphacyclododecane, $12aneP_3H_3$, by the molybdenum template cyclisation of three facially bound allylphosphine ligands,[1] Edwards and co-workers developed the further derivatization and demetallation of this type of macrocycle.[2] The liberation of the free macrocycle opened up the co-ordination chemistry of the $12aneP_3R_3$ ligands which has since been explored with a range of transition metals.[3] Attempts to synthesise smaller ring triphosphorus macrocycles by using vinylphosphines on $M(CO)_3$ (M = Cr, Mo) templates were unsuccessful.[2e] It was proposed that the long M-P bond lengths and the lack of steric compression from the carbonyl ligands precluded formation of these smaller ring P_3 macrocycles.[2e] Later investigations using cationic $[Cp^RFe]^+$ units, where R= H_5, Me_5, $SiMe_3$ or 1,3-$(SiMe_3)_2$, with inherently shorter M-P bond lengths and bulkier spectator ligands as templates allowed access to small ring-size triphosphorus macrocycles.[4] Using this approach, 9-membered triphosphorus macrocycles were synthesised by a Michael-type addition between a coordinated primary diphosphine (more specifically the phosphide derived from the phosphine upon addition of base) with a *bis*- or *tris*(vinyl)phosphine at the iron centre. The Cp^R spectator ligand in these systems assists the cyclisation by compressing the non-bonded P···P distances in the precursor complexes effectively bringing the reactive sites in close proximity for subsequent ring-closure. More rigid di- and tribenzo macrocycles were also prepared using the Fe(II) methodology with, instead of alkenyl phosphine electrophiles, *ortho*-fluoroaryl substituted phosphines which are susceptible to nucleophilic attack at the 2-fluoro carbon when an electron withdrawing group is present at the 1-position; a coordinated phosphine at this position is such an activator. This property was successfully exploited in the base activated template cyclisation of *o*-fluoro arylphosphines with primary phosphines resulting in rigid *o*-phenylene bridged 9-membered P_3 macrocycles.[5] This type of reaction is precedented by the observations of Saunders and co-workers who found C-C bond formation between penta(fluoro)phenylphosphine and Cp* ligands coordinated to Ir(I) and Rh(I) complexes.[6] In addition, the use of allyl functionalised monophosphines and diprimary phosphines gave asymmetric $10aneP_3$ systems through radical initiated trimerisation. Although the Fe(II) based systems are efficient templates for the formation of the cyclic 9-, 10- and 11-$aneP_3R_3$ ligands, the release of the macrocycles from the metal was only possible by oxidative methods leading to isolation of the macrocyclic trioxide which could not be reduced readily back to the desired P(III) state, hence other more suitable metal templates were sought.

The *fac*-$[(CO)_3Mn(CH_3CN)_3]^+$ fragment is isoelectronic with and structually analogous to *fac*-$[(CO)_3Cr(CH_3CN)_3]$ and *fac*-$[(CO)_3Mo(CH_3CN)_3]$. The cationic Mn(I) centre however has an intrinsically smaller radius than do the neutral metal atoms in the group 6 carbonyls which should help facilitate the closure of smaller ring systems. In addition, activation of the coordinated species towards cyclisation should be greater for the positively charged manganese species compared to the neutral group 6 systems enabling the chemistry to be performed under milder conditions, avoiding, for example, the use of very strongly basic organometallic reagents for initial

deprotonation.

The $[Mn(CO)_3]^+$ fragment has been used as a template to synthesise a 9-membered triphosphorus macrocycle.[7] The synthetic route involves the sequential substitution of acetonitrile ligands in the $[Mn(CO)_3(CH_3CN)_3]PF_6$ precursor by successive introduction of 1,2-*bis*{di-(2-fluorophenyl)phosphino}benzene and phenylphosphine. The intrinsically smaller $Mn(CO)_3^+$ template (covalent radius for Mn(I) = 1.13 Å) compared to the neutral group 6 metal tricarbonyls (covalent radii of 1.37 Å for Cr and 1.51 Å for Mo) enables the cyclisation chemistry through virtue of the shorter Mn-P and hence closer P···P contacts.[8] Initial efforts to liberate the macrocycle from the Mn(I) template were encouraging prompting further investigation of these systems which are detailed here. We have subsequently adopted this strategy for the formation of the first bis-phosphine-carbene macrocycles prepared on a similar Re template;[9] Hahn and co-workers have extended this approach to Mn, Ru and Fe systems.[10]



Scheme 1

Results and Discussion

Tribenzannulated 9-membered triphospha-macrocycles from ditertiary phosphines and monoprimary phosphines

The synthetic strategy is based upon that developed for the $[Cp^RFe]^+$ templates except using the $[Mn(CO)_3]^+$ core as the templating system. The weakly coordinated acetonitrile ligands in *fac*-$[(CO)_3Mn(CH_3CN)_3]^+$ are readily displaced by 1,2-*bis*[di(2-fluorophenyl)phosphino]benzene (dfppb) and subsequently phenylphosphine in stoichiometric reactions to afford the bisphosphine-monophosphine complex *fac*-$[(CO)_3Mn(dfppb)(PhPH_2)]^+$, **1**, as shown in scheme 1. The macrocycle complex **3** was subsequently produced after two intramolecular P-C bond ring-closure reactions as detailed previously for the Fe(II) template. The substitution of two CH_3CN ligands from *fac*-$[(CO)_3Mn(CH_3CN)_3]^+$ by dfppb is relatively slow and takes several hours to reach completion. It was found that removal of the volatile components in *vacuo* followed by addition of fresh solvent twice during the reaction facilitated the substitution resulting in shorter reaction times, presumably by removing competition for coordination by liberated acetonitrile. To prevent any structural isomerization of *fac*-$[(CO)_3Mn(dfppb)(CH_3CN)]^+$ (to *mer*-) at elevated temperature, reactions were performed at room temperature. The substitution was readily monitored by $^{31}P\{^1H\}$ NMR spectroscopy which showed the gradual disappearance of the resonance at δ -34.0 ppm due to free dfppb and the growth of a new resonance at δ 72.9 ppm attributed to coordinated dfppb. The relatively large $^3J_{P\text{-}F}$ coupling constant of 59 Hz observed in the $^{31}P\{^1H\}$ NMR spectrum of dfppb is completely lost in the $^{31}P\{^1H\}$ NMR spectrum of the complex where only a singlet is seen. The reaction was deemed complete when no further change was seen in the $^{31}P\{^1H\}$ NMR spectrum. The orange crystalline diphosphine mono-acetonitrile product was readily isolated in good yield. The $^{13}C\{^1H\}$ NMR spectrum of *fac*-$[(CO)_3Mn(dfppb)(CH_3CN)]^+$ showed a broadened CO resonance at δ_C 215 ppm due to the influence of the quadrupolar ^{55}Mn nucleus.[11] The presence of three strong υ_{CO} absorption bands observed in the IR spectrum (at 2031, 1961 and 1915 cm^{-1}) is consistent with the configuration of the complex being assigned as *fac*-.[12] An absorption band at 2344 cm^{-1} was assigned to υ_{CN} of the CH_3CN ligand. Replacement of the remaining acetonitrile ligand in *fac*-$[(CO)_3Mn(dfppb)(CH_3CN)]^+$ was achieved by reaction with one mol equivalent of phenylphosphine in CH_2Cl_2. The substitution was complete within 15 minutes of adding the $PhPH_2$ as evidenced by $^{31}P\{^1H\}$ spectroscopic analysis of the reaction mixture. The pale yellow $[(CO)_3Mn(dfppb)(PH_2Ph)]^+$, **1**, was then isolated in quantitative yield as its hexafluorophosphate salt after removal of the solvent. The IR spectrum of **1** shows the expected features (see experimental) with the slight increase in υ_{CO} being consistent with $PhPH_2$ being a slightly better π–acid (or poorer σ-base) than CH_3CN. The ^1H NMR spectrum of **1** showed a characteristic broad doublet for the PH protons at δ_H = 4.31 ppm ($^1J_{H\text{-}P}$ = 360 Hz) with all other resonances amassed in the aromatic region. No signals were observed for the CO ligands in the $^{13}C\{^1H\}$ NMR spectrum presumably because of broadening due to the effect of the ^{55}Mn quadrupolar nucleus as well as coupling to ^{31}P. The signals of coordinated dfppb and phenylphosphine appear as broad multiplets at δ 72.4 ppm and δ -17.6 ppm in the $^{31}P\{^1H\}$ NMR spectrum with both resonances being broadened by the influence of the ^{55}Mn quadrupolar nucleus and unresolved P-P and P-F coupling.

