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Synthesis and properties of a new nine-membered triphospha-macrocyclic complex via a manganese(I) tricarbonyl template

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ABSTRACT

Reaction of the primary diphosphine $H_2P(CH_2)_2PH_2$ with $[MnBr(CO)_5]$, followed by removal of the bromide by treatment with AgOTf (OTf = CF_3SO_3) and addition of PAr_3 (Ar = *o*-C_6H_4F), gives the acyclic precursor complex, fac-$[Mn(CO)_3\{H_2P(CH_2)_2PH_2\}(PAr_3)][OTf]$, thus positioning the primary phosphine functions adjacent to the o-fluorophenyl substituents. The identity of this species was confirmed by multinuclear NMR (^1H, $^{19}F\{^1H\}$, $^{31}P\{^1H\}$ and ^{55}Mn) and IR spectroscopic analysis, as well as from a single crystal X-ray analysis. Subsequent treatment of this complex with KO^{t}Bu (potassium tertiary butoxide) causes a double P-C coupling reaction, with defluorination of two aryl groups, and leads to formation of a nine-membered triphosphine macrocyclic complex. Methylation (KO^{t}Bu/MeI) of the two remaining secondary phosphine function yields the complex $[Mn(CO)_3(\mathbf{1})][OTf]$, which has been characterised similarly by multinuclear NMR and IR spectroscopy, and by electrospray mass spectrometry. A single crystal X-ray structure determination confirms the distorted octahedral coordination at Mn(I), with the triphosphine macrocycle occupying three mutually facial coordination sites. As expected, this complex is extremely thermodynamically stable and kinetically inert, being unaffected by prolonged refluxing with either Me_3NO or thiophenolate in MeCN.

1. Introduction

Tertiary phosphine ligands are among the most widely used and important classes of ligand in organometallic and coordination chemistry due to the broad applications of transition metal phosphine complexes in catalysis and the ease with which the electronic and steric properties can be tuned through variation of the P-bound substituents [1]. Moreover, while it is well known that chelating phosphine ligands have improved ligating ability over monodentate phosphines, macrocyclic phosphine ligands are expected to form more kinetically and thermodynamically stable complexes with metal ions than their acyclic multidentate counterparts, due to the macrocyclic effect [2]. Macrocyclic phosphine ligands may also favour coordination to the more electron rich metals and those in low oxidation states, as well as mismatched oxophilic hard early transition metal ions [3]. This may provide an entry into new classes of complexes and also stabilise active intermediates during catalytic reactions.

Of the known P-donor macrocycles, the triphosphine macrocycles containing three mutually syn phosphine groups are of particular interest due to their electronic analogy to η^5-cyclopentadienyl (η^5-Cp) ligand as a tridentate 6-electron donor and their structural character. The P_3-donor macrocycles are facially coordinating ligands that occupy three coordination sites. This can impart important structural consequences, forcing the remaining coordination (reaction) sites into a mutually cis arrangement and also causing geometric distortions within the coordination sphere with implications for modified reactivity.

Macrocyclic triphosphines, however, have not been extensively studied compared with well-known oxygen-, nitrogen- and sulfur-containing macrocycles, due to the difficulties in their synthesis [3(a)]. Reports on phosphine macrocycles are quite rare and are principally focused on the ligand synthesis aspect, reflecting the challenges associated with their preparation. Two main approaches for their synthesis have been studied, namely direct (high dilution) methods and template-mediated methods. In direct meth-

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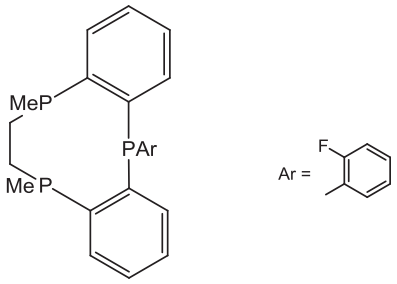
ods, the acyclic phosphine precursors are combined in dilute solution in a given ratio to yield the desired phosphine macrocycle. In the first such synthesis by Kyba and co-workers, an 11-membered triphospha-macrocycle was prepared via reaction of a dilithium organophosphide with a halogenophosphine [4]. The first direct synthesis of a nine-membered P_3-donor ring, 1,4,7-triphenyl-1,4,7-triphosphacyclononane (Ph_3[9]aneP_3), was through the reaction of lithium bis-(2-phenylphosphidoethyl)phenylphosphine with 1,2-dichloroethane [5]. This method is less effective, however, due to the unavoidable polymerisation side reaction and formation of the thermodynamic macrocyclic product as a mixture of the various possible stereoisomers, which are inherently difficult to separate.

