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Aspects of the Coordination Chemistry of *rac-trans*-1,2-diphosphinocyclohexane and the Preparation of Reinforced 9aneP_3 and 9aneN_2P Macrocycles

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Racemic *trans*-1,2-diphosphinocyclohexane (*t*-chxnP_2) has been synthesised and its coordination chemistry to Cu(I), Ag(I), Mn(I) and Fe(II) investigated. Compounds of empirical formula [Cu(*t*-chxnP_2)$_2$]BF_4 and [Ag(*t*-chxnP_2)$_2$]BF_4 have been prepared as isomeric mixtures and the solid-state structure of both complexes determined by single-crystal techniques. The Cu(I) complex is a monomeric species which crystallises with one ligand bearing the *R,R* configuration and the other being the *S,S* isomer whereas the Ag(I) complex crystallises as a polymer containing both chelating and bridging *t*-chxnP_2 ligands with 3- and 4-coordinate Ag(I) centres and argentophilic bonds. The bidentate diprimary phosphine has been coordinated to Mn(I) and Fe(II) templates and used as a P_2 unit for the formation of chiral (albeit racemic) 1,4,7-triphosphamacrocycles (9aneP_3). In addition 1*R*,2*R*- and 1*R*,2*S*-diaminocyclohexane (chxn) have been coordinated to Mn(I) and Fe(II) templates and similarly employed for the formation of new 1,4-diamino-7-phosphamacrocycle (9aneN_2P) complexes.

Introduction

Despite the synthesis of *trans*-1,2-*bis*(diethoxyphosphoryl)cyclohexane being reported over 15 years ago,[1] its reduction to *trans*-1,2-diphosphinocyclohexane (*t*-chxnP_2) has never been exploited. This is something of an oversight particularly as both enantiomers of the closely related *trans*-1,2-diphosphinocyclopentane have been prepared and utilised to good effect.[2] This omission is even more striking when the diamino analogue is considered; both *cis*- and *trans*-1,2-diaminocyclohexane has an extensive and very rich coordination chemistry with enantiomeric forms of the latter featuring in many chiral ligand systems. This apparent oversight prompted us to seek a viable preparative route to *trans*-chxnP_2 and to instigate an initial investigation of its coordination properties and its utilisation as a synthon for the template formation of triphosphorus macrocycles.

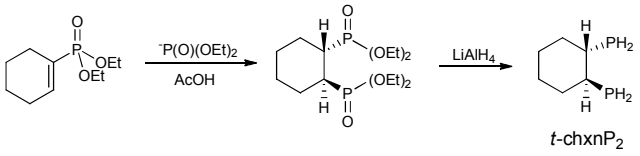
The $[(\eta^5\text{-}C_5Me_5)Fe]^+$ template synthesis of the first 9aneP_3 macrocycle was originally reported in 2000.[3] The construction of the macrocycle occurred through the formation of two new chelate rings via a Michael type addition of coordinated phosphides to activated vinylic functions. This was performed by a '2+1' method using a bidentate diprimary phosphine and a mondentate tertiary phosphine with at least two vinyl functions. The nature of the bidentate phosphine, the one variable substituent on the monodentate phosphine and the peripheral groups on the Cp ligand could be varied to give a range of derivatives.[4] The chemistry can be extended to benzannulated backbones which are prepared using the either the Fe(II) template or via $[(\eta^4\text{-}C_4Me_4)Co]^+$ and $[Mn(CO)_3]^+$ systems.[5]

Exchanging the vinyl groups for allyls leads to the formation of 10- and 11-aneP_3 systems through a radical-induced coupling.[6] However, there is little extant literature on similar systems where one or more of the P-donors have been replaced by different donors. One notable exception is the P_2C_{NHC} derivative originally reported in 2007.[7] Although some theoretical studies have been performed on 9aneN_2P ligands[8] there are no published articles describing their preparation and complexation. This is surprising given the vast amount of literature that exists on triazamacrocycles and their metal complexes. This paper seeks to redress some of these issues by reporting the first example of a 9aneN_2P macrocycle.

Results and Discussion.

Synthesis of *rac*, *trans*-1,2-diphosphinocyclohexane

Racemic *trans*-1,2-diphosphinocyclohexane, *t*-chxnP_2, has been prepared in reasonable yield by the synthetic route outlined in scheme 1. The key step in the synthesis is the nucleophilic Michael addition of sodium diethylphosphite to the cyclic allyl phosphonate which fixes the *trans* orientation of the two phosphorus-bearing groups. The desired diphosphine *t*-chxnP_2 is isolated as a pale yellow to colourless oil which proved sufficiently pure for use. The $^{31}P\{^1H\}$ NMR spectrum of *t*-chxnP_2 showed a singlet at -114.9 ppm that became a triplet of triplets in the ^{31}P NMR spectrum with a $^1J_{P\text{-}H}$ coupling of 200 Hz which is comparable to the values observed for other diprimary phosphines such as 1,2-diphosphinoethane ($^1J_{P\text{-}H}$ = 193Hz).[9] Further splitting of the major triplet to afford the observed triplet of triplets arises from $^{2,3}J_{P\text{-}H}$ couplings to the alpha and beta protons, which coincidentally have the same coupling constant of 21 Hz. A doublet of multiplets centred around 2.75 ppm is seen for the PH hydrogens of the primary phosphines in the ^1H NMR spectrum with the expected $^1J_{H\text{-}P}$ coupling constant of 200 Hz. The remaining hydrogens of the cyclohexane ring occur as a series of multiplets between 1.60 and 0.70 ppm. The expected three resonances are seen in the $^{13}C\{^1H\}$ NMR of *t*-chxnP_2 at 37.6 (t, $^{1,2}J_{C\text{-}P}$ = 6.4 Hz, P*C*H) 34.3 (s, PCHCH$_2$*C*H$_2$) and 27.4 ppm (t, $^{2,3}J_{C\text{-}P}$ = 2.9 Hz, PCH*C*H$_2$CH$_2$). A strong broad peak at 2318 cm^{-1} in the infrared spectrum of *t*-chxnP_2 confirms the presence of P-H bonds.



Scheme 1

Coordination of *t*-chxnP_2 to Cu(I) and Ag(I)

The coordination chemistry of *rac*,*trans*-1,2-diphosphinocyclohexane with the group 11 metals copper, silver and gold has been explored. The reaction of 2 molar equivalents of *t*-chxnP_2 with tetrakis(acetonitrile)copper(I) tetrafluoroborate in dichloromethane at room temperature afforded the tetrahedral *bis*(diphosphine)copper(I) complex $[Cu(t\text{-chxnP}_2)_2]BF_4$, **1**, as a white solid. The $^{31}P\{^1H\}$ NMR spectrum of **1** presented two broad signals at δ_P -72 and δ_P -81 ppm (width at half-height ~ 1200 Hz) which are shifted downfield compared to free *t*-chxnP_2 (δ_P -114.9 ppm). The magnitude of the coordination shift is similar to those of related complexes.[10] The presence of two peaks at room temperature may be indicative of the two possible isomers namely the *rac* pair $[Cu(R,R\text{-chxnP}_2)_2]^+$/$[Cu(S,S\text{-chxnP}_2)_2]^+$ and the *meso* complex $[Cu(R,R\text{-chxnP}_2)(S,S\text{-chxnP}_2)]^+$. The room temperature ^1H NMR spectrum of **1** is also broadened and showed a complex multiplet between δ_H 5.0 – 3.0 ppm assigned to the primary phosphine protons, and two doublets at δ_H 2.40 ppm ($^2J_{H\text{-}P}$ = 9.8 Hz) and δ_H 1.86 ppm ($^3J_{H\text{-}P}$ = 8.0 Hz) along with a multiplet centred at δ_H 1.45 ppm for the hydrogens of the cyclohexane ring. The $^{13}C\{^1H\}$ NMR spectrum is also consistent with the formulation of **1**, with three resonances at δ_C 37.0 (s), 34.5 (t) and 26.9 (s) assigned to each of the three carbon environments present in the cyclohexane backbone. In addition, the mass spectrum of **1** displayed the molecular ion peak at *m/z* 359.0422(100%) amu.

A single crystal of **1** suitable for single-crystal X-ray diffraction studies was obtained from slow evaporation of diethyl ether into a dichloromethane solution of **1** at 4 ºC (Figure 1). Extraordinarily there are no reported structures of Cu(I) complexes of diprimary phosphines and only one recorded structure with monodentate primary phosphines.[11] The solid-state structure confirms the expected composition of **1** and it is evident that the complex in the crystal is the mixed isomer where the two phosphine ligands on any given copper have the (*R*,*R*)(*S*,*S*) combination of configurations. The average Cu-P bond distance of 2.2606(15) Å is comparable to the observed bond lengths in other tetrahedral diphosphine copper systems such as $[Cu(dppe)_2]^+$ {av. 2.296(1)

Å},[12] $[Cu(dppb)_2]^+$ {av. 2.2999(9) Å}[13] and $[Cu(PH_2Mes)_4]^+$ {av. 2.283(2)}.[11] However, it is shorter than the Cu-P bond length reported for the phosphinine complex $[Cu\{octa(ethyl)diphosphaferrocene\}_2]^+$ (average 2.3177(6) Å).[14] The P-Cu-P bond angles of 88.62(5), 88.80(5), 112.61(5), 117.96(5), 120.99(6) and 129.89(5) clearly highlight the distorted tetrahedral structure of **1**. The smallest angles are those describing the chelate bite angles and the largest are non-chelate angles. It is unfortunate that the crystal structures of the primary phosphine complexes $[Cu(bpe)_2]^+$ and $[Cu(bpb)_2)]^+$,[15] where bpe is 1,2-*bis*(phosphine)ethane and bpb is 1,4-*bis*(phosphine)butane, have never been reported as they would have been valuable for comparison. However the angles reported here differ substantially from those observed in $[Cu(PH_2Mes)_4]^+$.[11]

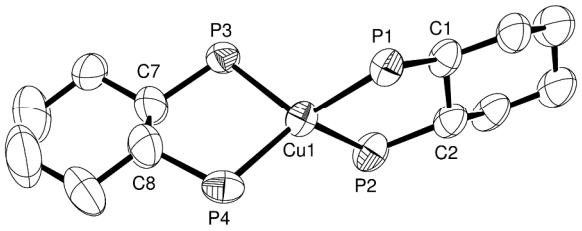


Figure 1 – The crystal structure of $[Cu(R,R\text{-chxnP}_2)(S,S\text{-chxnP}_2)]^+$, **1**. Thermal ellipsoids drawn at 50% probability, hydrogens and BF_4^- anion are omitted for clarity. Selected bond lengths (Å) and angles (º): Cu1-P1, 2.2570(14); Cu1-P2, 2.2715(14); Cu1-P3, 2.2694(13); Cu1-P4, 2.2443(15); P1-Cu1-P2, 88.80(5); P1-Cu1-P3, 117.96(5); P1-Cu1-P4, 129.89(5); P2-Cu1-P3, 112.61(5); P2-Cu1-P4, 120.99(6); P3-Cu1-P4, 88.62(5).

The reaction of 2 molar equivalents of *t*-chxnP$_2$ with silver triflate in dichloromethane at room temperature was anticipated to afford the analogous tetrahedral *bis*(diphosphine) silver(I) complex **2**. Upon work-up of the reaction mixture a white solid was obtained with a $^{31}P\{^1H\}$ NMR spectrum that showed one sharp singlet at δ_P -85.7 ppm. Although the shift of the resonance compared to the free phosphine confirms coordination, the lack of any observable ^{31}P-$^{107,109}Ag$ coupling suggests rapid Ag-P bond dissociation/reformation in solution at room temperature. The P*H*$_2$ hydrogens were present as a complex multiplet between δ_H 4.80 – 2.99 ppm in the ^1H NMR spectrum of **2** and complex resonances between δ_H 2.22 – 1.21 ppm were observed and assigned to the cyclohexane ring protons. The three resonances at δ_C 37.8 (s), 32.1 (t) and 26.2 (s) in the $^{13}C\{^1H\}$ NMR spectrum are each assigned to one of the three carbon environments present in the cyclohexane backbone. As for the Cu(I) complex the simplicity of the spectra reflect rapid exchange of the ligands such that the individual *rac*- and *meso*- forms of $[Ag(chxnP_2)_2]^+$ are not distinguishable. Detection of discrete species at low temperature did not prove possible as cooling the NMR sample to 193 K produced only an uninformative broad peak with some structure (principally a shoulder to low field) in the $^{31}P\{^1H\}$ spectrum. Microanalytical data for **2** was consistent with the formulation Ag : 2 *t*-chxnP$_2$: OTf$^-$.