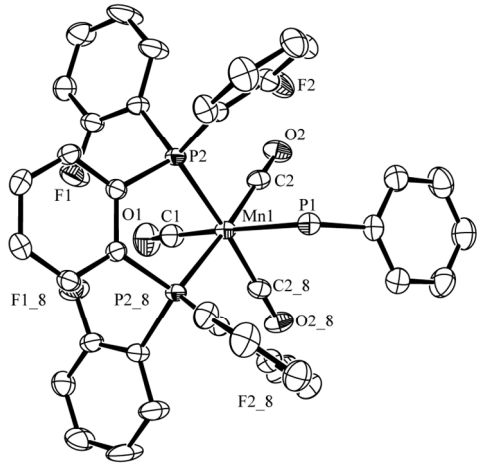


Fig. 1 Ortep view of the cation **1**. Thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å) and angles (°): Mn1-P1 2.3223(12), Mn1-P2 2.3327(8), Mn1-C1 1.841(4), Mn1-C2 1.821(3), P1-Mn1-P2 94.86(3), P1-Mn1-C1 169.51(14), P2-Mn1-C1 92.95(10).

The geometry of **1** was confirmed by determination of the crystal structure shown in Figure 1. The Mn centre of **1** possesses the expected distorted *fac*-octahedral geometry with facial CO ligands occupying three sites of one face and the dfppb chelate and the phenylphosphine on the opposing face. The structure has a mirror plane normal to the plane of the phenyl group of phenylphosphine passing through the P-C_{ipso} bond, one CO and the Mn centre. The dfppb ligand has slightly longer M-P bond lengths of 2.332(1) Å compared to the phenylphosphine ligand {2.322(1) Å} which may reflect the greater steric demand of the dfppb ligand but is more likely of electronic origin or a consequence of the relatively small ligand bite angle (see below). The Mn-C bond length *trans* to the phenylphosphine ligand is longer at 1.841(4) Å than those *trans* to the dfppb ligand which average 1.821(3) Å. This, and the relative Mn-P bond lengths above, indicate that the $PhPH_2$ ligand is a better donor than dfppb. The P-Mn-P bond angle of 83.61(4)° for dfppb in **1** is smaller than the ideal 90° but is similar to those observed in related 5-membered chelates, e.g. 81.98(6)° for $(CO)_3Mn(dppe)Cl$, 83.06(6)° in $(CO)_3Mn(H_2PC_6H_4PH_2)Cl$ and 84.14(10)° for $(CO)_3Mn(dppe)Br$.[13]

The cyclization reaction to produce the macrocycle complex, $[(CO)_3Mn\{1,4\text{-bis}(2\text{-fluorophenyl})\text{-}7\text{-phenyl-}[b,e,h]\text{tribenzo-}1,4,7\text{-triphosphacyclononane}\}]^+$,* **3**, was induced on addition of 2 mol equivalents of $KOBu^t$ to a solution of **1** in anhydrous THF. Upon adding the base a rapid colour change from yellow to red occurred which subsequently reverted back to a pale yellow and the poorly soluble complex **3** precipitated out as an off-white powder. The complex **3** is obtained as an air-stable solid that was only sparingly soluble in most common organic solvents. In order to improve the solubility of the complex, the PF_6^- anion was metathesised with BPh_4^- by anion exchange chromatography for analysis. It is reasonable to propose that the mechanism of ring closure involves initial deprotonation of phenylphosphine to produce a coordinated phosphide nucleophile (this species presumably gives rise to the red colour of the solution immediately after the addition of base), followed by intramolecular nucleophilic aromatic substitution of the *ortho* fluorine atom in the fluorophenyl group within the coordination sphere of manganese. The yield of **3** was found to be sensitive to the amount of $KOBu^t$ used and it was critical to avoid large excesses of $KOBu^t$ as this promoted loss of the dfppb ligand from **1** prior to cyclisation as observed by $^{31}P\{^1H\}$ NMR spectroscopy.

Only a single broad, complex resonance is seen in the $^{31}P\{^1H\}$ NMR spectrum of **3** at δ_P 109 ppm. The complexity of the peak is due to poorly resolved P-P and P-F coupling, quadrupolar broadening and the coincidence of the two unique sets of P atoms in the macrocycle. The single resonance observed in the ^{19}F NMR spectrum of **3** (δ_F = -96.4 ppm) is consistent with rapid rotation of fluorophenyl groups around the P-C_{exo} bonds and indicates relatively little steric hindrance between the CO ligands and the fluorophenyl group.

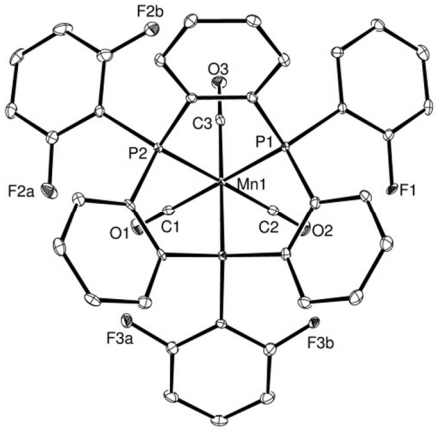
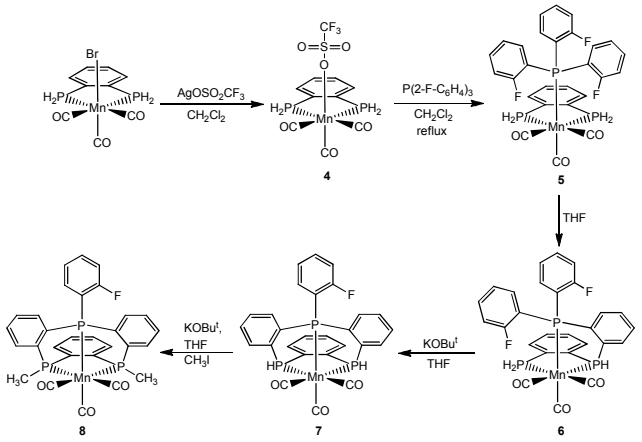


Fig. 2 Ortep view of the cation **3**. Thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å) and angles (°): Mn1-P1 2.2588(15), Mn1-P2 2.2582(15), Mn1-P3 2.2614(15), P1-Mn1-P2 84.22(5), P1-Mn1-P3 83.95(5), P2-Mn1-P3 83.79(5).