Within the template-directed methods, the phosphine precursors are first coordinated to a suitable metal centre, followed by a series of intramolecular P-C coupling reactions leading to the desired macrocycle coordinated to the metal template species. As well as increasing the range of P-C bond forming reactions available, the metal ion has three key roles. Firstly, it holds the phosphine precursors in close proximity to facilitate the ring closure reaction effectively, secondly, it stabilises the highly reactive precursors and, thirdly, it allows the formation of kinetic products with controlled stereochemistry as the P-containing precursors are pre-organised. However, while the yields of the P_3-macrocycles can be much higher than for the direct synthesis, there are also disadvantages associated with the template method, the most relevant of which are: i) identifying suitable metal templates to meet the conditions necessary for the synthesis of phosphine macrocycles; ii) once the phosphine macrocycle has been formed, the macrocyclic complexes produced are kinetically inert and thermodynamically stable and therefore may be resistant to demetallation.

The first 12-membered triphospha-macrocycle, 1,5,9-triphosphacyclododecane ([12]aneP_3), was prepared by Norman using the *fac*-$(CO)_3$Mo fragment as a template [6]. The liberation of the [12] aneP_3 ring was only achieved some years later. Edwards and co-workers demonstrated that by disrupting the Mo(0) (d^6) centre via oxidation with halogen to form a more kinetically labile Mo(II) (d^4) centre, followed by hydrolysis with aqueous base, yielded the metal-free [12] aneP_3 [7]. The synthesis and liberation of this macrocycle can also be achieved using the alternative $(CO)_3$Cr or $CpFe^+$ templates and a series of derivatives of 1,5,9-triphosphacyclododecane were also prepared by alkylation of the secondary phosphines and related complexes have been investigated [8], along with their application in organometallic chemistry and catalysis [3c,8]. As the chemistry of 1,5,9-triphosphacyclododecane and related derivatives developed, it became evident that ligands derived from the 12-membered ring are coordinatively flexible and that the formation of three six-membered chelate rings is not optimal for coordination of transition metal ions, hence the resulting complexes remain labile.

Triphosphamacrocycles with ring sizes smaller than 12 atoms, especially those with nine-membered rings [3(b)], should form more robust complexes with a wide range of metal ions since such macrocycles coordinate to the metal centre to form three fused five-membered chelate rings. In this regard, a small number of triphospha-macrocycle complexes with smaller ring sizes have been prepared using sterically bulky (η^5-C_5Me_5)Fe^+ [9] or (η^4-C_4Me_4)Co^+ [10] fragments as templates and mostly used base- or radical-induced hydrophosphination as the P-C bond forming strategy to achieve ring-closure.

An alternative base-induced cyclocondensation reaction strategy has been employed successfully using the $(CO)_3Mn^+$ fragment as template [11]. We present here the preparation and characterisation of the nine-membered triphosphine macrocycle (**1**) (as its $Mn^I(CO)_3$ complex) by P-C bond formation using a similar base-induced double defluorination of appended o-fluorophenyl groups via a cationictricarbonylmanganese(I) template



(**1**)