Crystals suitable for structural analysis by single-crystal X-ray techniques were obtained from the slow evaporation of diethyl ether into a dichloromethane solution of **2** at 4 ºC. The X-ray crystal structure did not, however, present the expected discrete tetrahedral silver complex but rather a silver polymer (Figures 2 and 3**)**. The polymer is of a ladder type with two distinct silver environments, one containing a distorted tetrahedral silver ion coordinated by one bidentate *t*-chxnP$_2$ and two monodentate *t*-chxnP$_2$ ligands and neighbouring Ag(I) centres which are trigonal planar with three monodentate *t*-chxnP$_2$ donors. The bridging diphosphines alternate between the *R,R* and *S,S* forms and the chelating phosphines show racemic disorder. Each of the trigonal planar silver ions has an argentophilic interaction to a like neighbour with the Ag-Ag bond being supported by the two bridging diphosphines. The Ag-Ag bond length of 3.2065(13) Å is within the expected limits according to the Cambridge Structural Database (CSD),[16,17] where similar bonds span the range from 2.543(5) Å[18] to 3.794(8) Å;[19] the average Ag-Ag bond length being 3.05 Å. The Ag-P bond lengths are also comparable with other 4-coordinate Ag-P bond distances which typically range from 2.449 Å[20] to 2.77 Å.[21] For the tetrahedral Ag the chelate bite angle is around 81° and the P-Ag-P angle for the bridging phosphines is expanded to around 122°; all other angles are closer to those expected for ideal tetrahedral coordination. The P-Ag-P bond angles range from 115° to 125° for the trigonal silver centres. Although this structure is observed in the isolated crystalline solid it is unlikely to persist in solution where rapid equilibration between a number of different species is to be expected.

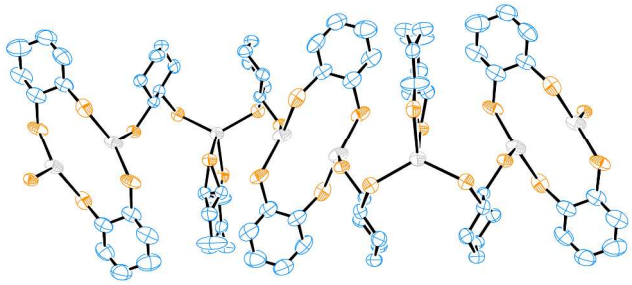


Figure 2 – A portion of the extended structure of **2**. Thermal ellipsoids drawn at 50% probability. Racemic disorder is evident in the chelating phosphines and hydrogens are omitted for clarity.

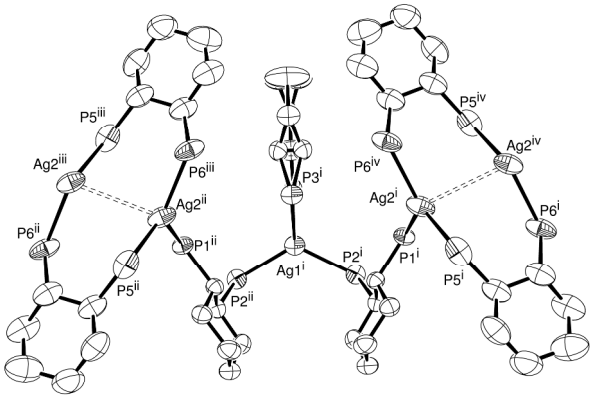


Figure 3 – The basic building block of polymeric **2** showing the argentophilic interactions. Thermal ellipsoids are drawn at 50% probability and hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (º): Ag1-P2, 2.4771(19); Ag1-P3, 2.526(3); Ag1-P4, 2.555(3); Ag2-P5, 2.471(3); Ag2-P6, 2.444(2); Ag2-P1, 2.4628(18); Ag2-Ag2, 3.2065(13); P2-Ag1-P2, 122.39(9); P2-Ag1-P3, 109.93(5); P2-Ag1-

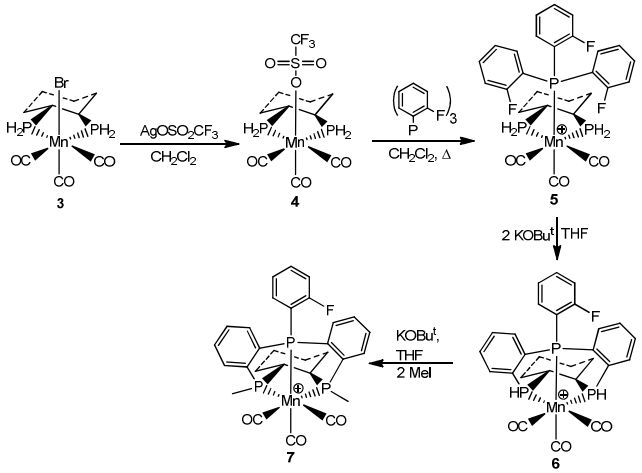
P4, 112.90(5); P4-Ag1-P3, 81.10(9); P1-Ag2-P5, 115.53(7); P1-Ag2-P6, 117.74(8); P5-Ag2-P6, 125.09(8).

Tetrahedral coordination with gold(I) has been observed with monodentate phosphines, for example $[Au(PMePh_2)_4]^+$ [22] and $[(TPA)_4Au]^+$ (where TPA = 1,3,5-triaza-7-phosphadamantane).[23] However, reports of tetrahedral gold(I) complexes with diphosphines are less prevalent.[24] A modification of a reported procedure for the preparation of $[Au(dppe)_2]^+$ was adopted in an attempt to synthesise a gold(I) complex of *t*-chxnP_2.[25] The addition of two molar equivalents of *t*-chxnP_2 to a dichloromethane solution of $[AuCl(SMe_2)]$ gave an immediate bright yellow precipitate which proved to be completely insoluble in all common solvents and was therefore presumed to be polymeric. No further attempts to prepare a monomeric tetrahedral gold (I) complex were made.

Coordination of *t*-chxnP_2 to Mn(I) and Fe(II) and the preparation of 9aneP_3 macrocyclic derivatives

$[Mn(CO)_3(Br)(t\text{-chxn}P_2)]$, **3**, was prepared from the 1:1 reaction of *t*-chxnP_2 and $[Mn(CO)_5Br]$ at reflux in $CHCl_3$. The reaction was followed by $^{31}P\{^1H\}$ NMR spectroscopy and shown to be complete after 4 hours. Simple evaporation to dryness and a single 40/60 petroleum ether wash gave **3** as a bright yellow solid in 76% yield. The $^{31}P\{^1H\}$ NMR spectrum of **3** showed the expected two downfield resonances at δ_P 9.5 and 2.8 ppm for the now inequivalent phosphines. These large downfield coordination shifts are typical for chelating phosphines bound to Mn(I). The ^1H NMR spectrum of **3** shows four distinct resonances for the P*H* hydrogens with the observation of a doublet at δ_H 5.26 ppm and three doublets of doublets at δ_H 4.87, 4.60 and 4.47 ppm respectively. The $^1J_{H\text{-}P}$ coupling constants of 335.4, 362.5, 353.3 and 317.5 Hz show the expected increase in magnitude induced upon coordination. Further $^2J_{H\text{-}H}$ coupling is responsible for the observed doublets of doublets for three of the resonances. The alpha hydrogens of the cyclohexane ring occur as a broad signal at δ_H 2.42 ppm and a multiplet between δ_H 2.02 – 1.03 ppm is assigned to the remaining eight CH_2 protons. In the $^{13}C\{^1H\}$ NMR spectrum of **3** two broad singlets are seen at δ_C 216.2 and 220.7 ppm arising from the two distinct types of CO ligand. Two doublets of doublets at δ_C 37.3 and 35.1 ppm represent the carbon atoms of the cyclohexane ring which are directly attached to the primary phosphine groups with $^1J_{C\text{-}P}$ values of 28.0 and 29.1 Hz and $^2J_{C\text{-}P}$ constants of 15.2 and 14.5 Hz respectively. Two further doublets of doublets at δ_C 34.9 and 34.0 ppm represent the two carbon atoms that are in positions 3 and 6 of the cyclohexane ring and the remaining two carbon atoms at positions 4 and 5 of the cyclohexane ring present as two doublets at δ_C 26.2 and 25.9 ppm with $^3J_{C\text{-}P}$ coupling constants of 5.5 Hz. The infrared spectrum of **3** shows a sharp ν_{PH} stretch at 2338 cm^{-1} and three strong ν_{CO} stretches at 2039, 1976 and 1926 cm^{-1}. High resolution mass spectrometry was used to confirm the presence of **3**, albeit with an acetonitrile ligand in place of the bromide.

The ability of the $[Mn(CO)_3]^+$ fragment to act as a template for the synthesis of nine-membered triphosphorus and mixed donor P_2NHC macrocycles is well established[5c, 26] and it was anticipated that this chemistry could be extended to systems built around *t*-chxnP_2 (scheme 2). To this end, the bromide ligand was replaced by a weakly coordinating triflate by treating **3** with an equimolar amount of silver triflate in dichloromethane. The reaction was followed in solution using infrared spectroscopy which showed complete loss of the three initial carbonyl stretches at 2039, 1976 and 1926 cm^{-1} after two hours of stirring; the conversion was accompanied by the growth of three new carbonyl peaks at slightly higher frequencies for the new complex $[Mn(CO)_3(t\text{-chxn}P_2)(OTf)]$ **4** at 2041 1985 and 1934 cm^{-1}. The shifts can be attributed to the greater electronegativity of the oxygen donor in OTf^- compared to Br^-. The $^{31}P\{^1H\}$ NMR spectrum of isolated **4** presented two doublets at δ_P 4.9 ($^2J_{P\text{-}P}$ = 43 Hz) and -1.7 ppm ($^2J_{P\text{-}P}$ = 43 Hz) assigned to the two non-equivalent primary phosphine groups. The ^1H NMR spectrum of **4** contained four doublets of doublets at δ_H 5.11 ($^1J_{H\text{-}P}$ = 356.5 Hz, $^2J_{H\text{-}H}$ = 7.1 Hz), 4.96 ($^1J_{H\text{-}P}$ = 355.3 Hz, $^2J_{H\text{-}H}$ = 6.9 Hz), 4.32 ($^1J_{H\text{-}P}$ = 345.7 Hz, $^2J_{H\text{-}H}$ = 8.0 Hz) and 4.28 ($^1J_{H\text{-}P}$ = 343.9 Hz, $^2J_{H\text{-}H}$ = 7.3 Hz) ppm for the primary phosphine protons, and a broad signal at δ_H 2.46 ppm and a multiplet centred at δ_H 1.54 ppm assigned to the cyclohexane protons. Further spectroscopic ($^{13}C\{^1H\}$ and ^{19}F NMR spectroscopy) and analytical data (MS) confirmed the nature of the complex.



Scheme 2

The introduction of the triflate ligand enabled its ready displacement by *tris*-2-fluorophenylphosphine to form the air sensitive monophosphine-bisphosphine complex **5** as a white solid in 77% yield (scheme 2). The reaction was followed by both $^{31}P\{^1H\}$ and ^{19}F NMR spectroscopy with the former showing the loss of the signals associated with **4** (δ_P 4.9 and -1.7 ppm) and the growth of three new broad singlets for **5** at δ_P 40.5, 3.6 and 0.8 ppm with time. The resonance at δ_P 40.5 ppm is assigned to the tertiary phosphine and the two latter resonances at δ_P 3.6 and 0.8 ppm are assigned to the primary phosphine groups which show $^1J_{P\text{-}H}$ coupling constants of 343 and 360 Hz respectively in the ^{31}P NMR spectrum. The coordination chemical shift for the *tris*-2-fluorophenylphosphine ligand is significantly downfield compared to the free ligand (δ_P -42.6 ppm, q, $^3J_{P\text{-}F}$ = 59 Hz). ^{19}F NMR spectroscopy complemented the use of $^{31}P\{^1H\}$ as a monitoring technique where growth of the signal associated with **5** was seen commensurate with the loss of the signal for uncoordinated P(*o*-F-C_6H_4)$_3$. The ^1H NMR spectrum confirmed the expected composition with resonances

for all aliphatic and aromatic hydrogens occurring at typical chemical shifts and the primary phosphine protons appearing as two sets of doublets of multiplets (δ_H 5.22 and 4.37 ppm), a doublet (δ_H 4.19 ppm) and a doublet of triplets (δ_H 3.62 ppm), reflecting the unique nature of each P*H* hydrogen. The $^{13}C\{^1H\}$ NMR spectrum of **5** was relatively uninformative but contained the expected resonances between δ_C 162.6 – 115.9 ppm for the aromatic protons along with those between δ_C 37.4 – 25.4 ppm assigned to the carbons of the cyclohexane ring. The separate carbonyls could not be distinguished and only a broad resonance at 215.4 ppm was observed in the $^{13}C\{^1H\}$ NMR spectrum. The infrared spectrum proved more useful as CO stretches at ν_{CO} 2041 and 1973 cm^{-1} were observable. The molecular ion was detected at *m/z* 603.0436 (100%) in the mass spectrum and satisfactory elemental analyses were obtained.