The crystal structure of **3** is presented in Figure 2. The tribenzannulated tribenzo-9aneP_3 ligand binds in the expected fashion to the Mn centre *via* three fused 5-membered chelate rings with three *trans* (to P) CO ligands making up the distorted octahedral configuration around the metal. The Mn-P bond lengths in **3** are significantly shorter than those in the acyclic **1** and in the larger ring complex, $[(12aneP_3Et_3)Mn(CO)_2Br]^+$, where values of 2.327(2), 2.243(2), and 2.331(2) Å were seen.[3b] The longer bond lengths for the latter 12aneP_3Et_3 example are associated with 6-membered chelate rings. The P-Mn-P angles are smaller than those in a related Co macrocycle complex due, at least in part, to the longer Mn-P bond lengths compared to those in the Co(III) system. The P-Mn-P angles in the more restricted 5-membered rings in **3** are also smaller than those in the 6-membered chelate rings in $(12ane\text{-}P_3Et_3)Mn(CO)_2Br$ {aver. 93.81(7)°}.[3b] The expanded Mn-P-C_{exo} (exocyclic phenyl or fluophenyl group) angles of around 119° indicate steric

* abbreviated to $[Mn(CO)_3(tribenzo\text{-}9aneP_3\text{-}Ph,Ph^F{}_2)]^+$; this notation is valid throughout the paper.

repulsion between the terminal phenyl or fluorophenyl groups and the CO spectator ligands. The Mn-P-C_{exo} angles are however considerably smaller than those in the bulkier $[(Cb^*)Co(tribenzo\text{-}9aneP_3\text{-}Ph,Ph^F{}_2)]^+$ analogue where the angles average 125.60(17)° highlighting significantly greater steric compression in the latter.



Scheme 2

Tribenzannulated 9-membered triphosphamacrocycles from diprimary phosphines and monotertiary phosphines

An alternative route to tribenzannulated macrocycles involves the base-induced coupling of a bidentate diprimary phosphine/phosphide with a monodentate tertiary phosphine ligand containing the necessary *ortho*-fluorophenyl groups. This is the exact reverse of the earlier synthetic protocol where the bidentate species had the electrophilic groups and the monodentate species provided the nucleophilic phosphide. The synthesis of the tribenzannulated 9-membered triphosphorus macrocycle, tribenzo-9aneP_3-H_2,Ph^F (**7**) by this second method is shown in scheme 2. The synthetic strategy involved substitution of two carbonyls in $Mn(CO)_5Br$ by 1,2-*bis*(phosphine)benzene to give the known compound *fac*-$Mn(CO)_3(H_2PC_6H_4PH_2)Br$.[13] The bromide was then substituted by the weakly coordinating triflate group leading to the diphosphine-triflate **4**. The formation of the neutral triflate complex **4** was followed in solution by IR spectroscopy. The three initial carbonyl bands of the *fac*-$Mn(CO)_3(H_2PC_6H_4PH_2)Br$ complex at 2039, 1976, and 1931 cm^{-1} were shifted to higher frequencies (2057, 1994, 1944 cm^{-1}) during the formation of **4**. This shift is attributed to the poorer electron-donating properties of the triflate group compared to bromide. The $^{31}P\{^1H\}$NMR spectrum of **4** shows a singlet at δ_P -3.3 ppm which becomes a triplet with $^1J_{P\text{-}H}$ = 341 Hz in the ^{31}P NMR spectrum. This, together with the infrared data, confirms the facial disposition of the ligands in **4**; a meridional isomer would give rise to an AB ^{31}P NMR pattern. The ^{31}P resonance is shifted slightly to high-field compared to the *fac*-$Mn(CO)_3(H_2PC_6H_4PH_2)Br$ precursor (δ_P -1.0 ppm, triplet, $^1J_{P\text{-}H}$ = 380 Hz) and the ^1H NMR spectrum shows a doublet at δ_H 5.97 ppm assigned to the protons of the primary phosphine with two broad singlets at δ_H 7.65 and 8.01 ppm for the aromatic protons. The $^{13}C\{^1H\}$ NMR spectrum shows a characteristic quartet at δ_C 118.9 ppm ($^1J_{C\text{-}F}$ = 321 Hz) for the quaternary carbon of the triflate group, whilst the virtual triplet at δ_C 131.0 ppm ($^{1,2}J_{C\text{-}P}$ = 45 Hz) is assigned to the *ipso* carbons. Two separate carbonyl resonances are observed as broad singlets in a 2:1 ratio at δ_C 213.7 and 218.1 ppm, respectively; the relative ratios identify the former signal as that arising from the two equivalent *trans*-P carbonyls and the latter as the unique *trans*-Br type. The broadness of the signals precludes resolution of $J_{C\text{-}P}$ and is caused largely by the ^{55}Mn quadrupole.[11] It was not necessary to isolate complex **4** and it was usually used *in situ* for the subsequent chemistry.

The weakly coordinating triflate group of **4** is readily displaced by the *tris*(2-fluorophenyl)phosphine ligand under mild conditions to yield **5**. The reaction was performed in dichloromethane and followed by $^{31}P\{^1H\}$ and ^{19}F NMR spectroscopy. As the substitution proceeded, the resonance for **4** at δ_P -3.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum decreased in intensity and two new signals at δ_P -1.9 and 39.7 ppm appeared and continued to grow as the reaction moved to completion. The reaction was deemed complete when no further trace of the signal for **4** was observed. Similarly, the ^{19}F NMR spectrum showed a decline in the resonance at -77.6 ppm for **4** and the growth of a new signal at δ_F -93.2 ppm for the product **5**. The rate of the reaction was shown to be dependent upon the concentration of the incoming-ligand such that reactions performed with a large excess of *tris*(2-fluorophenyl)phosphine occurred smoothly within reasonable times at room temperature, whereas reactions with a **4**:$P(Ph^F)_3$ ratio of 1:1.6 required heating and longer reaction times. The use of *tris*(2-fluorophenyl)phosphine in large excess was not recommended however, as, aside from the added issue of removing the ligand after the reaction, other unwanted side-reactions were observed during these experiments (*vide infra*).

After complete substitution of $CF_3SO_3^-$ for $P(Ph^F)_3$ compound **5** was isolated as an off-white, slightly air-sensitive solid in 59 % yield. The facial geometry of the complex is confirmed by the $^{31}P\{^1H\}$NMR spectrum of **5** (see above). The ^1H NMR spectrum of **5** displays two sets of doublets of doublets at δ_H 5.37 and 6.13 ppm which are assigned to the non-equivalent primary phosphine protons. These protons are coupled to the phosphorus atom to which they are directly attached ($^1J_{H\text{-}P}$ = 380, 386 Hz), and also to the phosphorus atom of the co-ordinated *tris*(2-fluorophenyl)phosphine ligand ($^3J_{H\text{-}P}$ = 14.4, 9.0 Hz). The $^{13}C\{^1H\}$ NMR spectrum of **5** also confirms the C_s symmetry of the complex. Nine different carbons from the co-ordinated 1,2-*bis*(phosphino)benzene and *tris*(2-fluorophenyl)phosphine ligands are observed (see experimental). In some cases these signals show coupling with the phosphorus and/or fluorine atoms. A broad resonance at δ_C 214.0 ppm is assigned to the carbonyl groups, with the signals for both the axial and equatorial carbonyls being coincident within the linewidth of the resonance. The number of bands in the carbonyl region of the infra red spectrum is consistent with a facial coordination of the ligands which was confirmed by a single-crystal X-ray study of the complex (Figure 3). Crystals of complex **5** were obtained by slow diffusion of hexane into a dichloromethane solution of the compound. The

structure of the cation **5** (Figure 3) shows the expected arrangement of ligands about the metal with the greater steric demand of the *tris*(2-fluorophenyl)phosphine ligand leading to a longer Mn-P(3) bond than that of the chelating 1,2-*bis*(phosphino)benzene ligand. These latter values are within the range of reported Mn-P bond lengths with primary phosphines such as $MnCl(CO)_3(H_2PC_6H_4PH_2)$ and $MnBr(CO)_3(H_2PC_6H_4PH_2)$.[13] The bite angle of 81.664(19)º for the chelate ring in **5** is similar to those observed in the related complexes $MnCl(CO)_3(H_2PC_6H_4PH_2)$ [83.06(6)º], and $MnCl(CO)_3(Ph_2PC_6H_4PPh_2)$ [81.97(6)º].[7,13]