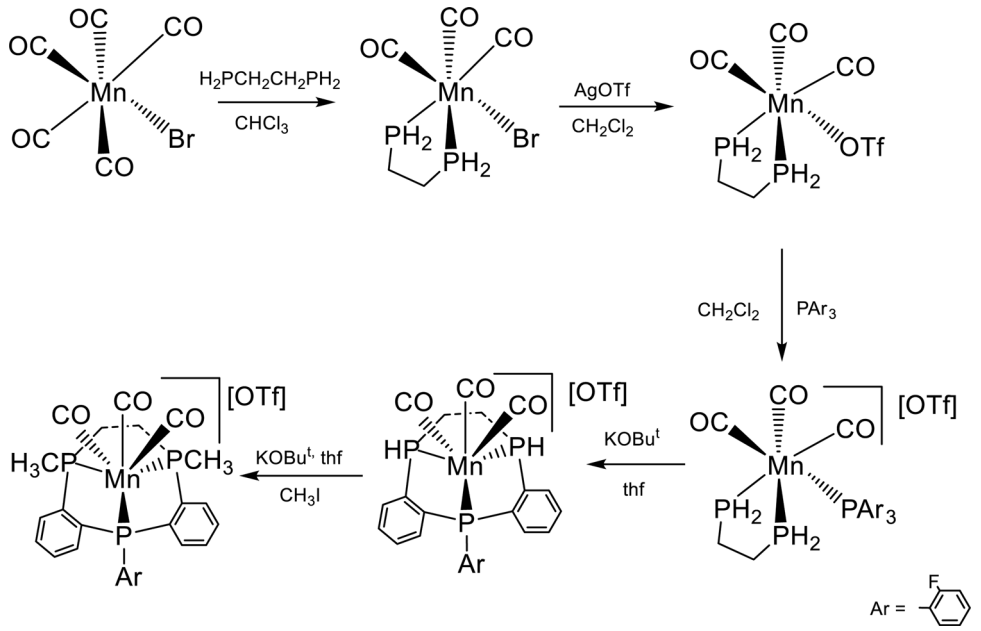
2. Results and discussion

The method employed for the preparation of the new triphospha-macrocycle (**1**) is shown in Scheme 1 and uses a double defluorination to form the two P-C bonds that cause ring-closure, using a modification of the method previously reported by Edwards et al [11].

The phosphine precursors were introduced sequentially, and the products at each stage were characterised by IR, ^{1}H, ^{31}P{^{1}H} and ^{55}Mn NMR spectroscopy, as well as elemental analysis and positive ion electrospray mass spectrometry for the final product. Thus, the primary diphosphine, $H_2P(CH_2)_2PH_2$ was reacted with $[MnBr(CO)_5]$ to liberate two CO ligands and form the distorted octahedral species, fac-$[MnBr(CO)_3\{H_2P(CH_2)_2PH_2\}]$ in > 90% yield. The spectroscopic data for this product are in accord with those of related primary diphosphine complexes [12], with three CO stretches in the IR spectrum, as expected for the C_s symmetry molecule, and show the expected two doublets associated with the P-H functions. The ^{1}H and ^{31}P{^{1}H} NMR resonances are broadened significantly by the ^{55}Mn quadrupole (^{55}Mn: I = 5/2, 100%, Q = 0.49 x 10^{-28} m^2) [13], while the ^{55}Mn NMR spectrum shows a broad resonance at −1374 ppm, consistent with the published data [12].

Subsequent removal of the bromide using AgOTf (OTf = $CF_3SO_3^-$), followed by the introduction of the second *P*-containing precursor, PAr_3 (Ar = *o*-C_6H_4F), gave the key precursor, fac-$[Mn(CO)_3\{H_2P(CH_2)_2PH_2\}(PAr_3)][OTf]$, also in very good yield (87%), with the formulation consistent with the microanalytical data. The ^{1}H NMR spectrum (CD_2Cl_2) of this product shows the expected resonances with integration ratios corresponding to the two distinct coordinated phosphines. While the ^{31}P{^{1}H} NMR resonance associated with the coordinated PAr_3 in this complex occurs at 43.1 ppm, the ^{31}P{^{1}H} NMR spectra for both this complex and its $[MnBr(CO)_3\{H_2P(CH_2)_2PH_2\}]$ precursor show a broadened resonance due to the coordinated $H_2P(CH_2)_2PH_2$, each with a very significant high frequency coordination shift compared to the primary diphosphine itself, and characteristic of the presence of a five-membered chelate ring [14]. The ^{55}Mn NMR resonance for $[Mn(CO)_3\{H_2P(CH_2)_2PH_2\}(PAr_3)][OTf]$ is broad as expected, with δ = -1273 ($w_{1/2}$ = 4600 Hz), some 100 ppm to high frequency of the bromo precursor complex, and in line with other fac-triphosphine complexes containing the $Mn(CO)_3^+$ fragment [15]. The ^{19}F{^{1}H} NMR spectrum shows the two singlets expected for the OTf anion and the PAr_3.

An X-ray crystal structure of this species (Fig. 1) confirmed its formula, showing the chelating primary diphosphine and the PAr_3 ligand positioned mutually facial. The Mn-P bond distance to the PAr_3 ligand is longer than those involving the chelating $H_2P(CH_2)_2PH_2$, in line with expectations due to steric and electronic effects. The P1-Mn-P2 bond angle within the chelate ring is < 90 °, whereas the P-Mn-P angles involving P3 are both > 90 °,



Scheme 1. Mn(I)-mediated template synthesis of a nine-membered triphosphine macrocyclic complex, [Mn(CO)$_3$(**1**)][OTf].