Addition of 2 mole equivalents of potassium *tert*-butoxide to **5** in THF at -78 ºC caused a colour change from colourless to yellow reflecting the formation of the disecondary phosphine macrocycle complex $[Mn(CO)_3$(dibenzo,chxn-9aneP$_3$-H$_2$,Ph^F)]OTf, **6**. When isolated, bright yellow **6** proved indefinitely stable in the solid state but appeared unstable in solution and was therefore usually used for subsequent reactions without prior isolation. The $^{31}P\{^1H\}$ NMR spectrum of **6** showed two broad singlets at δ_P 108.8 and 79.0 ppm representing the tertiary and secondary phosphines respectively. The broadness of the signals, which is due to the quadrupolar manganese nucleus, precluded acquisition of the P-H coupling constant in the ^{31}P NMR spectrum. Unfortunately this data could not be obtained from the ^1H NMR spectrum either as the necessary resonances overlapped with some of those arising from the aromatic hydrogens. The infrared spectrum did confirm the presence of P-H functions with a sharp band at 2364 cm^{-1} and was also consistent with the facial geometry assigned to **6** as only two bands were present in the carbonyl region at 2038 and 1954 cm^{-1}. The ^{19}F NMR spectrum displayed two singlets at -78.8 and -96.6 ppm assigned to the triflate anion and the *o*-F-aryl group respectively. The mass spectrum of **6** showed the molecular ion at *m/z* 563.0303 (100%)

The solution instability (presumably due to the secondary phosphine groups) of **6** prompted us to further functionalise these P-donors. Deprotonation of the coordinated secondary phosphine groups of **6** using potassium *tert*-butoxide in tetrahydrofuran at -78 ºC, followed by alkylation with methyl iodide successfully afforded the dimethylated complex $[Mn(CO)_3$(dibenzo,chxn-9aneP$_3$-Me$_2$,Ph^F)](OTf/I), **7** which proved completely stable in both solution and solid state. The $^{31}P\{^1H\}$ NMR spectrum of the isolated off-white solid displayed three broad signals at 104.0, 102.6 and 99.3 ppm for the three non-equivalent phosphorus atoms in **7**. The ^1H NMR spectrum presented several multiplets from δ_H 8.11 – 6.87 ppm assigned to the aromatic protons and overlapping multiplets between δ_H 2.15 and -0.01 ppm assigned to all of the aliphatic protons. The $^{13}C\{^1H\}$ NMR spectrum showed only an unresolved broad multiplet between 219.7 and 216.1 ppm for the carbonyl carbons, in addition to a multitude of resonances for the aromatic carbon atoms within the 163.7 – 118.1 ppm range and resonances associated with the cyclohexane ring between 49.8 and 25.1 ppm. Two doublets at δ_C 11.0 ($^1J_{C\text{-}P}$ = 28.8 Hz) and 9.1 ppm ($^1J_{C\text{-}P}$ = 26.5 Hz) were assigned to the two non-equivalent methyl groups.

Single crystals suitable for X-ray diffraction studies were obtained from the slow evaporation of an acetone solution of **7** at room temperature. The X-ray crystal structure of **7** confirmed the expected composition as highlighted in Figure 5. The molecular structure shows a distorted octahedral arrangement of donors around the manganese metal centre with the three carbonyls occupying coordination sites *trans* to the triphosphacyclononane ligand. The Mn-P distances average 2.260(6) Å which is comparable to the closely related compounds $[Mn(CO)_3$(tribenzo-9aneP$_3$-Ph,Ph$^F_2$)]$^+$ (average 2.260(15) Å)[27] and $[Mn(CO)_3$(tribenzo-9aneP$_3$-Me$_2$,Ph^F)]$^+$ (average 2.255(16) Å).[28] However it is notably shorter than for other Mn-P$_{tert}$ bond distances including that of [MnBr(CO)$_3$(dppe)] (2.3305(3)Å) and [MnCl(CO)$_3${*o*-C$_6$H$_4$(PPh$_2$)$_2$}] (2.3225(2)Å).[29] The average M-C metal carbonyl bond distance (1.811Å) is similar to those observed in both $[Mn(CO)_3$(tribenzo-9aneP$_3$-Me$_2$,Ph^F)]$^+$ (average 1.825(3)Å)[29] and $[Mn(CO)_3$(tribenzo-9aneP$_3$-{C$_6$H$_{11}$}$_2$,Ph^F)]$^+$ (average 1.812(13)Å). The bite angles of 83.77(16) (P1-Mn1-P2) and 84.0(2)° (P2-Mn1-P2^i) for the chelate rings in **7** are smaller than the 90º expected in an ideal octahedron. The values are in harmony with those observed for $[Mn(CO)_3$(tribenzo-9aneP$_3$-Ph,Ph$^F_2$)]$^+$ (average 83.99°), and $[Mn(CO)_3$(tribenzo-9aneP$_3$-Me$_2$,Ph^F)]$^+$ (average 84.19°).[27,28]

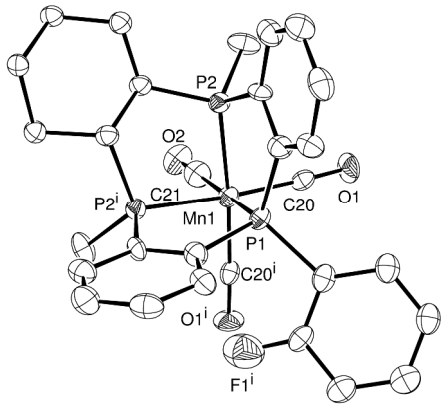


Figure 5 – The molecular structure of one of the two independent molecules of **7** in the asymmetric unit. Thermal ellipsoids drawn at 30% probability. Positional disorder in the cyclohexane ring, *o*-F-aryl rotational disorder, solvent, counterions and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (º): Mn1-P1, 2.250(6); Mn1-P2, 2.270(4); Mn1-C20, 1.832(16); Mn1-C21, 1.79(3); C20-O1, 1.143(17); C21-O2, 1.14(3); C8-F1, 1.342(5); C13-C18, 1.520(5); P1-Mn1-P2, 83.77(16); P2-Mn1-P2^i, 84.0(2).

In an effort to selectively remove one of the remaining carbonyl ligands in 7 the complex was reacted with 4-methylmorpholine N-oxide. However as any CO removal requires a ligand to coordinate at the vacated site the OTf/I$^-$ counterions were first replaced with Br$^-$ by passing a methanolic solution of **7(OTf/I)** through a column of anion exchange resin in the bromide form. Following anion exchange, the reactivity with 4-methylmorpholine N-oxide was studied by the addition of one mole equivalent of the N-oxide to a dichloromethane solution of **7(Br)** at –78 °C. Within a short period of time the mixture changed from an off-white suspension to a bright yellow solution. However, the isolated solid **8** was clearly a mixture (see

experimental) so no selectivity was apparent; ^{19}F NMR spectroscopy was used primarily to determine this as three broad singlets were observed in an approximate 1:1:1 ratio. This was supported where possible by ^{31}P and ^{1}H NMR spectroscopy but not $^{13}C\{^{1}H\}$ as the complex was very poorly soluble in all common deuterated solvents. Mass spectrometry was used to confirm the presence of the $[Mn(CO)_2(Br)(dibenzo,chxn\text{-}9aneP_3\text{-}Me_2Ph^F)]^+$ molecular ion as its ammonium adduct at *m/z*: 660.0192 (100%).

In a similar manner to the chemistry described for Mn(I), the coordination and subsequent cyclisation chemistry of *t*-chxnP_2 was attempted on an iron(II) template. Initial coordination of *t*-chxnP_2 to the $[Fe(\eta^5\text{-}C_5H_5)]^+$ unit through the photolytically activated substitution of *p*-xylene in $[(\eta^6\text{-}p\text{-xylene})(\eta^5\text{-}C_5H_5)Fe]PF_6$ gave dark red $[Fe(\eta^5\text{-}C_5H_5)(NCMe)(t\text{-chxnP}_2)]PF_6$, **9**. In common with the previous complexes, the $^{31}P\{^{1}H\}$ NMR spectrum of **9** was characterised by two doublets at δ_P 18.1 ($^2J_{P\text{-}P}$ = 49.2 Hz), and 13.7 ppm ($^2J_{P\text{-}P$ = 49.2 Hz) as the phosphine groups of the coordinated diphosphine are not equivalent. The ^{1}H NMR spectrum of **9** presented four resonances at 5.45 (dm, $^1J_{H\text{-}P}$ = 352.5 Hz), 4.90 (dm, $^1J_{H\text{-}P}$ = 340.8 Hz), 4.83 (dd, $^1J_{H\text{-}P}$ = 340.5 Hz, $^2J_{H\text{-}H}$ = 11.1 Hz) and 4.13 ppm (dd, $^1J_{H\text{-}P}$ = 324.7 Hz, $^2J_{H\text{-}H}$ = 12.0 Hz) assigned to the protons of the primary phosphines with the hydrogens on the cyclopentadienyl ring occuring as a singlet at 4.32 ppm and the acetonitrile methyl at 2.11 ppm. The remaining hydrogens of the cyclohexyl ring occurred as complex multiplets between δ_H 2.33 and 1.05 ppm. The ν_{PH} and ν_{CN} stretches were observed at 2319 and 2265 cm^{-1} respectively in the infrared spectrum of **9**. The coordinated acetonitrile ligand of **9** was replaced with *tris*-2-fluorophenylphosphine upon gentle heating in dichloromethane for 5 days to afford the monophosphine/diphosphine complex $[Fe(\eta^5\text{-}C_5H_5)(P\{o\text{-}F\text{-}Ph\}_3)(t\text{-chxnP}_2)]PF_6$, **10**. A colour change from dark red to yellow was observed during the reaction. The usual coordination shift was seen for the *tris*-2-fluorophenylphosphine ligand in the $^{31}P\{^{1}H\}$ NMR spectrum of **10** which contains an apparent triplet at 63.4 ppm with $^2J_{P\text{-}P}$ = 51 Hz for the tertiary phosphine and broad unresolved peaks at 19.6 and 15.9 ppm for the primary phosphines. The ^{1}H NMR spectrum shows all of the anticipated resonances in typical regions (see experimental) and the PH stretch was observed at 2333 cm^{-1} in the infrared spectrum.

The molecular structure of **10** determined by single-crystal x-ray techniques is presented in figure 6. The structure is much as expected with the chelating diphosphine and *tris*-2-fluorophenylphosphine occupying one face of the distorted octahedron and the cyclopentadienyl ligand occupying the opposite face. The average Fe-P bond length of 2.201(9) Å is similar to the analogous bond distances in other iron cyclopentadienyl complexes of acyclic phosphines such as $[(\eta^5\text{-}C_5H_5)Fe(1,2\text{-}C_6H_4\text{-}\{PMePh\}_2)(PHMePh)]^+$ (average 2.179(2) Å)[30] and other known cyclopentadienyl iron complexes of triphosphamacrocycles such as $[(\eta^5\text{-}C_5H_5)Fe(9aneP_3Et_3)]^+$ (average 2.194(2) Å)[3] and $[(\eta^5\text{-}C_5H_5)Fe(1,4\text{-bis}(2\text{-fluorophenyl})\text{-}7\text{-phenyl-}[b,e,h]tribenzo\text{-}[9]aneP_3)]^+$ (average 2.164(1) Å).[31] The P2-Fe-P3 bite angle of 84.87(3)º is smaller than would be expected in a regular octahedron and confirms the earlier statement suggesting that **10** is distorted.

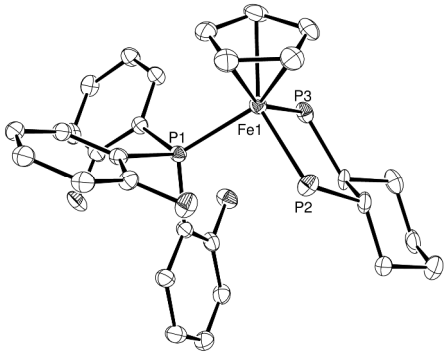


Figure 6 – The molecular structure of one of the isomers of the cation of **10**. Thermal ellipsoids drawn at 50% probability. Racemic disorder, counterion and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (º):Fe1-P1, 2.2195(8); Fe1-P2, 2.1880(9); Fe1-P3, 2.1950(9); P1-Fe1-P2, 94.29(4); P1-Fe1-P3, 99.50(3); P2-Fe1-P3, 84.87(3).