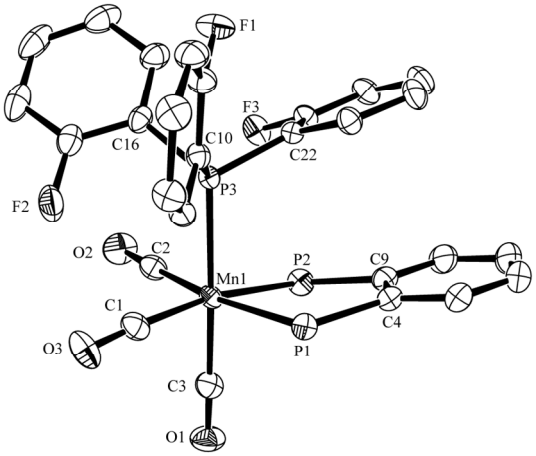


Fig. 3 Ortep view of the cation **5**. Thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å) and angles (º): Mn1-P1 2.3068(5), Mn1-P2 2.2927(5), Mn1-P3 2.3749(5), P1-Mn1-P2 81.664(19), P1-Mn1-P3 90.198(18), P2-Mn1-P3 96.398(18).

Facial tricarbonylmanganese(I) complexes with phosphine donor ligands are known to isomerise from the facial to the meridional isomer at room temperature or by boiling in different solvents.[14] No evidence (NMR) of isomerisation of **5** to the meridional isomer was observed under any of the conditions employed during the synthesis of the compound. However, upon dissolution of a small amount of **5** in THF a rapid colour change from colourless to pale yellow was observed. The $^{31}P\{^1H\}$ NMR and ^{19}F NMR spectra of the solution indicated the formation of a new compound as the major component of the solution. The $^{31}P\{^1H\}$ NMR spectrum showed a resonance at δ_P -1.7 ppm and a broadened signal with structure around δ_P 72 ppm; this pattern was identical to that observed for the by-product formed during the reaction of **4** with an excess of *tris*(2-fluorophenyl)phosphine. The peak at δ_P -1.7 ppm became an identifiable triplet with $^1J_{P\text{-}H}$ of 374 Hz in the ^{31}P NMR spectrum and the peak at 72 ppm became a recognisable superposition of a secondary phosphine resonance with $^1J_{P\text{-}H}$ = 404 Hz and a tertiary phosphine signal. It was then evident that excess $P(Ph^F)_3$ or the change in solvent to THF had lead to partial cyclisation of **5** to give complex **6** containing a linear tridentate triphosphine which was isolated as a pale yellow, slightly air-sensitive solid and is, to the best of our knowledge, the first example of a complex which contains a primary, secondary and tertiary phosphine donor at a single metal centre (certainly in a single acyclic ligand). The $^{31}P\{^1H\}$ NMR spectrum of the isolated complex is as detailed above and the ^{19}F NMR spectrum shows two signals for the non-equivalent fluorine atoms of the 2-fluorophenyl groups at δ_F -95.9 and -96.8 ppm. In the ^1H NMR spectrum of **6** two sets of doublets of multiplets at δ_H 4.56 and 5.82 ppm are attributed to the two non-equivalent protons of the primary phosphine. A further doublet of doublets centred at δ_H = 7.55 ppm with $^1J_{H\text{-}P}$ = 411 Hz and $^3J_{H\text{-}P}$ = 6.0 Hz is assigned to the P*H* of the central secondary phosphine of the linear triphosphine ligand. The peaks at δ_H 5.52, 6.62, 8.47 and 8.84 ppm are assigned to the new benzannulated chelate ring. The remaining protons are observed as multiplets between 7.02-7.89 ppm. The $^{13}C\{^1H\}$ NMR spectrum of **6** shows a complicated pattern resulting from the C_1 symmetry of the complex with a single broad multiplet at δ_C 214.2 ppm being assigned to the carbonyl groups. The IR spectrum of **6** shows only one P-H stretch at 2367 cm^{-1} and two strong bands at 2045, 1957 cm^{-1} characteristic of the presence of the *fac*-$Mn(CO)_3$ group.

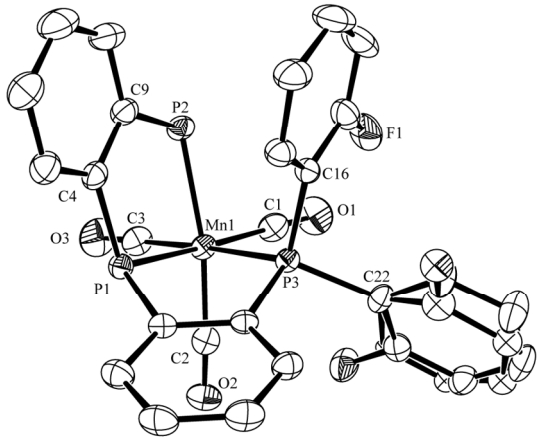


Fig. 4 Ortep view of the cation **6**. Thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å) and angles (º): Mn1-P1 2.2657(6), Mn1-P2 2.2817(6), Mn1-P3 2.3373(6), P1-Mn1-P2 83.86(2), P1-Mn1-P3 80.49(2), P2-Mn1-P3 94.59(2).

Crystals of **6** suitable for structure determination by single-crystal X-ray techniques were obtained from a saturated solution of the complex in $CDCl_3$. The complex crystallises as a racemate and one of the enantiomers of the cation is shown in Figure 4. The partially cyclised ligand is clearly visible from the figure with the P(1) and P(3) donors defining the new chelate ring. As anticipated, the Mn-P(1)/P(2)/P(3) distances are shorter than those observed in complex **5** with the central Mn-P(1) bond distance being the shortest. The remaining P-Mn-P bond angles are disparate highlighting a considerable distortion from a regular octahedron. The 2-fluorophenyl group perpendicular to the plane defined by the P(1), Mn and P(2) atoms exhibits positional disorder as shown in figure 4.

The intermediate **6** was stable in the absence of additional base, but further coupling to give the desired macrocyclic complex **7** was induced upon the addition of a suitable base.

Thus, addition of two mole-equivalents of $KOBu^t$ to a THF solution of **5** led to an immediate colour change from colourless to yellow. The $^{31}P\{^1H\}$ NMR spectrum of the solution showed the rapid formation of a new compound **7** identified by the presence of two broadened signals at δ_P 74.4 and 110.5 ppm. The former is assigned to the secondary phosphines whilst the latter is attributed to the tertiary phosphine. The ^{19}F NMR spectrum of **7** displays two peaks at δ_F -79.3 and -96.9 ppm for the triflate counter-anion and the fluorine of the aryl group respectively. Complex **7** was relatively unstable in solution (especially in chlorinated solvents) presumably due to the relative acidity of the secondary phosphines and was therefore not isolated but converted immediately to the more stable tritertiary macrocyclic complex **8** (see below).