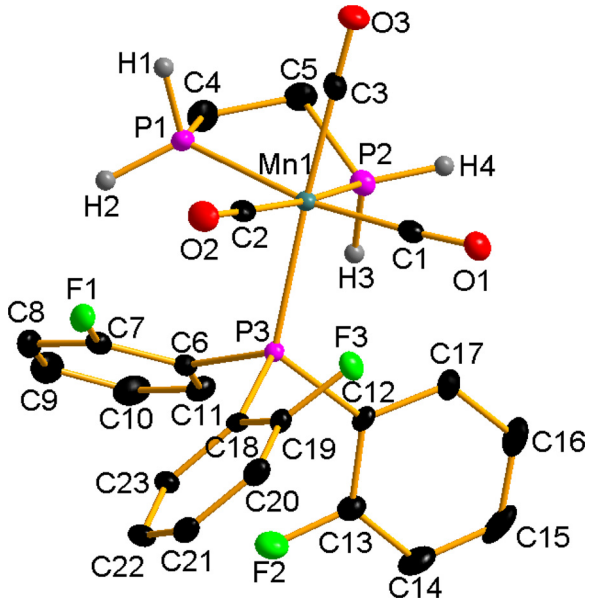


Fig. 1. View of the structure of the cation present in *fac*-[Mn(CO)$_3${H$_2$P(CH$_2$)$_2$PH$_2$}(PAr$_3$)][OTf] with numbering scheme adopted. Ellipsoids are shown at the 50% probability level and H atoms, other than those bound to P are omitted for clarity. Selected bond lengths (Å) and angles (°): Mn(1)-C(2) = 1.824(2), Mn(1)-C(1) = 1.831(2), Mn(1)-C(3) = 1.836(2), Mn(1)-P(2) = 2.2944(6), Mn(1)-P(1) = 2.3130(7), Mn(1)-P(3) = 2.3611(6), P(2)-Mn(1)-P(1) = 81.20(2), P(2)-Mn(1)-P(3) = 91.24(2), P(1)-Mn(1)-P(3) = 97.78(2).

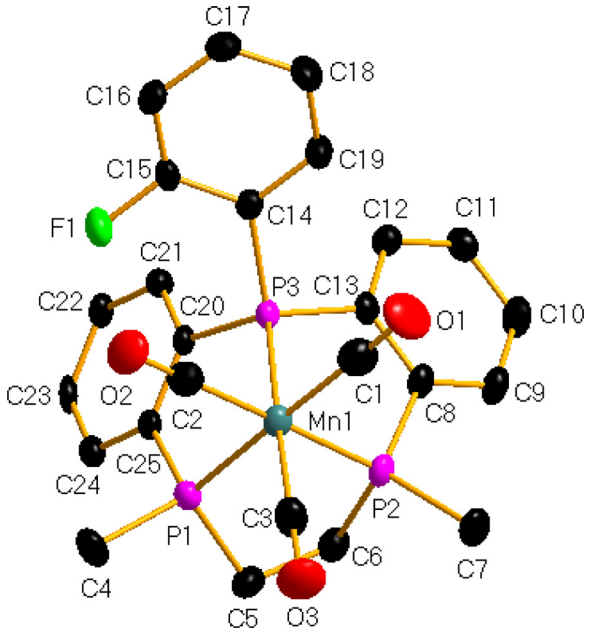


Fig. 2. View of the structure of fac-[Mn(CO)$_3$(**1**)][OTf] with numbering scheme adopted. Ellipsoids are shown at the 50% probability level and H atoms, other than those bound to P, are omitted for clarity. Selected bond lengths (Å) and angles (°): Mn(1)-C(3) = 1.817(5), Mn(1)-C(2) = 1.823(5), Mn(1)-C(1) = 1.832(6), Mn(1)-P(3) = 2.2469(13), Mn(1)-P(1) = 2.2616(14), Mn(1)-P(2) = 2.2719(14), P(3)-Mn(1)-P(1) = 85.22(5), P(3)-Mn(1)-P(2) = 82.38(5), P(1)-Mn(1)-P(2) = 83.51(5).

reflecting the steric requirements of the Ar groups and the absence of a chelate ring.