Analogous to the Mn(I) complex, the addition of two equivalents of potassium *tert*-butoxide to a tetrahydrofuran suspension of **10** at -78 °C leads to ring-closure affording the disecondary triphosphorus macrocycle compound $[(\eta^5\text{-}C_5H_5)Fe(dibenzo,chxn\text{-}9aneP_3\text{-}H_2,Ph^F)]PF_6$, **11** as a yellow solid. The $^{31}P\{^{1}H\}$ NMR spectrum of **11** shows downfield shifted peaks for all resonances compared to **10** as highlighted by the presence of signals at 122.6 ppm (apparent t, $^2J_{P\text{-}P}$ = 35.6 Hz) assigned to the *o*-fluoroarylphosphine and two multiplets centred at 102.8 and 94.3 ppm for the two non-equivalent secondary phosphines. The ^{1}H NMR spectrum showed characteristic peaks at 6.72 (d, $^1J_{H\text{-}P}$ = 376.4) and 6.40 (d, $^1J_{H\text{-}P}$ = 368.4 Hz) ppm for the P*H* protons along with a singlet at δ_H 4.42 ppm for the cyclopentadienyl ligand. The infrared spectrum had a sharp peak at 2312 cm^{-1} for the P-H stretch.

Functionalisation of the secondary phosphine groups of **11** was performed in a manner similar to that for the Mn(I) complex above except that 1-iodohexane was employed as the alkylating agent. The $^{31}P\{^{1}H\}$ NMR spectrum of the obtained pale yellow solid $[(\eta^5\text{-}C_5H_5)Fe(dibenzo,chxn\text{-}9aneP_3\text{-}\{C_6H_{11}\}_2,Ph^F)]PF_6$, **12** displayed a complex pattern at 298K suggesting the presence of rotamers through restricted rotation of the fluoroaryl group. However at 393K, three apparent triplets at δ_P 124.7 ($^2J_{P\text{-}P}$ = 37.2 Hz), 122.2 ($^2J_{P\text{-}P}$ = 38.7 Hz) and 121.1 ppm ($^2J_{P\text{-}P}$ = 37.2 Hz) were seen consistent with the presence of three inequivalent phosphorus environments. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were in agreement with the assigned structure which was confirmed by high resolution mass spectrometry (molecular ion; *m/z* 713.2681, 100%) and elemental analyses (see experimental).

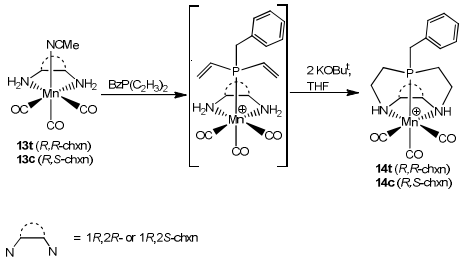
Coordination of 1*R*,2*R*- and 1*R*,2*S*-diaminocyclohexane to Mn(I) and the preparation of 9anePN$_2$ macrocycles

The success of the macrocyclisation chemistry with *t*-chxnP_2 prompted us to explore the possibility of making hitherto unknown 9anePN$_2$ macrocyles using a similar template approach but substituting the diprimary phosphine for the analogous diamine (scheme 3). To remove any possibility of isomeric complications, we used the readily available chiral form of the diamine namely 1*R*,2*R*-diaminocyclohexane (*R,R*-chxn) in addition to the *meso* form, 1*R*,2*S*-chxn which was employed in order to explore the influence of the relative disposition of the

two nitrogens.

Chelate complexes of both 1*R*,2*R*- and 1*R*,2*S*-chxn with Mn(I) were prepared by addition of a stoichiometric amount of the appropriate diamine to solutions of $[(Mn(CO)_3(MeCN)_3]PF_6$ in CH_2Cl_2. The reactions were followed by infrared spectroscopy which showed the gradual disappearance of carbonyl bands associated with the starting complex and the emergence of those of the products, $[Mn(CO)_3(1R,2R\text{-chxn})(MeCN)]PF_6$, **13t** and $[Mn(CO)_3(1R,2S\text{-chxn})(MeCN)]PF_6$, **13c**. The IR spectra of the isolated complexes are similar with the number of carbonyl stretches consistent with low symmetry *fac*-$Mn(CO)_3$ complexes as evidenced by the presence of two bands at 2045, and 1932 (a composite band with structure) for **13t**, and 2033, 1922 and 1883 cm^{-1} for **13c**. Two bands are observed for the symmetric and asymmetric N-H stretches at 3347 and 3298 cm^{-1} and 3344 and 3288 cm^{-1} respectively and the coordinated acetonitrile C≡N stretches are at 2359 and 2333 cm^{-1}.

There are some interesting differences in the ^1H NMR spectra of the two complexes. Both **13t** and **13c** show four distinct broad resonances for the inequivalent NH hydrogens between δ_H 5.18 and 4.00 ppm in the former and δ_H 4.45 and 3.80 ppm in the latter. The methyl resonance of the acetonitrile donor appears at δ_H 2.50 ppm in **13t** and 1.95 ppm in **13c,** reflecting downfield and upfield shifts respectively with regard to uncoordinated acetonitrile. The opposite trend is seen with the two inequivalent CH hydrogens which occur at δ_H 2.38 and 2.34 ppm in the *trans* isomer and δ_H 3.17 and 3.09 ppm in the *cis*. The difference in chemical shift between the two isomers represents significant differences in the nature of the coordinated 1,2-diaminocyclohexane isomers as is well-known. Surprisingly, both complexes were observed to decompose readily in a range of solvents over a relatively short timeframe. Therefore, they were used immediately for the subsequent chemistry.



Scheme3

The substitution of acetonitrile by benzyldivinylphosphine in **13t** and **13c** was achieved upon addition of the phosphine in CH_2Cl_2. The reactions were followed by ^{31}P NMR spectroscopy which showed the formation of numerous irresolute signals downfield from that of the free ligand in both instances. Such complexity indicated that simple ligand substitution had not occurred and that the vinyl groups had become activated upon coordination. The most likely outcome of this activation was a coordination-induced intramolecular hydroamination to form a linear P_3 ligand and ultimately a P_3 macrocycle. This was probably promoted by unbound benzyldivinylphosphine acting as a base to abstract a proton from the acidic NH_2 groups enabling attack of the liberated nitrogen lone pair at a coordinated benzyldivinylphosphine. In order to confirm this and promote complete reaction to the macrocyclic species, the solvent was removed *in vacuo,* the residues dissolved in THF and the solution treated with potassium *tert*-butoxide. This resulted in the formation and isolation of the macrocyclic complexes $[Mn(CO)_3(trans\text{-chxn-9anePN}_2\text{-Bz},H_2)]PF_6$, **14t** and $[Mn(CO)_3(cis\text{-chxn-9anePN}_2\text{-Bz},H_2)]PF_6$, **14c**. Judged by the yield of the two complexes, the formation of **14c** appears to be less efficient than **14t**. This may be a consequence of the different orientation of the cyclohexyl rings in the *cis* and *trans* isomers. In the *trans* isomer the diamine chelate assumes the λ conformation and the cyclohexyl ring is orientated largely in the equatorial plane of the metal.[32] This configuration is sterically the most unobtrusive, and the incumbent phosphine is able to occupy the remaining coordination site with little steric hindrance. In the *cis* analogue, the diamine chelate adopts a δ conformation which may bring the cyclohexyl ring in close proximity to the outgoing MeCN ligand providing a greater steric obstacle for phosphine coordination and/or macrocyclisation.

The ^{31}P NMR chemical shifts of **14t** and **14c** are characteristically downfield (δ_P 104 and 103 ppm, respectively) and the IR spectra show a reduced number of NH stretches with only a single band being observed in each case at 3291 and 3500 cm^{-1}, respectively. The carbonyl stretching frequencies are at 2016 and 1918 (composite) cm^{-1} for **14t** and 2019 and 1910 (composite) cm^{-1} for **14c**. The NH hydrogens are characteristically broad singlets at δ_H 5.43 and 5.14 ppm in the ^1H NMR spectrum of **14t** and at 4.69 and 2.38 ppm for **14c**. The benzyl CH_2 protons are doublets at 3.62 ($^2J_{H\text{-}P}$ = 10.8 Hz) and 3.65 ($^2J_{H\text{-}P}$ = 14.4 Hz) ppm for **14t** and **14c** respectively. It is noteworthy that we were unable to find any examples of related complexes containing both aliphatic diamines and triarylphosphines coordinated to the $[Mn(CO)_3]^+$ fragment for comparison. All the aromatic and aliphatic resonances are observed in the $^{13}C\{^1H\}$ NMR spectra but the carbonyl peaks could not be detected due to loss of intensity through quadrupolar broadening and coupling to the phosphorus atoms.

Attempts to make 11anePN$_2$ macrocycles

The success of the template approach to synthesising 9anePN$_2$ macrocycles encouraged us to investigate the possibility of making larger 10- and/or 11anePN$_2$ macrocycles by a method well-known for the analogous P_3 systems. The synthetic protocol requires a radical-induced ring-closure using a diallyl functionalised tertiary phosphine, in this case diallylphenylphosphine. Addition of diallylphenylphosphine to **13t** led to the gradual disappearance of the $^{31}P\{^1H\}$ NMR signal for the uncoordinated phosphine and the commensurate emergence of a broad signal at δ_P 37 ppm. After formation of the desired complex was complete, **15t** was isolated as a yellow solid. The infrared spectrum of **15t** showed N-H stretches at 3352 and 3258 cm^{-1} and υCO bands at 2004 and 1907 (composite) cm^{-1}. The alkenic hydrogens were visible in the ^1H NMR spectrum at δ_H 5.89 and 5.77 ppm while the methylene protons appear as doublets of doublets at δ_H 5.32 and 5.20 ppm. The *cis* analogue, **15c** was prepared similarly and showed the two N-H stretches at 3337 and 3297 cm^{-1} and two υCO bands at 2029 and 1917 (composite) cm^{-1} in the IR spectrum. The $^{31}P\{^1H\}$ NMR spectrum gave a singlet at 48 ppm and the ^1H and $^{13}C\{^1H\}$

NMR spectra were as expected with the former being broadened. The molecular structure of **15c** was confirmed by a single-crystal x-ray diffraction study (Figure 7). The chelating diamine adopts the δ conformation at the metal which forces the cyclohexyl backbone to fold inwards towards the *cis*-orientated carbonyl. As a consequence, this carbonyl group is bent away from the cyclohexyl backbone with a Mn-C-O bond angle of 171.3(4)°. This contrasts with the remaining Mn-C-O angles which are closer to linearity at around 177°. In addition, the sterically compromised CO has the longest Mn-C bond length of 1.841(5)Å partly as a consequence of the steric strain but also because it is *trans* to the phosphine; the other Mn-C bonds are 1.800(5) and 1.799(4)Å, respectively. Unsurprisingly, at 1.139(5)Å , the C-O bond length of the *trans*-P carbonyl is significantly shorter than those of the carbonyls *trans* to the N-donors (1.149(5) and 1.150(5)Å). However, all three metal-carbon bonds are shown to be in line with those of related facial tricarbonyl complexes of group 15 donors that approximate to 1.80Å.[33] At 79.7(12)° the N-Mn-N bond angle is the most acute as expected for a 5-membered chelate.

Attempts to ring close complexes **15t** and **15c** to produce 10- and/or 11-membered macrocycles proved unsuccessful. Heating either complex in toluene with the free radical initiator, 1,1'-azobis(cyclohexanecarbonitrile) at 80 °C for 12 hours gave mixtures from which the only identifiable phosphorus-containing compounds were the starting complexes. This lack of reactivity is likely due to the less facile homolytic cleavage of the N-H bond and lower stability of nitrogen-based radicals compared to the phosphorus analogues.

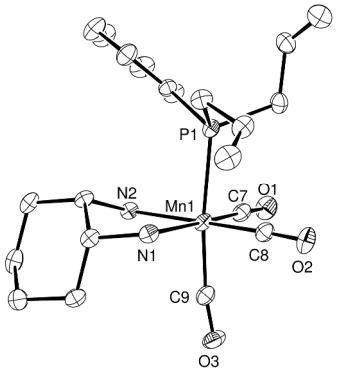


Figure 7 – The molecular structure of one of the two independent molecules of **15c** in the asymmetric unit. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Mn1-P1, 2.3543(13); Mn1-N1, 2.099(3); Mn1-N2, 2.101(3); Mn1-C7, 1.800(4); Mn1-C8, 1.799(4); Mn1-C9, 1.841(5); C7-O1, 1.149(5); C8-O2, 1.150(5); C9-O3, 1.139(5); N1-Mn1-N2, 79.70(12); N1-Mn1-N2, 79.70(12); N1-Mn1-P1, 92.65(10); N2-Mn1-P1, 90.92(10); N1-Mn1-C9, 91.61(17); N2-Mn1-C9, 94.98(16); Mn1-C9-O3, 171.4(4); Mn1-C7-O1, 177.3(4); Mn1-C8-O2, 177.4(4).

Attempts to liberate the macrocycles by reductive or oxidative methods proved largely unsuccessful. The NMR scale reaction of **14t** or **14c** with a large excess of morpholine N-oxide over an extended time period (3 weeks) produced a signal at δ_P 36 ppm in the 31P NMR spectrum which was assigned to the liberated P-oxide of the macrocycle. This was confirmed by mass spectrometry which showed the parent ion peak at 335 amu. However the reactions were not clean and the compound was never isolated pure. Similar results were obtained using bromine in a mixture of DCM and water or acidified aqueous hydrogen peroxide solutions. However, yields were variable and attempts to reduce the resultant mixtures using $LiAlH_4$ in THF were unsuccessful.