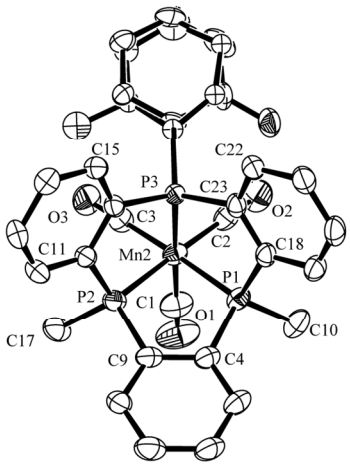


Fig. 5 Ortep view of the cation **8**. Thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å) and angles (º): Mn2-P1 2.2578(15), Mn2-P2 2.2565(17), Mn2-P3 2.2499(16), P1-Mn2-P2 84.40(6), P1-Mn2-P3 84.23(6), P2-Mn1-P3 83.95(6).

Although something of a frustration in the attempted isolation of **7**, the reactivity of the phosphorus-hydrogen bond of the secondary phosphines offers great synthetic potential for further derivatization of **7**. 12-membered macrocycles are readily functionalised through coordinated secondary phosphines by hydrophosphination and/or deprotonation/alkylation procedures.[2a,b] The apparent instability of **7** prompted us to alkylate the secondary phosphine groups of the complex so as to preclude any undesirable reactivity resulting from the P-H functions. Addition of two equivalents of $KOBu^t$ to a solution of **7** in THF at -78 °C produced a colour change from yellow to brown indicating the formation of the neutral mono-phosphide and/or anionic di-phosphide complex. The addition of an excess of methyl iodide to this solution at -78 ºC causes the slow precipitation of a white solid identified as the tri-tertiary macrocycle complex, **8**, in good yield (65 % based on **5**). Compound **8** was isolated as a mixed salt containing both triflate and iodide counterions. The $^{31}P\{^1H\}$ NMR spectrum of **8** displays a broad resonance from δ_P 95.4 to 107.1 ppm with the signals corresponding to the two different types of phosphorus donor overlapping. The ^1H NMR spectrum of **8** displays a virtual triplet at δ_H 2.57 ppm ($^2J_{H\text{-}P}$ = 4.8 Hz) assigned to the protons of the methyl groups and the $^{13}C\{^1H\}$ NMR spectrum shows a doublet of doublets at δ_C 13.9 ppm for the methyl carbons with coupling constants of $^{1,3}J_{C\text{-}P}$ = 19.0 and 18.7 Hz and a broad resonance for the carbonyl ligands at 218 ppm. The iodide salt of **8** had a lower solubility in $CDCl_3$ and when a saturated solution of the mixed salt was left to slowly evaporate, crystals of **8** as the iodide were obtained the structure of which is shown in figure 5. The molecular structure shows three fused 5-membered rings of the triphosphorus 9-membered macrocycle coordinating in a facial mode to the Mn. The Mn-P distances (average 2.255 Å) are significantly shorter than those observed for **5** and **6** but are similar to those reported for $[Mn(CO)_3(tribenzo\text{-}P_3\text{-}Ph,Ph^F{}_2)]^+$ (average 2.259 Å).[7] The average P-Mn-P angles (84.19°) also compare favourably with those reported for the latter complex (average 83.99°).[7] The residual 2-fluorophenyl group also exhibits a positional disorder.

Although the Mn(I) templates reported here are favourable for the formation of the benzannulated macrocycles, in a similar manner to the previously reported Fe(II) templates, they are too robust to allow ready release of the $9aneP_3$ macrocycles. Several attempts to achieve liberation where attempted including reductive methods using boro- or aluminium hydrides and oxidative methods using Br_2 or H_2O_2. In all cases either only starting materials were recovered or intractable mixtures resulted. When a solution of complex **8** in benzonitrile was heated near reflux in air and constantly irradiated with UV light a small amount of a Mn(II) complex containing partially oxidised macrocycle (two of the three phosphorus centres being converted to phosphine oxides) and benzamide (from hydrolysis of benzonitrile) was obtained. However the yield was very poor with the majority of recovered material being unreacted **8**.

Experimental

Methods and materials

Unless otherwise stated all manipulations were carried out using standard Schlenck techniques, under an atmosphere of dry nitrogen. All solvents were dried and degassed by refluxing over standard drying agents under a nitrogen atmosphere. The compounds 1,2-bis(phosphino)benzene, $[(CO)_3Mn(CH_3CN)_3]PF_6$[15], phenylphosphine[16], tris-*o*-fluorophenylphosphine and $MnBr(CO)_3(H_2PC_6H_4PH_2)$[13] were prepared according to literature methods. *t*-BuOK was obtained from Aldrich Chemical Company and was purified by sublimation. $MnBr(CO)_5$ and AgOTf were obtained from Aldrich Chemical Company and used without further purification. MeI and all deuterated solvents were dried over 3 or 4 Å molecular sieves and degassed by freeze-thaw methods prior to use. The NMR spectra were recorded on a Bruker DPX-500 instrument at 500 MHz (^1H) and 125.8 MHz (^{13}C), Bruker DPX-400 instrument at 400 MHz (^1H) and 100 MHz (^{13}C), Jeol Lamda Eclipse 300 at 121.7 MHz (^{31}P), 75.6 MHz (^{13}C), 282.8 MHz (^{19}F). ^1H and ^{13}C chemical shifts are quoted in ppm relative to residual solvent peaks, and ^{31}P chemical

shifts are quoted in ppm relative to external 85% H_3PO_4. ^{19}F chemical shifts are quoted in ppm relative to external $CFCl_3$. Infra-red spectra were recorded on a Nicolet 500 FT-IR spectrometer and the samples were prepared under N_2 as a KBr disk or as a solution. Mass Spectra of all the samples have been collected by direct injection into a Waters Low Resolution ZQ Mass Spectrometer fitted with a ESCI source. Elemental Analyses were performed by Warwick Analytical Services, University of Warwick. X-ray diffraction data collection was carried out on a Nonius Kappa CCD diffractometer at the University of Bath.

Syntheses

***fac*-[(CO)$_3$Mn{(Ph^F)$_2$PC$_6$H$_4$P(Ph^F)$_2$}(CH$_3$CN)]PF$_6$.** To a solution of [(CO)$_3$Mn(CH$_3$CN)$_3$]PF$_6$ (0.15 g, 0.368 mmol) in 20 ml CH_2Cl_2 was added dfppb (0.19 g, 0.368 mmol) with stirring. After 2 hours, the solvent was evaporated in *vacuo* and the residue redissolved in CH_2Cl_2 (20 ml) and left to stir for a further 2 hours. The $^{31}P\{^1H\}$ NMR spectrum at this stage showed the growth of a resonance due to coordinated dfppb at δ_P 72.9 ppm. The volatiles were subsequently removed in *vacuo* and the solid residue washed with a mixture of Et_2O and 40/60 petroleum ether. Orange crystals of the desired compound were obtained after diffusion of diethyl ether into a solution of the solid in CH_2Cl_2. Yield = 0.30 g (98%). $^{31}P\{^1H\}$ (CD_2Cl_2, 121.7 MHz): 72.9 (s br), -144.1 (sept, PF_6^-, $^1J_{P\text{-}F}$ = 714 Hz) ppm. ^{19}F (CD_2Cl_2, 282.8 MHz): -94.5 (s), -95.0 (s), -73.1 (d, PF_6^-) ppm. $^{13}C\{^1H\}$ (CD_2Cl_2, 100.1 MHz): 215 (CO, br), 135-115 (aromatics), 2.4 (s) ppm. ^1H (CD_2Cl_2): 7.6 to 6.4 (20H, m, H_{aryl}), 1.15 (3H, s, CH_3CN). IR: 2344w (CN), 2031s (CO), 1961s (CO), 1915s (CO) cm^{-1}.