The key ring closure step, via formation of two new P-C bonds, used a base-induced double defluorination reaction promoted by treatment of the acyclic precursor complex with KO^{t}Bu in thf (Scheme 1). Methylation of the resulting disecondary phosphine macrocyclic complex was achieved by further treatment with KO^{t}Bu and MeI, affording fac-[Mn(CO)$_3$(**1**)][OTf] as an orange/yellow coloured solid and containing the κ^3-coordinated nine-membered triphosphine macrocycle, (**1**), as intended. As well as the resonances associated with the aromatic H atoms and the CH$_2$ groups, the ^{1}H NMR spectrum shows a doublet corresponding to the two P-bound Me substituents, and the complete consumption of the P-H resonances associated with the [Mn(CO)$_3${H$_2$P(CH$_2$)$_2$PH$_2$}(PAr$_3$)][OTf] precursor, caused by the P-C coupling to effect ring closure, and the installation of the terminal methyl groups. The ^{31}P{^{1}H} NMR spectrum shows a single, broad and asymmetric resonance centred at 108.2 ppm, and spanning the range 102-114 ppm. The asymmetry is attributed to the two different P environments that lie within the envelope of the broad signal caused by the ^{55}Mn quadrupole, which also masks the P-P couplings. Similar behaviour was observed for the Mn(CO)$_3$-templated

Table 1
Crystallographic parameters[a]

Complex	$[Mn(CO)_3\{H_2P(CH_2)_2PH_2\}(PAr_3)][OTf]$	$[Mn(CO)_3(\mathbf{1})][OTf]$
Formula	$C_{24}H_{20}F_6MnO_6P_3S$	$C_{26}H_{22}F_4MnO_6P_3S$
M	698.31	686.35
Crystal system	Monoclinic	Monoclinic
Space group (no.)	$P2_1/c$ (14)	$P2_1/c$ (14)
a /Å	10.6173(3)	13.8745(5)
b /Å	10.7762(3)	13.6209(3)
c /Å	24.7601(7)	16.1505(5)
α /°	90	90
β /°	99.909(2)	110.796(4)
γ /°	90	90
U /Å^3	2790.65(14)	2853.32(15)
Z	4	4
μ(Mo-K$_\alpha$)/mm^{-1}	0.799	0.770
F(000)	1408	1392
Total number reflns	9996	27825
R_{int}	-	0.037
Unique reflns	9996	5585
No. of params, restraints	383/0	372/0
GOF	1.066	1.071
R_1, wR_2 [$I > 2\sigma(I)$] [b]	0.038, 0.099	0.062, 0.180
R_1, wR_2 (all data) [b]	0.040, 0.100	0.071, 0.189

[a] common data: T = 100 K; wavelength (Mo-K$_\alpha$) = 0.71073 Å; θ(max) = 27.5°
[b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$.

benzannulated P_3-macrocylic analogue reported previously [11(a)], and the $^{31}P\{^1H\}$ chemical shift is consistent with the presence of three fused five-membered chelate rings [14],[9(f)]. The ^{55}Mn NMR spectrum of this complex occurs at δ = -933 and is also broad.

The positive ion electrospray mass spectrum of this macrocyclic product also supports the formulation of the cation as $[Mn(CO)_3(\mathbf{1})]^+$. Final confirmation of the successful formation of the complex was obtained from a single crystal X-ray structure analysis. The structure of the cation is shown in Fig. 2, containing three mutually fac CO ligands lying trans to the nine-membered cyclic triphosphine. The Mn-P bond distances range between 2.2469(13) and 2.2719(14) Å, i.e. slightly contracted compared to the acyclic precursor complex (above). Further, in contrast to the acyclic precursor in Fig. 1, the P-Mn-P bond angles in the macrocyclic complex are all significantly below 90 °, ranging from 82.38(5) to 85.22(5) °, due to the constraints of the nine-membered macrocycle and the fused five-membered chelate rings.

Finally, several attempts were made to liberate the ligand (**1**) from the manganese(I) tricarbonyl fragment, either by heating the $[Mn(CO)_3(\mathbf{1})][OTf]$ salt with either Me_3NO in MeCN to promote decarbonylation or with sodium thiophenolate to sequester the manganese, however these have proved unsuccessful to-date. This confirms that the macrocyclic complex is both highly thermodynamically stable and kinetically inert, consistent with previous work on metal templated triphosphacyclononane complexes.