Experimental

Materials and methods

All synthetic procedures were carried out under an atmosphere of dry nitrogen using standard Schlenk line techniques. All solvents were freshly distilled under nitrogen from sodium (diethyl ether, petroleum ether and tetrahydrofuran) or calcium hydride (acetonitrile, dichloromethane and chloroform) before use. Tris-2-fluorophenylphosphine,[34] tetrakis(acetonitrile)copper(I) tetrafluoroborate[35] and $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_8H_{10})]PF_6$[36] were prepared according to literature procedures. All other chemicals were purchased from commercial sources and used as received. ^{1}H NMR spectra were obtained using Bruker 250, 400 and 500 MHz spectrometers referenced to tetramethylsilane (δ = 0 ppm). ^{31}P, ^{19}F and ^{13}C NMR spectra were recorded on a Jeol Eclipse 300 MHz spectrometer operating at 121.7 MHz, 282.8 MHz and 75.6 Mhz respectively. ^{31}P and ^{19}F chemical shifts are referenced to external 85% H_3PO_4 (δ = 0 ppm) and external $CFCl_3$ respectively. All NMR spectra were recorded at 293K unless otherwise stated. Infrared spectra were recorded in solution unless otherwise noted 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.[37]

Syntheses

Rac,trans-1,2-diphosphinocyclohexane, t-chxnP$_2$ A solution of *rac,trans*-1-2-*bis*(diethoxyphosphoryl)cyclohexane (4.2 g, 11.8 mmol) in diethyl ether (10 mL) was added dropwise to a suspension of lithium aluminium hydride (1.43 g, 37.8 mmol) in diethyl ether (40 mL) at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred overnight. Water (1.5 mL), 12% (w/v) aqueous sodium hydroxide (1.5 mL) and finally water (4.5 mL) were added at 0 °C before the resulting sludge was filtered onto magnesium sulphate and stirred for 2 hours. The reaction mixture was then filtered and all solvents and volatiles were removed *in vacuo* leaving *t*-chxnP$_2$ as a colourless to pale yellow oil; Yield = 1.33 g (76%). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz): δ -114.9 (s) ppm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.75 (dm, 4H, $^1J_{H\text{-}P}$ 200.0 Hz; PH_2), 1.45 (m, 2H), 1.26 (m, 2H), 1.07 (m, 2H), 0.80 (m, 4H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75.6 MHz): δ 37.6 (vt, $^{1,2}J_{C\text{-}P}$ 6.4 Hz, CH), 34.3 (s, CH_2), 27.4 (vt, $^{2,3}J_{C\text{-}P}$ 2.9 Hz, CH_2) ppm. IR ($CDCl_3$ soln.): 2318 cm^{-1} (PH).

[Cu(t-chxnP$_2$]BF$_4$, 1 *t*-chxnP$_2$ (148 mg, 1.00 mmol) and *tetrakis*(acetonitrile)copper(I) tetrafluoroborate (150 mg, 0.48 mmol) were dissolved in dichloromethane (15 mL) giving a colourless solution. The reaction mixture was allowed to stir for 2 hours at room temperature before all solvents and volatile materials were removed *in vacuo*. The residual solid was then washed with diethyl ether (3 x 10 mL) and recrystallised from a 1:1 dichloromethane/diethyl ether solvent combination at 4 ºC

affording **1** as colourless crystals. Yield = 147 mg (69%). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 121.7 MHz): δ -71.6 (br), -79.7 (br) ppm. ^{1}H NMR (CD_2Cl_2, 250 MHz): δ 5.31 – 2.73 (m, 8H, P*H*), 2.40 (d, 4H, $^{2}J_{H-P}$ 9.8 Hz), 1.86 (d, 4H, $^{3}J_{H-P}$ 8.0 Hz), 1.71 – 1.19 (m, 12H) ppm. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 75.6 MHz): δ 37.0 (s; CH_2), 34.5 (vt, $^{1,2}J_{C-P}$ 15.6 Hz, CH), 26.9 (s, CH_2) ppm. IR (KBr): 2333 (PH) cm^{-1}. HRMS (ES): expected 359.0438; observed 359.0422 amu (100%) [M^+]. Anal. Calcd for ($CuC_{12}H_{28}P_4F_4B$): C 32.27% H 6.32%. Found: C 32.22% H 6.26%.

[Ag(t-chxnP$_2$)]OTf, 2 *t-c*hxnP$_2$ (241 mg, 1.63 mmol) and silver(I) triflate (200 mg, 0.78 mmol) were dissolved in dichloromethane (15 mL) giving a colourless solution. The reaction mixture was allowed to stir for 1 hour at room temperature before all solvents and volatile materials were removed *in vacuo*. The residual solid was then washed with diethyl ether (3 x 10 mL) and dried under high vacuum affording **2** as a white solid. Yield = 349 mg (81%). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 121.7 MHz): δ -85.7 (s) ppm. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 4.80 – 2.99 (m, 8H, P*H*), 2.22 (d, 4H, $^{2}J_{H-P}$ 12.4 Hz), 1.75 (d, 8H, $^{3}J_{H-P}$ 7.2 Hz), 1.52 – 1.21 (m, 8H) ppm. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 75.6 MHz): δ 37.8 (s, CH_2), 32.1 (vt, $^{1,2}J_{C-P}$ 14.4 Hz, CH), 26.2 (s, CH_2) ppm. IR (KBr):2344 (PH) cm^{-1}. Anal. Calcd for ($AgC_{13}H_{28}P_4F_3O_3S$): C 28.23% H 5.10%. Found: C 27.92% H 4.98%.

[Mn(CO)$_3$(Br)(t-chxnP$_2$)], 3 Bromopentacarbonylmanganese(I) (500 mg, 1.82 mmol) and *t*-chxnP$_2$ (296 mg, 2.03 mmol) were dissolved in chloroform (12 mL) affording a bright yellow solution. The reaction mixture was heated at reflux for 4 hours, filtered and all solvents and volatiles removed *in vacuo*. The residual solid was washed with petroleum ether (5 x 10 mL) and dried under high vacuum leaving compound **3** as a bright yellow solid. Yield = 512 mg (77%). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.7 MHz): δ 9.5 (s br), 2.8 (s br) ppm. ^{31}P NMR ($CDCl_3$, 121.7 MHz): δ 9.2 (t, $^{1}J_{P-H}$ 357 Hz), 2.5 (t, $^{1}J_{P-H}$ 338 Hz) ppm. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 5.26 (d, 1H, $^{1}J_{H-P}$ 335.4 Hz, P*H*), 4.87 (dd, 1H, $^{1}J_{H-P}$ 362.5 Hz, $^{2}J_{H-H}$ 9.1 Hz, P*H*), 4.60 (dd, 1H, $^{1}J_{H-P}$ 353.3 Hz, $^{2}J_{H-H}$ 10.1 Hz, P*H*), 4.47 (dd, 1H, $^{1}J_{H-P}$ 317.5 Hz, $^{2}J_{H-H}$ 9.6 Hz, P*H*), 2.42 (s br, 2H), 2.02 – 1.03 (m, 8H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.6 MHz): δ 220.8 (s br, axial CO), 216.2 (s br, equatorial CO), 37.3 (dd, $^{1}J_{C-P}$ 28.0 Hz, $^{2}J_{C-P}$ 15.2 Hz, CH), 35.0 (dd, $^{1}J_{C-P}$ 29.1 Hz, $^{2}J_{C-P}$ 14.5 Hz, CH), 34.9 (dd, $^{2}J_{C-P}$ 29.8 Hz, $^{3}J_{C-P}$ 14.8 Hz, CH_2), 34.0 (dd, $^{2}J_{C-P}$ 31.1 Hz, $^{3}J_{C-P}$ 15.2 Hz, CH_2), 26.2 (d, $^{3}J_{C-P}$ 5.5 Hz, CH_2), 25.9 (d, $^{3}J_{C-P}$ 5.5 Hz, CH_2) ppm. IR ($CDCl_3$ soln.): 2338 (PH), 2039, 1976, 1926 (CO) cm^{-1}. HRMS (ES): expected 328.0064; observed 328.0069 amu (100%) [M^+ - Br^- + NCMe].

[Mn(CO)$_3$(OSO$_2$CF$_3$)(t-chxnP$_2$)], 4 Compound **3** (350 mg, 0.95 mmol) was dissolved in dichloromethane (15 mL) affording a bright yellow solution. In the absence of light, the solution was then added to a suspension of silver triflate (245 mg, 0.95 mmol) in dichloromethane (5 mL) and the reaction mixture allowed to stir for 2 hours. The solution was subsequently filtered through celite and all solvents and volatiles removed *in vacuo* to give **4** as a bright yellow solid. Yield = 369 mg (89%). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 121.7 MHz): δ 4.9 (d, $^{2}J_{P-P}$ 43 Hz), -1.7 (d, $^{2}J_{P-P}$ 43 Hz) ppm. ^{31}P NMR (CD_2Cl_2, 121.7 MHz): δ 4.8 (td, $^{1}J_{P-H}$ 350 Hz, $^{2}J_{P-P}$ 42.2 Hz), -1.9 (td, $^{1}J_{P-H}$ 350.4 Hz, $^{2}J_{P-P}$ 40.4 Hz) ppm. ^{1}H NMR (CD_2Cl_2, 250 MHz): δ 5.11 (dd, 1H, $^{1}J_{H-P}$ 356.5 Hz, $^{2}J_{H-H}$ = 7.1 Hz, P*H*), 4.96 (dd, 1H, $^{1}J_{H-P}$ 355.3 Hz, $^{2}J_{H-H}$ 6.9 Hz; P*H*), 4.32 (dd, 1H, $^{1}J_{H-P}$ 345.7 Hz, $^{2}J_{H-H}$ 8.0 Hz, P*H*), 4.28 (dd, 1H, $^{1}J_{H-P}$ 343.9 Hz, $^{2}J_{H-H}$ 7.3 Hz, P*H*), 2.46 (s br, 2H), 1.97 – 1.10 (m, 8H) ppm. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 75.6 MHz): δ 219.7 (br, axial CO), 214.7 (br, equatorial CO), 36.6 (dd, $^{1}J_{C-P}$ 29.8 Hz, $^{2}J_{C-P}$ 15.2 Hz, CH), 35.0 (m, CH and CH_2), 33.7 (dd, $^{2}J_{C-P}$ 28.6 Hz, $^{3}J_{C-P}$ 15.2 Hz, CH_2), 25.9 (s, CH_2) ppm. ^{19}F NMR (CH_2Cl_2, 282.8 MHz): δ -77.5 (s, CF_3) ppm. IR (CH_2Cl_2 soln.): 2354 (PH), 2041, 1985, 1934 (CO) cm^{-1}. HRMS (ES): expected 328.0064; observed 328.0065 amu (100%) [M^+ - Br^- + NCMe].

[Mn(CO)$_3${P(C$_6$H$_4$F)$_3$}(t-chxnP$_2$)]OTf, 5 Compound **4** (250 mg, 0.57 mmol) was dissolved in dichloromethane (10 mL) and a solution of *tris*-2-fluorophenylphosphine (272 mg, 0.86 mmol) in dichloromethane (5 mL) added thereto. The reaction mixture was refluxed for 72 hours in absence of light before all solvents and volatiles were removed *in vacuo*. The remaining solid was washed with diethyl ether (3 x 25 mL) and dried under high vacuum leaving compound **5** as a white solid; Yield = 330 mg (77%). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 121.7 MHz): δ 40.5 (br, P{*o*-F-C_6H_5}$_3$), 3.6 (br, PH_2), 0.7 (br, PH_2) ppm. ^{31}P NMR (CD_2Cl_2, 121.7 MHz): δ 40.4 (br, P{*o*-F-C_6H_5}$_3$), 3.7 (t, $^{1}J_{P-H}$ 343.1 Hz, PH_2), 0.8 (t, $^{1}J_{P-H}$ 360.1 Hz, PH_2) ppm. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.65 – 7.54 (m, 3H), 7.44 – 7.11 (m, 9H), 5.22 (dm, 1H, $^{1}J_{H-P}$ 359.2 Hz, P*H*), 4.37 (dm, 1H, $^{1}J_{H-P}$ 343.0 Hz, P*H*), 4.19 (d, 1H, $^{1}J_{H-P}$ 363.5 Hz, P*H*), 3.62 (dt, 1H, $^{1}J_{H-P}$ 344.1 Hz, $^{2,3}J_{H-H}$ 14.0 Hz, P*H*), 2.35 (s br, 1H), 2.12 (d, 1H, $^{2}J_{H-P}$ 12.8 Hz), 1.82 – 1.67 (m, 2H), 1.41 – 0.91 (m, 5H), 0.42 – 0.28 (m, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 75.6 MHz): δ 215.4 (br, CO), 162.6 (d, $^{1}J_{C-F}$ 248.1 Hz, C-F), 135.4 (d, *J* 9.2 Hz), 133.9 (s), 125.9 (d, *J* 8.1 Hz), 117.4 (d, *J* 23.1 Hz), 115.9 (dd, *J* 16.5 Hz, 41.5 Hz), 37.4 (dd, $^{1}J_{C-P}$ 32.9 Hz, $^{2}J_{C-P}$ 13.3 Hz, CH), 34.9 – 33.8 (m, CH and CH_2), 26.0 (d, $^{3}J_{C-P}$ 6.9 Hz, CH_2), 25.4 (d, $^{3}J_{C-P}$ 6.9 Hz, CH_2) ppm. ^{19}F NMR (CD_2Cl_2, 282.8 MHz): δ -78.6 (s, CF_3), -93.0 (s, P{*o*-F-C_6H_5}$_3$) ppm. IR (KBr): 2372 (PH), 2041, 1973 (CO) cm^{-1}. HRMS (ES): expected 603.0427; observed 603.0436 amu (100%) [M^+]. Anal. Calcd for ($MnC_{28}H_{26}F_6O_6P_3S$): C 44.70% H 3.48%. Found: C 44.99% H 3.60%.