***fac*-[(CO)$_3$Mn{(Ph^F)$_2$PC$_6$H$_4$P(Ph^F)$_2$}(PhPH$_2$)]PF$_6$, 1.** To a solution of [(CO)$_3$Mn{(Ph^F)$_2$PC$_6$H$_4$P(Ph^F)$_2$(CH$_3$CN)]PF$_6$ (0.20 g, 0.22 mmol) in CH_2Cl_2 (20 ml) was added phenylphosphine (0.03 g, 0.27 mmol) in toluene. After stirring for 15 minutes, the $^{31}P\{^1H\}$ NMR spectrum showed the growth of a broad resonance for coordinated phenylphosphine at δ –17.6 ppm. The resonance for coordinated dfppb became very broad at δ 72.4 ppm. The reaction mixture was filtered, the solvent removed in *vacuo* and the residue triturated with diethyl ether to remove excess phenylphosphine. The yellow powder that remained was dissolved in CH_2Cl_2 and the solution concentrated. Yellow crystals of **1** were obtained by diffusion of diethyl ether vapour into the solution. Yield = 197 mg (98%). $^{31}P\{^1H\}$ (CD_2Cl_2, 121.7 MHz): 72.4 (s br), -143.3 (sept, PF_6^-, $^1J_{P\text{-}F}$ = 714 Hz) ppm. $^{19}F\{^1H\}$ (CD_2Cl_2, 282.8 MHz): -93.2 (s), -94.4 (s), -73.2 (d, PF_6^-) ppm. $^{13}C\{^1H\}$ (CD_2Cl_2, 100 MHz): 135-115 (aromatics) ppm. ^1H (CD_2Cl_2, 400 MHz): 7.4 to 6.7 (m, 25H, H_{aryl}), 4.31 (d, 2H, PH, $^1J_{P\text{-}H}$ = 360 Hz) ppm. IR: 2365m (PH), 2037s (CO), 1974s (CO), 1964s (CO) cm^{-1}. MS(APCI): 767.9 (M^+).

***fac*-[Mn(CO)$_3$(tribenzo-9aneP$_3$-Ph,Ph^F$_2$)]BPh$_4$, 3.** To a solution of **1** (0.27 g, 0.29 mmol) in THF (30 ml) was added KOBu^t (65 mg, 0.58 mmol). The colour of the solution changed from yellow to red within one minute, then to a very pale yellow with the formation of a white precipitate. After filtering, the white precipitate was dissolved in CH_2Cl_2 and a $^{31}P\{^1H\}$ NMR spectrum recorded which showed a broad complex multiplet significantly shifted downfield at δ_P 109 ppm. In order to get decent spectroscopic data, the poorly soluble PF_6^- salt of **3** was converted into the BPh_4^- salt by anion exchange in THF. Yield = 0.2 g (80%). $^{31}P\{^1H\}$ (CD_3NO_2, 121.7 MHz): 109.0 (m br), -144.7 (sept, PF_6^-, $^1J_{P\text{-}F}$ = 714 Hz) ppm. $^{13}C\{^1H\}$ (CD_2Cl_2, 100 MHz): 135-115 (aromatics) ppm. ^{19}F (CD_2Cl_2, 282.8 MHz): -96.4 (s), -73.4 (d, PF_6^-) ppm. ^1H (CD_2Cl_2, 400 MHz): 7.6 to 7.1 (m, H_{aryl}) ppm. IR (KBr): 2030s (CO), 1974s (CO), 1962s (CO) cm^{-1}. MS(APCI): 728.0 (M^+). Anal. Calcd for $C_{63}H_{45}B_1F_2Mn_1O_3P_3$ (**3**·BPh$_4$, M = 1046.71 gmol^{-1}): C, 72.29; H, 4.33. Found: C, 72.08; H, 4.23.

***fac*-[Mn(CO)$_3$(H$_2$PC$_6$H$_4$PH$_2$)(OTf)], 4.** To a solution of MnBr(CO)$_3$(H$_2$PC$_6$H$_4$PH$_2$) (0.5 g, 1.38 mmol) in dichloromethane (15 mL) protected from light was added AgOTf (0.354 g, 1.38 mmol) in one portion. The reaction mixture was stirred in the absence of light for 2 hours during which time a grey precipitate formed. The solution was then filtered through Celite and all volatiles removed *in vacuo* to leave a yellow solid in quantitative yield which was used without further purification (this compound was normally synthesised and used *in situ* for the next step). ^1H NMR ($CDCl_3$, 400 MHz): 8.01 (m, 2H, Ph), 7.65 (m, 2H, Ph), 5.97 (d, 4H, $^1J_{P\text{-}H}$ = 341 Hz, PH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): 118.9 (q, $^1J_{C\text{-}F}$ = 321 Hz, CF_3), 131.0 (t, $^1J_{C\text{-}P}$ = 45 Hz, *ipso*-C), 132.3 (s, Ph), 135.4 (s, Ph), 213.7 (s br, CO eq), 218.1 (s br, CO ax) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): -3.3 ppm. ^{19}F NMR ($CDCl_3$, 282.8 MHz): -77.6 ppm. IR (CH_2Cl_2): 2057s (CO), 1994s (CO), 1944s (CO) cm^{-1}. MS (ES): 322 (70%, [M^+ - OTf$^-$ + MeCN]).

***fac*-[Mn(CO)$_3$(H$_2$PC$_6$H$_4$PH$_2$){P(Ph^F)$_3$}]OTf, 5.** [Mn(CO)$_3$(H$_2$PC$_6$H$_4$PH$_2$)(OTf)], **4** (0.59 g, 1.38 mmol) was dissolved in DCM (20 mL) and a solution of *tris*(*o*-fluorophenyl)phosphine (0.70 g, 2.2 mmol) in dichloromethane (5 mL) added thereto. The reaction mixture was refluxed for 1 day in the absence of light and the solvent subsequently removed *in vacuo*. The reesultant solid was washed with Et_2O (5 x 10 mL) leaving an off-white solid (0.61 g, 59 %). Single crystals of **5** were obtained by slow diffusion of hexane into a dichloromethane solution of **5** at room temperature. ^1H NMR δ ppm ($CDCl_3$, 500 MHz): 8.02 (m, 2H, Ph), 7.63 (m, 2H, Ph), 7.57 (m, 3H, *o*-F-Aryl-H), 7.47 (m, 3H, *o*-F-Aryl-H), 7.36 (m, 3H, *o*-F-Aryl-H), 7.05 (m, 3H, *o*-F-Aryl-H), 6.13 (dd, 2H, $^1J_{H\text{-}P}$ = 386 Hz, $^3J_{H\text{-}P}$ = 9.1 Hz, PH), 5.37 (dd, 2H, $^1J_{H\text{-}P}$ = 380 Hz, $^3J_{H\text{-}P}$ = 14.4 Hz, PH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): 214.0 (br, CO), 167.3 (dd, $^1J_{C\text{-}F}$ = 246 Hz, $^2J_{C\text{-}P}$ = 2.5 Hz, *o*-F-Aryl-C), 135.1 (d, $^3J_{C\text{-}P}$ = 8.8 Hz, Ph), 134.7 (t, $^2J_{C\text{-}P}$ = 6.3 Hz, $^3J_{C\text{-}F}$ = 6.3 Hz, *o*-F-Aryl-CH), 133.5 (d, $^3J_{C\text{-}F}$ = 5.0 Hz, *o*-F-Aryl-CH), 132.1 (s, Ph), 130.1 (t, $^1J_{C\text{-}P}$ = 45.3 Hz, Ph), 125.7 (d, $^3J_{C\text{-}P}$ = 8.8 Hz, *o*-F-Aryl-CH), 116.9 (dd, $^2J_{C\text{-}F}$ = 25.9 Hz, $^3J_{C\text{-}P}$ = 2.5 Hz, *o*-F-Aryl-CH), 115.2 (dd, $^1J_{C\text{-}P}$ = 43.2 Hz, $^2J_{C\text{-}F}$ = 16.0 Hz, *o*-F-Aryl-C) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): 39.7 {s br,