3. Experimental

Syntheses were performed using standard Schlenk and glovebox techniques under a dry N_2 atmosphere. Solvents were dried by distillation from CaH_2 (CH_2Cl_2, $CHCl_3$) or Na/benzophenone ketyl (thf, toluene, n-hexane, diethyl ether). $[MnBr(CO)_5]$, AgOTf and potassium tert-butoxide were obtained from Sigma-Aldrich. $H_2P(CH_2)_2PH_2$ [16], and $P(o\text{-}C_6H_4F)_3$ [17] were prepared by the literature methods. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer in the range 4000–200 cm^{-1}, with samples prepared either as Nujol mulls between CsI plates or in a solution cell with NaCl windows as solutions in CH_2Cl_2 or $CHCl_3$. ^1H, $^{19}F\{^1H\}$, $^{31}P\{^1H\}$ and ^{55}Mn NMR spectra were recorded using a Bruker AV400 spectrometer and are referenced to the residual protio-solvent (^1H), external $CFCl_3$ (^{19}F), external 85% H_3PO_4 (^{31}P) and external aqueous $K[MnO_4]$ (^{55}Mn). Microanalyses on new compounds were undertaken by London Metropolitan University or Medac Ltd. ESI$^+$ mass spectra were obtained in MeCN solution using a Waters Acquity Platform.

3.1. *fac-[MnBr(CO)$_3${H$_2$P(CH$_2$)$_2$PH$_2$}]*

To a suspension of $[MnBr(CO)_5]$ (0.274 g, 1 mmol) in $CHCl_3$ (20 mL). $H_2P(CH_2)_2PH_2$ (0.100 g 1.06 mmol) in toluene (10 mL) was added via dropping funnel with stirring. After addition the mixture was heated to reflux for 4 h. After cooling to room temperature, the solvent and volatiles were removed *in vacuo*. The yellow-orange solid residue was collected and washed with petroleum ether (BPt = 40–60 °C) and dried *in vacuo*. Yield = 0.284 g, 91%. Anal. required for $C_5H_8BrMnO_3P_2$: C,19.2; H, 2.6%. Found: C, 19.5; H, 2.9%. ^1H NMR (CD_2Cl_2): δ = 5.09 (PH, [2H], dd, $^1J_{PH}$ = 332 Hz), 4.90 (PH, [2H], dd, $^1J_{PH}$ = 372 Hz), 2.28 (br m, CH, [2H]), 2.07 (br m, CH, [2H]). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = −9.6 (br s). ^{55}Mn NMR (CH_2Cl_2): δ = −1374 ($w_{1/2}$ = 4300 Hz). IR (Nujol): 2343br (PH), 2024 (CO), 1968 (CO), 1932 (CO).

3.2. *fac-[Mn(CO)$_3${H$_2$P(CH$_2$)$_2$PH$_2$}(PAr$_3$)][OTf]*

To a solution of $[MnBr(CO)_3\{H_2P(CH_2)_2PH_2\}]$ (0.156 g, 0.5 mmol) in CH_2Cl_2 (20 mL) was added AgOTf (0.128 g 0.5 mmol) with stirring. The reaction was continued overnight producing a cloudy yellow solution. After filtering to remove the AgBr, PAr_3 (0.158 g, 0.5 mmol) was added to the filtrate, which was stirred for 2 h. The solvent and volatiles were then removed *in vacuo*. The solid residue was washed with petroleum ether (BPt = 40–60 °C) and the light yellow solid was then dried *in vacuo*. Yield = 0.305 g, 87%) Anal. required for $C_{24}H_{20}F_6MnO_6P_3S$: C, 41.3; H, 2.9%. Found: C, 41.5; H: 3.1%. ^1H NMR (CD_2Cl_2): δ = 7.62-7.57(m, aromatic C-H, [3H]), 7.30-7.28(m, aromatic C-H, [6H]), 7,19-7.13(m, aromatic C-H, [3H]) 5.0 (br d, $^1J_{PH}$ = 388 Hz, P-H, [2H]), 4.0 (br d, $^1J_{PH}$ = 372 Hz, P-H, [2H]), 2.20-1.85 (br m, CH_2, [4H]). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 43.1 (PAr_3, [1P]), -7.3 ($H_2P(CH_2)_2PH_2$, [2P]). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): -79.0 (OTf^-, [3F]), -93.9 (Ar-F, 3F). IR(Nujol): 2359 (PH),

2044 (CO), 1965 (CO), 1926sh (CO). ^{55}Mn NMR (CH_2Cl_2): δ = -1273 ($w_{1/2}$ = 4600 Hz).