[Mn(CO)$_3$(dibenzo,chxn-9aneP$_3$-H$_2$,Ph^F)]OTf, 6 Compound **5** (300 mg, 0.40 mmol) was dissolved in tetrahydrofuran (20 mL) and cooled to -78°C. A solution of potassium *tert*-butoxide (98 mg, 0.88 mmol) in tetrahydrofuran (10 mL) was then added slowly to afford a bright yellow solution. The reaction mixture was allowed to warm slowly to room temperature before all solvents and volatiles were removed in *vacuo*. The residual solid was then washed with degassed water (10 mL) and dried under high vacuum leaving compound **6** as a bright yellow solid. Yield = 208 mg (73%). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 121.7 MHz): δ 108.8 (br, P{*o*-F-C_6H_5}$_3$), 79.0 (br, PH) ppm. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.01 – 7.46 (m, 9H), 7.30 – 6.97 (m, 4H), 6.57 – 6.22 (m, 1H), 2.65 – 2.32 (m, 2H), 2.21 – 1.15 (m, 5H), 0.92 – 0.04 (m, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 75.6 MHz): δ 215.7 (br, CO), 163.4 (d, $^{1}J_{C-F}$ 252.7 Hz, C-F), 142.5 – 130.0 (aromatics), 125.7 (s br), 125.0 (s br), 119.3 – 115.3 (aromatics), 48.0 (CH),

38.6 (CH), 31.5 (CH_2), 25.5 (CH_2) ppm. ^{19}F NMR (CD_2Cl_2, 282.8 MHz): δ -78.8 (s, CF_3), -96.6 (s br, P{*o*-F-C_6H_5}$_3$) ppm. IR (KBr): 2364 (PH), 2038, 1954 (CO) cm^{-1}. HRMS (ES): expected 563.0303; observed 563.0276 amu (100%) [M^+].

[Mn(CO)$_3$(dibenzo,chxn-9aneP$_3$-Me$_2$,Ph^F)](OTf/I), ***7*** Compound **6** (600 mg, 0.84 mmol) was dissolved in tetrahydrofuran (40 mL) and cooled to -78˚C. A solution of potassium *tert*-butoxide (208 mg, 1.86 mmol) in tetrahydrofuran (10 mL) was then added slowly causing a colour change from yellow to brown. The reaction mixture was then allowed to warm slowly to room temperature before re-cooling to -78˚C whereupon an excess of methyl iodide (2 mL) was added. The solution was allowed to warm slowly to room temperature before all solvents and volatiles were removed *in vacuo* and the residual solid washed with water (3 x 25 mL) and diethyl ether (3 x 25 mL). The residue was then dried under high vacuum leaving compound **7** as an off-white solid. Yield = 559 mg (91%). $^{31}P\{^1H\}$ NMR ($(CD_3)_2SO$, 121.7 MHz): δ 104.0 (br), 102.6 (br), 99.3 (br) ppm. ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.11 – 7.88 (m, 4H), 7.67 – 7.51 (m, 5H), 7.31 – 7.18 (m, 2H), 7.03 – 6.87 (m, 1H), 2.15 – 1.83 (m, 8H), 1.58 – 1.21 (m, 4H), 1.13 – 0.45 (m, 3H), 0.21 – 0.01 (m, 1H) ppm. $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$, 75.6 MHz): δ 219.7 – 216.1 (br, CO), 163.7 (d, $^1J_{C\text{-}F}$ 251.5 Hz, C-F), 143.0 – 138.1 (aromatics), 136.2 (d, *J* 9.2 Hz), 134.6 – 132.8 (aromatics), 132.4 (d, *J* 13.8 Hz), 130.2 (d, *J* 15.0 Hz), 126.8 (d, *J* 8.1 Hz), 119.7 – 118.1 (aromatics), 49.8 (dd, $^1J_{C\text{-}P}$ 31.2 Hz, $^2J_{C\text{-}P}$ 15.4 Hz, CH), 42.5 (dd, $^1J_{C\text{-}P}$ 27.8 Hz, $^2J_{C\text{-}P}$ 13.4 Hz, CH), 28.8 (dd, $^2J_{C\text{-}P}$ 15.0 Hz, $^3J_{C\text{-}P}$ 7.3 Hz, CH_2), 26.9 (CH_2), 26.1 (d, $^3J_{C\text{-}P}$ 11.5 Hz, CH_2), 25.1 (d, $^3J_{C\text{-}P}$ 6.9 Hz, CH_2), 11.0 (d, $^1J_{C\text{-}P}$ 28.8 Hz, CH_3), 9.1 (d, $^1J_{C\text{-}P}$ 26.5 Hz, CH_3) ppm. ^{19}F NMR ($(CD_3)_2SO$, 282.8 MHz): δ -77.1 (s, CF_3), -97.0 (s, P{*o*-F-C_6H_5}$_3$) ppm. IR (KBr): 2025, 1952 (CO), cm^{-1}. HRMS (ES): expected 591.0616; observed 591.0597 amu (100%) [M^+]. Anal. Calcd for $MnC_{29}H_{28}P_3O_3FBr$: C 51.89% H 4.20%. Found: C 51.35% H 4.29%.

[Mn(CO)$_2$(Br)(dibenzo,chxn-9aneP$_3$-Me$_2$,Ph^F)], **8** A solution of 4-methylmorpholine N-oxide monohydrate (30 mg, 0.22 mmol) in dichloromethane (5 mL) was added slowly to a suspension of **7(Br)** (150 mg, 0.22 mmol) in dichloromethane (10 mL) at -78 °C. The colour of the solution changed from an off white suspension to a bright yellow solution almost immediately. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight during which time a bright yellow solid precipitated. All solvents and volatiles were then removed *in vacuo* before column chromatography (100% dichloromethane) was used to isolate compound **8** as a bright yellow solid. Yield = 115 mg (80%). $^{31}P\{^1H\}$ NMR ({CD_3}$_2$SO, 121.7 MHz): δ 128.5 (t, $^2J_{P\text{-}P}$ 24.5 Hz), 122.4 (t, $^2J_{P\text{-}P}$ 24.5 Hz), 119.1 (t, $^2J_{P\text{-}P}$ 24.5 Hz), 100.5 – 99.6 (br m), 99.1 (t, $^2J_{P\text{-}P}$ 31.1 Hz), 98.0 (dd, $^2J_{P\text{-}P}$ 22.3, 35.6 Hz), 95.9 (dd, $^2J_{P\text{-}P}$ 26.8, 35.6 Hz), 94.8 – 93.4 (m), 90.9 – 89.6 (m) ppm. ^1H NMR ({CD_3}$_2$SO, 400 MHz): δ 8.27 – 7.61 (m), 7.49 – 7.33 (m), 7.19 – 7.00 (m), 2.61 – 0.73 (m), 2.23 (d, $^2J_{H\text{-}P}$ 9.5 Hz, CH_3), 2.18 (d, $^2J_{H\text{-}P}$ 9.1 Hz, CH_3), 2.15 (d, $^2J_{H\text{-}P}$ 9.4 Hz, CH_3), 2.13 (d, $^2J_{H\text{-}P}$ 9.4 Hz, CH_3), 1.95 (d, $^2J_{H\text{-}P}$ 9.1 Hz, CH_3), 1.86 (d, $^2J_{H\text{-}P}$ 9.0 Hz, CH_3), 0.47 - -0.07 (m) ppm. ^{19}F NMR ({CD_3}$_2$SO, 282.8 MHz): δ -95.6 (s br), -97.3 (s br), -98.2 (s br.) ppm. IR (DCM soln.): 1947, 1888 (CO), 1605 (C=C) cm^{-1}. HRMS (ES): expected 660.0194; observed 660.0192 amu (100%) [M + NH_4^+]. Anal. Calcd for $MnC_{28}H_{28}P_3O_2BrF$: C 52.28% H 4.39%. Found: C 51.89% H 4.30%.

[Fe(η^5-C$_5$H$_5$)(NCMe)(t-chxnP$_2$)]PF$_6$, **9** [η^6-(*p*-xylene)Fe(η^5-C_5H_5)] hexafluorophosphate (500 mg, 1.34 mmol) and *t*-chxnP_2 (199 mg, 1.34 mmol) were dissolved in acetonitrile (10 mL) and the reaction mixture stirred in the presence of sunlight for 48 whereupon the solution colour changed from dark yellow to deep red. The solution was filtered through celite and all volatiles removed *in vacuo*. The solid residue was washed with 40/60 petroleum ether (3 x 25 mL) and dried under high vacuum leaving compound **9** as a red solid. Yield = 514 mg (84%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.7 MHz): δ 18.1 (d, $^2J_{P\text{-}P}$ 49.2 Hz), 13.7 (d, $^2J_{P\text{-}P}$ 49.2 Hz), -143.9 (sept, $^1J_{P\text{-}F}$ 713 Hz, PF_6^-) ppm. ^{31}P NMR (CD_2Cl_2, 121.7 MHz): δ 18.2 (ddd, $^1J_{P\text{-}H}$ 324.4 Hz, $^1J_{P\text{-}H}$ 352.0 Hz, $^2J_{P\text{-}P}$ 49.8 Hz), 13.7 (td, $^1J_{P\text{-}H}$ 340.2 Hz, $^2J_{P\text{-}P}$ 50.1 Hz), -143.8 (sept, $^1J_{P\text{-}F}$ 713 Hz, PF_6^-) ppm. ^1H NMR (CD_2Cl_2, 400 MHz): δ 5.45 (dm, 1H, $^1J_{H\text{-}P}$ = 352.5 Hz, P*H*), 4.90 (dm, 1H, $^1J_{H\text{-}P}$ 340.8 Hz, P*H*), 4.83 (dd, 1H, $^1J_{H\text{-}P}$ 340.5 Hz, $^2J_{H\text{-}H}$ 11.1 Hz; P*H*), 4.32 (s, 5H; C_5H_5) 4.13 (dd, 1H, $^1J_{H\text{-}P}$ 324.7 Hz, $^2J_{H\text{-}H}$ 12.0 Hz, P*H*), 2.33 (d, 2H, $^2J_{H\text{-}P}$ 12.0 Hz), 2.11 (s, 3H, $NCCH_3$), 1.75 – 1.64 (m, 2H), 1.39 – 1.05 (m, 6H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.6 MHz): δ 133.1 (s, N*C*CH_3), 77.2 (s, C_5H_5), 40.6 (dd, $^1J_{C\text{-}P}$ 36.3 Hz, $^2J_{C\text{-}P}$ 18.0 Hz, CH), 36.9 (dd, $^1J_{C\text{-}P}$ 33 Hz, $^2J_{C\text{-}P}$ 15 Hz, CH), 34.9 – 34.2 (CH_2), 26.3 (br, CH_2), 4.8 (s, NC*C*H_3) ppm. IR (KBr): 2319 (PH), 2265 (C≡N) cm^{-1}. HRMS (ES): expected 310.0577; observed 310.0579 amu (100%) [M^+].