$P(Ph^F)_3\}$, -1.9 (s br, PH_2) ppm. ^{19}F NMR ($CDCl_3$, 282.8 MHz): -77.7 (s, CF_3), -93.2 {s, $P(Ph^F)_3\}$ ppm. IR (KBr): 2383s (PH), 2053s (CO), 1983s br (CO) cm^{-1}. MS (ES): 577 (95%, $[M^+ - HF]$). Anal Calc. for $C_{28}H_{20}F_6MnO_6P_3S$ (745.95): C, 45.05; H, 2.70. Found: C, 45.24; H, 2.66%.

***fac*-[(CO)$_3$Mn{H$_2$PC$_6$H$_4$P(H)C$_6$H$_4$P(Ph^F)$_2$}]OTf, 6**. $[Mn(CO)_3(H_2PC_6H_4PH_2)\{P(Ph^F)_3\}]OTf$, **5**, (0.1 g, 0.1 mmol) was dissolved in THF (2 mL), and the solution was allowed to stir for 7 days at room temperature. The solvent was then removed *in vacuo* and no further purification was necessary. Single crystals of **6** were obtained by slow diffusion of hexane into a dichloromethane solution at room temperature. ^1H NMR ($CDCl_3$, 500 MHz): 8.84 (m, 1H, Ph), 8.47 (m, 1H, Ph), 7.89 (m, 1H, Ph), 7.55 (dd, 1H, $^1J_{H-P}$ = 411 Hz, $^3J_{H-P}$ = 6.0 Hz), 7.02-7.73 (m, 12H, Ph), 6.62 (m, 1H, Ph), 5.82 (dd, 1H, $^1J_{H-P}$ = 374 Hz, $^3J_{H-P}$ = 14.4 Hz, PH), 5.52 (m, 1H, Aryl-H), 4.56 (d, 1H, $^1J_{H-P}$ = 374 Hz, PH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): 214.2 (m br, CO), 163.3 (d, $^1J_{C-F}$ = 250 Hz, *o*-F-Aryl-C), 161.7 (d, $^1J_{C-F}$ = 253 Hz, *o*-F-Aryl-C), 130.5 - 138.8 (m, *o*-F-Aryl-CH, Ph), 125.5 (s, *o*-F-Aryl-CH), 125.2 (s, *o*-F-Aryl-CH), 117.6 (d, $^2J_{C-F}$ = 22.4 Hz, *o*-F-Aryl-CH), 116.5 (d, $^2J_{C-F}$ = 21.2 Hz, *o*-F-Aryl-CH) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): 71.9 (s br, $^1J_{H-P}$ = 404 Hz, PH), 71.9 {s br, $P(Ph^F)_2\}$, -1.7 (s br, PH_2) ppm. ^{19}F NMR ($CDCl_3$, 282.8 MHz): -78.8 (s, CF_3), -95.9 {s, $P(Ph^F)_2\}$, -96.8 {s, $P(Ph^F)_2\}$ ppm. IR (KBr): 2367s (PH), 2045s (CO), 1957s br (CO) cm^{-1}. MS (ES): 577 (100 %, $[M^+]$). Anal Calc. for $C_{28}H_{19}F_5MnO_6P_3S$ (725.94): C, 46.30; H, 2.64. Found: C, 46.13; H, 2.57%.

***fac*-[Mn(CO)$_3$(tribenzo-9aneP$_3$-H$_2$,Ph^F)]OTf, 7**. To a solution of $[Mn(CO)_3(H_2PC_6H_4PH_2)\{P(Ph^F)_3\}](OTf)$, **5**, (0.175 g, 0.23 mmol) was in THF (10 mL) at -78 ºC was added a pre-cooled solution of potassium *tert*-butoxide in THF (0.142 M, 3.30 ml, 0.47 mmol). The colourless solution instantly changed to yellow. The solution was allowed to warm slowly to room temperature before the solvent was removed *in vacuo* and the residue triturated with degassed water (5 mL). The remaining solid was dissolved in THF (25 mL) and dried over $MgSO_4$. The yellow solution was filtered and the solvent was removed *in vacuo* to give a pale yellow powder. Due to the apparent instability of the complex in solution, this compound was normally synthesised *in situ* without isolation and used directly for the next step. ^1H NMR (d_4-MeOD, 400 MHz): 8.31 (m, 4H, Ph), 8.01 (m, 2H, Ph), 7.63-7.78 (m, 8H, Ph), 7.34-7.44 (m, 4H, Ph) ppm. $^{13}C\{^1H\}$ NMR (d_4-MeOD, 100 MHz): 164.7 (d, $^1J_{C-F}$ = 251 Hz, *o*-F-Aryl-C), 132.3-140.9 (m, Ph, *o*-F-Aryl-CH), 126.8 (d, $^3J_{C-P}$ = 9.4 Hz, *o*-F-Aryl-CH), 118.5 (d, $^2J_{C-F}$ = 22.0 Hz, *o*-F-Aryl-CH) ppm. $^{31}P\{^1H\}$ NMR (d_4-MeOD, 121.7 MHz): 110.47 {s br, $P(Ph^F)\}$, 74.4 (s br, PH) ppm. ^{19}F NMR (d_4-MeOD, 282.8 MHz): -79.3 (s, CF_3), -96.9 {s, $P(Ph^F)\}$ ppm. IR (KBr): 2044s (CO), 1970s br (CO) cm^{-1}. MS (ES): 557 (100 %, $[M^+]$).