[Fe(η^5-C$_5$H$_5$)(P{o-F-C$_6$H$_5$}$_3$)(t-chxnP$_2$)]PF$_6$, **10** Compound **9** (300 mg, 0.66 mmol) was dissolved in dichloromethane (10 mL) to which a solution of *tris*-2-fluorophenylphosphine (313 mg, 0.99 mmol) in dichloromethane (10 mL) was added and the reaction mixture subsequently refluxed for 5 days whereupon a gradual colour change from red to yellow was observed. All solvents and volatiles were removed *in vacuo* and the remaining solid washed with diethyl ether (5 x 15 mL). The remaining residue was then dried under high vacuum leaving compound **10** as a bright yellow solid. Yield = 342 mg (71%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.7 MHz): δ 63.4 (t, $^2J_{P\text{-}P}$ 51.2 Hz, P{*o*-F-C_6H_5}$_3$), 19.6 (br, PH_2), 15.9 (m, PH_2), -143.6 (sept, $^1J_{P\text{-}F}$ 713 Hz, PF_6^-) ppm. ^{31}P NMR (CD_2Cl_2, 121.7 MHz): δ 63.4 (t, $^2J_{P\text{-}P}$ 51.2 Hz, P{*o*-F-C_6H_5}$_3$), 23.4 – 12.3 (m, PH_2), -143.7 (sept, $^1J_{P\text{-}F}$ 713 Hz, PF_6^-) ppm. ^1H NMR (CD_2Cl_2, 500 MHz): δ 7.58 – 7.14 (m, 9H), 7.05 (s br, 3H), 5.41 (dd, 1H, $^1J_{H\text{-}P}$ 349.4 Hz, $^2J_{H\text{-}H}$ = 6.5 Hz, P*H*), 4.98 (dd, 1H, $^1J_{H\text{-}P}$ 341.2 Hz, $^2J_{H\text{-}H}$ 8.5 Hz, P*H*), 4.62 (d br, 1H, $^1J_{H\text{-}P}$ 363.6 Hz, P*H*), 4.22 (s, 5H, C_5H_5), 3.42 (d br, 1H, $^1J_{H\text{-}P}$ 341.3 Hz, P*H*), 2.21 (d, 1H, $^2J_{H\text{-}P}$ 11.0 Hz), 2.13 (d, 1H, $^2J_{H\text{-}P}$ 11.0 Hz), 1.75 – 1.58 (m, 2H), 1.46 – 0.78 (m, 5H), 0.50 – 0.39 (m, 1H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.6 MHz): δ 162.6 (d, $^1J_{C\text{-}F}$ 246.9 Hz, C-F), 134.3 (d, *J* 9.2 Hz), 125.4 (d, *J* 9.2 Hz), 119.8 (dd, *J* 29.6, 41.5 Hz), 116.9 (d, *J* 23.1 Hz), 81.1 (s, C_5H_5), 40.9 (dd, $^1J_{C\text{-}P}$ 33.5 Hz, $^2J_{C\text{-}P}$ 16.2 Hz, CH), 37.3 (dd, $^1J_{C\text{-}P}$ 32.9 Hz, $^2J_{C\text{-}P}$ 15.4 Hz, CH), 34.8 – 33.9 (CH_2), 26.6 (d, $^3J_{C\text{-}P}$ 7.0 Hz, CH_2), 25.8 (d, $^3J_{C\text{-}P}$ 6.8 Hz, CH_2) ppm. ^{19}F NMR (CD_2Cl_2, 282.8 MHz): δ -72.4 (d, $^1J_{F\text{-}P}$ 713 Hz, PF_6^-), -95.8 (s, P{*o*-F-C_6H_5}$_3$) ppm. IR (KBr): 2333 (PH) cm^{-1}. HRMS (ES): expected 585.0940;

observed 585.0930 amu (100%) [M^+]. Anal. Calcd for $FeC_{29}H_{31}P_4F_9$: C 47.70% H 4.28%. Found: C 47.28% H 4.36%.

[(η^5-C_5H_5)Fe(dibenzo,chxn-9aneP_3-H_2,Ph^F)]PF_6, **11** Compound **10** (200 mg, 0.27 mmol) was suspended in tetrahydrofuran (25 mL) and cooled to -78 ˚C. A solution of potassium *tert*-butoxide (61 mg, 0.55 mmol) in tetrahydrofuran (10 mL) was then added slowly affording a bright yellow solution. After warming slowly to room temperature all solvents and volatiles were removed *in vacuo* and the residual solid washed with degassed water (10 mL) and dried under high vacuum to give **11** as a bright yellow solid. Yield = 132 mg (70%). $^{31}P\{^1H\}$ NMR ($\{CD_3\}_2CO$, 121.7 MHz): δ 122.6 (t, $^2J_{P-P}$ 35.6 Hz, P$\{o$-F-$C_6H_5\}_3$), 102.9 (m, PH), 94.3 (m, PH), -144.7 (sept, $^1J_{P-F}$ 713 Hz, PF_6^-) ppm. ^1H NMR ($\{CD_3\}_2CO$, 400 MHz): δ 8.07 – 7.79 (m, 3H), 7.69 – 7.44 (m, 6H), 7.38 – 7.03 (m, 3H), 6.72 (dd, 1H, $^1J_{H-P}$ 376.4 Hz, $^3J_{H-H}$ 8.0 Hz, PH), 6.40 (dd, 1H, $^1J_{H-P}$ 368.4 Hz, $^3J_{H-H}$ 8.1 Hz, PH), 4.42 (s, 5H, C_5H_5), 2.41 (d, 1H, $^2J_{H-P}$ 8.0 Hz), 2.35 (d, 1H, $^2J_{H-P}$ 12.0 Hz), 2.11 (m, 1H), 1.54 (m, 3H), 1.16 (m, 2H), 0.79 (m, 1H), -0.03 (m, 1H) ppm. $^{13}C\{^1H\}$ NMR ($\{CD_3\}_2CO$, 75.6 MHz): δ 164.4 (d, $^1J_{C-F}$ 248.0 Hz, C-F), 135.8 – 132.5 (aromatics), 126.8 – 126.0 (aromatics), 118.1 (d, *J* 23.1 Hz), 80.5 (s, C_5H_5), 52.2 (dd, $^1J_{C-P}$ 32.3 Hz, $^2J_{C-P}$ 17.3 Hz, CH), 42.2 (dd, $^1J_{C-P}$ 35.2 Hz, $^2J_{C-P}$ 11.0 Hz, CH), 32.9 – 32.2 (CH_2), 32.1 – 31.6 (CH_2), 27.3 (d, $^3J_{C-P}$ 6.9 Hz, CH_2), 26.4 (d, $^3J_{C-P}$ 8.1 Hz, CH_2) ppm. ^{19}F NMR ($\{CD_3\}_2CO$, 282.8 MHz): δ -71.2 (d, $^1J_{F-P}$ 713 Hz, PF_6^-), -95.3 (s, P$\{o$-F-$C_6H_5\}_3$) ppm. IR (KBr Disk): 2312 (PH) cm^{-1}. Anal. Calcd for $FeC_{29}H_{29}P_4F_7$: C 50.46% H 4.23%. Found: C 49.59% H 4.24%.

[(η^5-C_5H_5)Fe(dibenzo,chxn-9aneP_3-{C_6H_{11}}$_2$,Ph^F)]PF_6, **12** To a cooled solution of **11** (300 mg, 0.43 mmol) in tetrahydrofuran (50 mL) at -78 ˚C was added a solution of potassium *tert*-butoxide (98 mg, 0.87 mmol) in tetrahydrofuran (10 mL). The addition caused a colour change from yellow to red and the reaction mixture was subsequently allowed to warm slowly to room temperature before cooling once more to -78 ˚C and adding an excess of 1-iodohexane (2 mL). After warming to RT, all volatiles were removed *in vacuo* and the residual solid washed with water (3 x 25 mL) and diethyl ether (3 x 25 mL). The residue was then dried under high vacuum leaving compound **12** as a pale yellow solid. Yield = 321 mg (86%). $^{31}P\{^1H\}$ NMR ($\{CD_3\}_2SO$, 393K, 121.7 MHz): δ 124.7 (t, $^2J_{P-P}$ 37.2 Hz), 122.2 (t, $^2J_{P-P}$ 38.7 Hz), 121.1 (t, $^2J_{P-P}$ 37.2 Hz), -142.5 (sept, $^1J_{P-F}$ 713 Hz, PF_6^-) ppm. ^1H NMR ($\{CD_3\}_2SO$, 393K, 500 MHz): δ 8.20 – 8.13 (m, 1H), 8.07 – 7.88 (m, 4H), 7.80 – 7.67 (m, 4H), 7.65 – 7.43 (m, 3H), 4.57 (s, 5H, C_5H_5), 3.07 – 2.96 (m, 1H), 2.88 – 2.53 (m, 4H), 2.33 (d, 1H, *J* 11.0 Hz), 2.25 – 2.15 (m, 1H), 1.92 – 1.84 (m, 2H), 1.81 – 1.67 (m, 5H), 1.64 – 1.43 (m, 12H), 1.40 – 1.28 (m, 1H), 1.23 – 1.03 (m, 7H), 0.91 – 0.80 (m, 1H), 0.03 – -0.06 (m, 1H) ppm. $^{13}C\{^1H\}$ NMR ($\{CD_3\}_2SO$, 75.6 MHz): δ 165.4 (d, $^1J_{C-F}$ 253.8 Hz, C-F), 134.3 (d, *J* 8.1 Hz), 133.1 (d, *J* 25.4 Hz), 132.1 – 128.8 (aromatics), 127.3 (dd, *J* 16.2, 34.6 Hz), 125.9 – 125.1 (aromatics), 122.3 – 121.3 (aromatics), 117.8 – 116.8 (aromatics), 78.9 (s, C_5H_5), 52.4, 43.0, 33.8, 31.5, 31.1 (dd, *J* 8.1, 22.0 Hz), 30.3, 29.3 (dd, *J* = 6.9, 15.0 Hz), 27.5 (dd, *J* = 4.6, 15.0 Hz), 26.4 (d, *J* = 6.9 Hz), 25.63 – 23.77, 22.8, 14.0, 7.8 ppm. The $^{13}C\{^1H\}$ NMR spectrum is more complicated than would be expected due to the presence of rotamers at room temperature. ^{19}F NMR ($\{CD_3\}_2SO$, 393K, 282.8 MHz): δ -69.8 (d, $^1J_{F-P}$ 713 Hz, PF_6^-), -97.7 (s, *o*-F-aryl) ppm. HRMS (ES): expected 713.2694; observed 713.2681 amu (100%) [M^+]. Anal. Calcd for $FeC_{41}H_{53}P_4F_7$: C 57.36% H 6.22%. Found: C 56.79% H 6.35%.

[$Mn(CO)_3$(1R,2R-chxn)(MeCN)]PF_6 **13t** To a stirred solution of $[Mn(CO)_3(MeCN)_3]PF_6$ (150 mg, 3.68 x 10^{-4} mol) in MeCN (15 mL), was added one equivalent of 1R,2R-diaminocyclohexane (0.04 g) and the solution allowed to stir overnight under an atmosphere of dinitrogen whereupon a slight yellow precipitate formed. The solution was pumped to dryness and washed sequentially with 40/60 petroleum ether (10 mL) and diethyl ether (10 mL). The resultant yellow powder was dried *in vacuo* to yield **13t** (125 mg, 76 %). ^1H NMR ($\{CD_3\}_2CO$, 500 MHz): δ 5.18 (br s, 1H, N*H*), 4.94 (br s, 1H, N*H*), 4.15 (br s, 1H, N*H*), 4.00 (br s, 1H, N*H*), 2.80 (m, 2H), 2.50 (s, 3H), 2.38 (br, 1H), 2.34 (br, 1H), 1.00-1.80 (m, 6H) ppm. IR : 3347, 3298 (NH), 2359 (C≡N), 2045, 1932 (CO) cm^{-1}. HRMS (ES): expected 294.0651; observed 294.0653 amu (100%) [M^+]. The compound proved to be relatively unstable and gave unsatisfactory elemental analyses. For this reason it was used immediately for the subsequent chemistry.

[$Mn(CO)_3$(1R,2R-chxn-9anePN_2-Bz,H_2)]PF_6, **14t** To a solution of **13t** (150 mg, 3.42 x 10^{-4} mol) in CH_2Cl_2 (10 mL) was added a solution of benzyldivinylphosphine (0.05 g from a standard solution in toluene). and the solution stirred until completion (*ca*. 4 h as determined by disappearance of the benzyldivinylphosphine resonance in the $^{31}P\{^1H\}$ NMR spectrum) The reaction mixture was pumped to dryness, the solid residue dissolved in THF and an excess of potassium *tert*-butoxide (0.1 g) added thereto. The colour of the solution turned from pale yellow to dark red instantly upon addition of the base. The reaction was stirred under dinitrogen for 2 days and all solvent was removed under reduced pressure. The red solid was washed with degassed water (5 mL), and the resultant yellow solid isolated by filtration. The solid was sequentially washed with 40/60 petroleum ether (10 mL) and diethyl ether (10 mL) to give **14t**. Yield 160 mg (82%). $^{31}P\{^1H\}$ NMR (CD_3CN, 121.7 MHz): δ 104 (s), -144.7 (sept, $^1J_{P-F}$ 713 Hz, PF_6^-) ppm. ^1H NMR (CD_3CN, 500 MHz): δ 7.50-7.70 (m, 5H), 5.43 (s, 1H, N*H*), 5.14 (s, 1H, N*H*), 3.62 (d, $^2J_{H-P}$ 10.8 Hz, 2H, CH_2Ph), 2.70 (q, *J* 6.8 Hz, 1H), 2.51 (d, *J* 10.0 Hz, 1H), 2.46 (t, *J* 11.6 Hz, 1H), 2.27 (m, 1H), 2.19 (m, 2H), 2.06 (m, 2H), 1.72 (m, 2H), 1.64 (m, 2H), 1.24 (m, 2H), 1.06 (m, 2H), 0.81 (m, 2H) ppm. $^{13}C\{^1H\}$ DEPT NMR (CD_3CN, 125.8 MHz): δ 133.7 (d, *J* 7.8 Hz), 131.3 (s), 129.7 (d, *J* 3.9 Hz), 129.1 (d, *J* 2.9 Hz), 128.7 (s), 127.4 (d, *J* 4.4 Hz), 68.9 (s), 58.9 (s, CH), 51.1 (d, $^2J_{C-P}$ 8.5 Hz, CH_2N), 43.0 (d, $^2J_{C-P}$ 8.0 Hz, CH_2N), 31.8 (d, $^1J_{C-P}$ 24.2 Hz, CH_2Ph), 30.6 (s, CH_2), 30.2 (s, CH_2), 29.8 (s, CH_2), 29.8 (d, $^1J_{C-P}$ 21.8 Hz, CH_2P), 23.9 (s, CH_2), 21.9 (d, $^1J_{C-P}$ 19.0 Hz, CH_2P) ppm. IR : (KBr) 3291 (NH), 2016, 1918 (CO) cm^{-1}; (CH_2Cl_2) 2020, 1941, 1919 (CO) cm^{-1}. HRMS (ES): expected 429.1140; observed 421.1130 amu (100%) [M^+]. *Anal.* Calcd for $MnC_{20}H_{27}P_2N_2O_3F_6$: C, 41.83; H, 4.74; N, 4.80. Found: C, 41.79; H, 4.72; N, 4.78.

[$Mn(CO)_3$(1R,2R-chxn){$PBz(C_3H_5)_2$}]PF_6 **15t** To a solution of

13t (150 mg, 3.4 x 10^{-4} mol) in CH_2Cl_2 (20 mL) was added 1.1 equivalents of diallylphenylphosphine. The solution was stirred for ca. 2 days, pumped to dryness and the residue washed successively with diethyl ether (10 mL) and 40/60 petroleum ether (10 mL) Yield 150 mg (66%). $^{31}P\{^1H\}$ NMR ($\{CD_3\}_2CO$, 121.7 MHz): δ 37.1 (s), -144.7 (sept, $^1J_{P-F}$ 713 Hz, PF_6^-) ppm. ^1H NMR ($\{CD_3\}_2CO$, 500 MHz): δ 7.66 (t, *J* 7.2 Hz, 2H), 7.56 (m, 2H), 7.23 (m, 1H), 5.89 (br, 1H), 5.77 (br, 1H), 5.32 (dd, $^2J_{H-P}$ 33.0 Hz, $^2J_{H-H}$ 17.1 Hz, 2H), 5.20 (dd, $^2J_{H-P}$ 26.8 Hz, $^2J_{H-H}$ 10.0 Hz, 2H), 4.83 (m, 2H), 4.25 (br, 1H), 3.33 (m, 3H), 3.00 (br, 1H), 2.18 (m, 1H), 1.80 (m, 2H), 1.46 (m, 3H), 1.17 (m, 1H), 0.94 (m, 2H), 0.57 (m, 1H) ppm. $^{13}C\{^1H\}$ DEPT NMR ($\{CD_3\}_2CO$, 125.8 MHz): δ 133.1 (d, J 17.5 Hz), 131.8 (d, *J* 7.5 Hz), 131.0 (d, *J* 8.8 Hz), 130.1 (d, *J* 6.5 Hz), 129.9 (d, *J* 6.5 Hz), 122.0 (d, *J* 6.3 Hz), 121.9 (d, *J* 6.3 Hz), 60.8 (CH), 59.4 (CH), 35.6 (CH_2), 34.5 (CH_2), 24.8 (d, *J* 13.8 Hz, CH_2) ppm. IR : 3352, 3258 (NH), 2004, 1907 (CO) cm^{-1}. *Anal.* Calcd for $C_{21}H_{29}P_2N_2F_6O_3Mn$: C, 42.87; H, 4.97; N, 4.76. Found: C, 42.99; H, 4.82; N, 4.81.

[Mn(CO)$_3$(1R,2S-chxn)(MeCN)]PF$_6$ **13c** Prepared exactly as detailed for **13t**. Yield = 110 mg (69%). ^1H NMR ($\{CD_3\}_2CO$, 500 MHz): δ 4.45 (br, 1H), 4.18 (br, 1H), 3.93 (br, 1H), 3.80 (br, 1H), 3.17 (br, 1H), 3.09 (br, 1H), 2.39 (br, 1H), 1.93 (s, 3H), 1.54 (br m, 4H), 1.32 (br, 2H) ppm. IR : 3344, 3288 (NH), 2333 (C≡N), 2033, 1922, 1883 (CO) cm^{-1}. HRMS(ES): expected 294.0651; 294.0658 amu (100%) [M^+]. The compound proved to be relatively unstable and gave unsatisfactory elemental analyses. For this reason it was used immediately for the subsequent chemistry.

[Mn(CO)$_3$(1R,2S-chxn-9anePN$_2$-Bz,H$_2$)]PF$_6$, **14c** The compound was prepared in an analogous fashion to **14t**. Yield = 75 mg (40 %). $^{31}P\{^1H\}$ NMR (CD_3CN, 121.7 MHz): δ 103.0, -144.7 (sept, $^1J_{P-F}$ 713 Hz, PF_6^-) ppm. ^1H NMR (CD_3CN, 500 MHz): δ 7.34 (m, 1H), 7.30 (m, 2H), 7.29 (m, 2H), 4.69 (br s, 1H), 3.65 (d, $^2J_{H-P}$ 14.4 Hz, 2H), 3.21 (m, 2H), 2.65 (m, 2H), 2.51 (br m, 2H), 2.37 (m, 2H), 2.21 (m, 2H), 1.86 (obs, 1H), 1.59 (m, 2H), 1.49 (m, 2H), 1.38 (m, 2H), 1.23 (m, 2H) ppm. $^{13}C\{^1H\}$ DEPT NMR (CD_3CN 125.8 MHz): δ 133.6, 129.5 (d, *J* 4.0 Hz), 128.8 (d, *J* 1.8 Hz), 127.2, 66.0 (CH), 61.7 (CH), 53.4 (d, *J* 17.5 Hz, CH_2), 32.0 (d, $^1J_{C-P}$ 25.0 Hz, CH_2), 25.7 (CH_2), 25.3 (d, *J* 18.8 Hz, CH_2), 21.1 (CH_2), 20.8 (CH_2), 19.4 (CH_2) ppm. MS(ES): expected 429.11; observed 338.15 amu [M^+ – Bz]. IR : 3500 (NH), 2019, 1910 (CO) cm^{-1}. *Anal.* Calcd for $MnC_{20}H_{27}P_2N_2O_3F_6$: C, 41.83; H, 4.74; N, 4.80. Found: C, 41.90; H, 4.86; N, 4.74.

[Mn(CO)$_3$(1R,2S-chxn)(PPh{C$_3$H$_5$}$_2$)]PF$_6$ ***15c*** Prepared in an analogous manner to **15t**. Yield = 75 mg (38%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ 48.2 (s), -144.7 (sept, $^1J_{P-F}$ 713 Hz, PF_6^-) ppm. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.7 – 7.2 (5H), 4.85 (br s, 1H), 4.68 (br s, 1H), 3.90 (br s, 2H), 3.0 – 1.5 (br m, 14H) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$ 125.8 MHz): δ 129.5, 127.7, 121.2, 117.1 (br, CH_2), 78.2 (CH), 53.5 (CH), 31.0 (CH_2), 29.8 (CH_2), 27.7 (br, CH_2), 25.0 (CH_2), 20.0 (CH_2) ppm. IR : 3337, 3297 (NH), 2029, 1917 (CO) cm^{-1}. *Anal.* Calcd for $C_{21}H_{29}P_2N_2F_6O_3Mn$: C, 42.87; H, 4.97; N, 4.76. Found: C, 42.69; H, 5.11; N, 4.69.

Crystallography

Data collection was carried out at 150 K on a Nonius Kappa CCD diffractometer using graphite monochromoated Mo Kα radiation (λ(Mo-Kα) = 0.71073 Å) equipped with an Oxford Cryosystems cooling apparatus. The structures were solved using direct methods and refined with SHELX suite of programs.[38] 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. The cyclohexane rings in the complexes **10**, **2** and **7** and the counter ions for **10** (PF_6^-), **2** (OTf^-) and **1** (BF_4^-) ions are disordered and were refined with constrained geometry and displacement parameters. Crystal structure and refinement data are collected in Table 1.

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

	1	**2**	**7**	**10**	**16c**
Empirical formula	$C_{12}H_{28}F_4BP_4Cu$	$C_{33}H_{50}F_9O_9P_{10}S_3Ag_3$	$C_{32}H_{34}FlMnO_4P_3$	$C_{29}H_{31}F_9FeP_4$	$C_{21}H_{31}Cl_2F_6MnN_2O_3P_2$
Formula weight	446.57	1491.22	776.34	730.27	673.27
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	P-1	P21/m	C2/m	Pbca	P-1
a/Å	8.7911(5)	9.8754(3)	35.176(5)	13.02100(10)	14.2290(2)
b/Å	8.9433(3)	23.0437(9)	10.9232(15)	15.2570(2)	14.4430(3)
c/Å	12.8881(6)	13.1527(3)	20.217(2)	30.5590(3)	16.8230(4)
α/°	80.312(3)				72.1450(10)
β/°	83.702(2)	99.030(2)	113.514(9)		73.3360(10)
γ/°	88.708(3)				72.4180(10)
U/Å^3	992.79(8)	2956.01(16)	7122.9(16)	6070.89(11)	3064.40(11)
Z	2	2	8	8	4
D_c/Mg m^{-3}	1.494	1.675	1.448	1.598	1.459
Reflections collected	4487	6912	3944	6923	13925
Independent reflections	2872	4542	2895	5784	8990
R_{int}	0.0329	0.0424	0.0992	0.0293	0.0415

Final $R1$, $wR2$ [$I>2\sigma(I)$]	0.0650, 0.1678	0.0749, 0.1911	0.0836, 0.2070	0.0516, 0.1095	0.0692, 0.1680
(all data)	0.1054, 0.1971	0.1155, 0.2190	0.1175, 0.2331	0.0641, 0.1140	0.1156, 0.1930

[a] Footnote text.

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ARTICLE TYPE

Conclusions

Rac,trans-1,2-diphosphinocyclohexane *t*-chxnP$_2$ has been prepared *via* a lithium aluminium hydride reduction of *rac,trans*-1,2-*bis*(diethoxyphosphoryl)cyclohexane. The coordination chemistry of *t*-chxnP$_2$ has been explored with copper(I) and silver(I) affording tetrahedral [Cu(*t*-chxnP$_2$)$_2$]BF$_4$ **1** and polymeric {[Ag(*t*-chxnP$_2$)$_2$]OTf}$_n$ **2**. The latter contains an unusual combination of tetrahedral and trigonal planar Ag(I) centres with both chelating and bridging *t*-chxnP$_2$. Coordination of *t*-chxnP$_2$ to manganese(I) and iron(II) metal centres provided suitable precursors for the preparation of the complexes [Mn(CO)$_3$(dibenzo,chxn-9aneP$_3$-Me$_2$,Ph^F)](OTf/I), ***7*** and [(η^5-C$_5$H$_5$)Fe(dibenzo,chxn-9aneP$_3$-{C$_6$H$_{11}$}$_2$,Ph^F)]PF$_6$, **12** containing structurally reinforced triphosphamacrocycles.

In addition, both 1*R*,2*R* and 1*R*,2*S*-diaminocyclohexane have been used as synthons in the assembly of 9-membered PN$_2$ macrocycles *via* intramolecular hydroamination of coordinated P-vinyl functions on a cationic manganese centre. The resultant 9anePN$_2$ macrocycles are the first of their kind. Similar attempts to make larger ring macrocycles by using P-allyl derivatives instead of P-vinyl were unsuccessful. This has been attributed to the different synthetic approach which relies upon the formation of relatively stable N-based radicals; such species are apparently not sufficiently stable to promote the cyclisation in this case.

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

1 A. Name, B. Name and C. Name, *Journal Title*, 2000, **35**, 3523; A. Name, B. Name and C. Name, *Journal Title*, 2000, **35**, 3523.

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