***fac*-[Mn(CO)$_3$(tribenzo-9aneP$_3$-Me$_2$,Ph^F)]I/OTf, 8**. A solution of potassium *tert*-butoxide in THF (0.213 M, 1.25 mL, 0.26 mmol) was added to a solution of **7** (0.095 g, 0.13 mmol) in THF (20 mL) at -78 ºC. The colour of the solution changed from yellow to reddish-brown. The reaction mixture was allowed to warm slowly to room temperature after which time it was re-cooled to -78 ºC and an excess of MeI (0.05 ml, 0.8 mmol) added thereto. The solution was allowed to warm to room temperature and stirred overnight during which time a white solid precipitated. All the volatiles were then removed *in vacuo*, the crude material dissolved in dichloromethane and filtered and the product precipitated by adding cold Et_2O. **8** was isolated as a white solid (64 mg, 65 % based on **7**). Single crystals of **8** were obtained from a saturated solution in $CDCl_3$. ^1H NMR (CD_2Cl_2, 400 MHz): 8.23-8.30 (m, 4H, Ph), 7.57-7.76 (m, 9H, Ph), 7.24-7.38 (m, 3H, Ph), 2.57 (t, 6H, $^2J_{H-P}$ = 4.8 Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz): 163.2 (dd, $^1J_{C-F}$ = 251 Hz, $^2J_{C-P}$ = 2.3 Hz, *o*-F-Aryl-C), 139.2 (t, $^1J_{C-P}$ = 42.0 Hz, Ph), 135.0 (d, J_{C-P} = 9.2 Hz, *o*-F-Aryl-CH), 133.2 (s, Ph), 133.1 (s, Ph), 132.8 (d, $^1J_{C-P}$ = 6.9 Hz, Ph), 132.6 (d, $^3J_{C-F}$ = 6.9 Hz, *o*-F-Aryl-CH), 130.1 (d, J_{C-P} = 16.1 Hz, Ph), 130.1 (s, Ph), 129.8 (t, J_{C-P} = 9.1 Hz, Ph), 125.3 (dd, $^3J_{C-P}$ = 9.2 Hz, $^4J_{C-F}$ = 2.3 Hz, *o*-F-Aryl-CH), 117.4 (dd, $^2J_{C-F}$ = 21.9 Hz, $^3J_{C-P}$ = 4.6 Hz, *o*-F-Aryl-CH), 13.9 (dd, $^1J_{C-P}$ = 18.7 Hz, $^3J_{C-P}$ = 19.0 Hz, CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.7 MHz): 95.4 - 107.1 {m, PCH_3, $P(Ph^F)\}$ ppm. ^{19}F NMR (CD_2Cl_2, 282.8 MHz): -76.9 (s, CF_3), -94.3 {s, $P(Ph^F)\}$ ppm. IR (KBr): 2025s (CO), 1965s br (CO) cm^{-1}. MS (ES): 585 (100 %, $[M^+]$).

Crystallography

Data collection was carried out on a Bruker-Nonius Kappa CCD diffractometer using graphite monochromoated 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[17] and HKL SCALEPACK.[18] Data reduction was applied using HKL DENZO and SCALEPACK.[18] The structures were solved using direct methods (Sir92)[19] and refined with SHELX-97.[20] Absorption corrections were performed using SORTAV.[21] Unless stated otherwise, all non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were inserted in idealised positions with Uiso set at 1.2 or 1.5 times the Ueq of the parent atom, except in some specific cases for hydrogens attached to phosphorus atoms (see below). Complex **1** was crystallised as its PF_6^- salt and complex **3** as its SbF_6^- salt. F4 and F5 from the anion in **1** were disordered over 2 positions. These fractional occupancy fluorines were refined with some ADP restraints to assist convergence. H1A (attached to P1) was located and refined freely. The two F atoms of the fluorophenyl groups in **3** are refined and distributed in five *ortho* positions of three phenyls with disordered model of approximate occupancy factor of 0.65:0.57:0.12:0.44:0.22 for F1, F2A, F2B, F3A and F3B respectively. Fractional occupancy fluorines were refined with similar restraints to those in **1**. It was also noted that the asymmetric unit in **3** contained two molecules of acetonitrile. The hydrogens attached to the phosphorus atoms in **5** were located and refined subject to having similar P-H distances. For complex **6** there was some disorder in the ring based on C22 (85:15 ratio) with C22 being common to both fragments.

The minor component of the disordered ring was treated isotropically. Once again, the hydrogens attached to phosphorus atoms were located and refined subject to having similar P-H distances. The crystal quality of complex **8** was not as good as the previous complexes with the asymmetric unit containing 4.2 molecules of chloroform in addition to one molecule of the salt. The fluorinated arene is disordered in a 75:25 ratio over 2 sites, and the aromatic partial carbons therein have been refined as rigid hexagons. Residual electron density is in the solvent region and probably reflects some minor disorder as well as the somewhat average crystal quality. Crystal structure and refinement data are collected in Table 1.

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

	1	**3**	**5**	**6**	**8**
Empirical formula	$C_{39}H_{27}F_{10}MnO_3P_4$	$C_{43}H_{31}F_8MnN_2O_3P_3Sb$	$C_{28}H_{20}F_6MnO_6P_3S$	$C_{28}H_{19}F_5MnO_6P_3S$	$C_{33.20}H_{26.20}Cl_{12.60}FIMnO_3P_3$
Formula weight	912.43	1045.30	746.35	726.34	1213.56
Crystal system	Orthorhombic	Triclinic	Monoclinic	Triclinic	Orthorhombic
Space group	*qll*	*P*-1	$P2_1/c$	*P*-1	*Pbnb*
a/Å	18.2370(2)	9.0240(2)	10.8280(1)	9.0220(1)	15.8680(1)
b/Å	21.3400(3)	15.6510(3)	14.9880(1)	13.4210(1)	21.7160(2)
c/Å	19.5450(3)	15.9190(4)	19.0140(2)	13.6260(2)	28.1150(3)
α/°		75.1480(10)		69.978(1)	
β/°		80.1430(10)	100.439(1)	80.994(1)	
γ/°		77.2800(10)		76.824(1)	
U/Å^3	7606.48(18)	2104.11(8)	3034.71(5)	1503.80(3)	9688.13(15)
Z	8	2	4	2	8
D_c/Mg m^{-3}	1.594	1.650	1.634	1.604	1.664
Reflections collected	53306	32820	43985	24905	146990
Independent reflections	3995	8594	6913	8430	11027
R_{int}	0.0781	0.1244	0.0467	0.0485	0.0538
Final *R*1, *wR*2 [$I>2\sigma(I)$]	0.0437, 0.1049	0.0608, 0.1482	0.0335, 0.0808	0.0451, 0.1089	0.0708, 0.1794
(all data)	0.0541, 0.1104	0.0887, 0.1660	0.0431, 0.0860	0.0640, 0.1196	0.0855, 0.1888

[a] Footnote text.

Conclusions

Nine-membered triphosphamacrocycles with unsaturated benzo-backbones have been prepared by a template method utilising the $[Mn(CO)_3]^+$ core. The cyclisation involves the attack of a coordinated phosphide 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. The base-promoted cyclisation of the precursor complex *fac*-$[(CO)_3Mn(dfppb)(PHPH_2)]^+$, **1**, where dfppb = 1,2-*bis*[di(2-fluorophenyl)phosphino]benzene, results in the direct formation of the macrocyclic compound *fac*-$[Mn(CO)_3$(tribenzo-9aneP_3-Ph,Ph^F_2)$]^+$, **3**. A second precursor, namely *fac*-$[(CO)_3Mn(1,2\text{-bpb})\{P(Ph^F)_3\}]^+$, **5**, where 1,2-bpb = 1,2-*bis*(phosphino)benzene, undergoes spontaneous partial macrocyclisation when dissolved in THF to give the intermediate complex *fac*-$[(CO)_3Mn\{H_2PC_6H_4P(H)C_6H_4P(Ph^F)_2\}]^+$, **6**, which contains a linear tridentate phosphine with the unusual combination of a primary, secondary and tertiary phosphine donor. The desired macrocyclic complex *fac*-$[Mn(CO)_3$(tribenzo-9aneP_3-H_2,Ph^F)$]^+$, **7**, is formed upon addition of base to **6**. The complex was further functionalised through reaction of the remaining two secondary phosphines with methyl iodide in the presence of base.

Notes and references

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