3.3. fac-[Mn(CO)$_3$(1)][OTf)]

To a solution of [Mn(CO)$_3${H$_2$P(CH$_2$)$_4$PH$_2$}(PAr$_3$)][OTf] (0.174 g, 0.25 mmol) in thf (20 mL), potassium tert-butoxide (0.057 g 0.50 mmol) was added with stirring. After stirring for 30 min., further potassium tert-butoxide (0.057 g 0.50 mmol) was added and stirring was continued for 30 min. CH_3I (0.075 g, 0.5 mmol) was then added, followed by stirring for one hour. The solvent and volatiles were then removed *in vacuo*. The orange/yellow solid residue was extracted with CH_2Cl_2 (40 mL) and crystals of the target complex were obtained by vapour diffusion of diethyl ether into a concentrated CH_2Cl_2 solution. Yield = 0.111 g, 65%. Anal. required for: $C_{26}H_{22}F_4MnO_6P_3S$: C, 45.5; H, 3.2%. Found: C, 45.3; H, 3.3%. ^{1}H NMR (CD_2Cl_2): 7.95 (m, [2H]), 7.74 (m, [2H]), 7.65 (m, [2H]), 7.55 (m, [3H]), 7.3 (m, [1H]) 7.2 (m, [2H]) all aromatic H, 2.40 (br, CH_2, [2H]), 2.20 (d, $^2J_{PH}$ = 12 Hz, Me, [6H]), 1.96 (br, CH_2, [2H]). ^{31}P{^{1}H} (CD_2Cl_2): 108.2 (br). ^{19}F{^{1}H} (CD_2Cl_2): δ = -78.9 (s, OTf^-), -96.6 (s, Ar-F). ^{55}Mn NMR (CH_2Cl_2): δ = -933 ($w_{1/2}$ = 4200 Hz). IR (Nujol): 2026 (CO), 1949br (CO), 1918 (CO). ESI$^+$ MS (MeCN): found *m/z* = 537.2 Calculated for [Mn(CO)$_3${$C_{22}H_{22}F_1P_3$}]$^+$: *m/z* = 537.

3.4. X-Ray experimental

Crystals suitable for X-ray analysis were grown by diethyl ether vapour diffusion into CH_2Cl_2 solutions of the complexes. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum (λ = 0.71073 Å) rotating anode generator with VHF Varimax optics (70 μm focus) with the crystal held at 100 K or an Agilent Xcalibur Gemini S diffractometer with a CCD plate detector using Mo-Kα (λ = 0.71073 Å) radiation with the crystal held at 100 K. [Mn(CO)$_3${H$_2$P(CH$_2$)$_2$PH$_2$}(PAr$_3$)][OTf] is a non-merohedral twin. Structure solution and refinement were performed using SHELX(S/L)97, SHELX-2013, or SHELX-2014/7 and were generally routine [18]. Crystallographic parameters are presented in Table 1.

4. Conclusions

We have reported the successful preparation, spectroscopic and structural characterisation of a new triphosphacyclononane macrocyclic ligand, (**1**) formed on a Mn(CO)$_3^+$ template through a based-induced P-C coupling reaction, accompanied by defluorination of two o-fluoroaryl groups. Multinuclear NMR and IR spectroscopic analysis of the precursor complex and the final macrocyclic complex are fully consistent with the solid state structures of each, determined by X-ray crystallography. The Mn(I) tricarbonyl fragment is shown to be a reliable template for the cyclisation reaction to form the rare triphosphacyclononane ligands, and contrasts with the reports using Mo(O) tricarbonyl as the template, which has proved to be unsuitable for formation of nine-membered P_3 rings [6].

The complex containing the new nine-membered triphosphine macrocycle is extremely resistant to demetallation, indicating that its complex with the d^6 Mn^I(CO)$_3$ cation fragment is highly stable and inert, as anticipated.

Declaration of Competing Interest

The authors have no conflicts to declare.

CRediT authorship contribution statement

Wenjian Zhang: Conceptualization, Methodology, Writing – review & editing. **William Levason:** Conceptualization, Writing – review & editing. **Gillian Reid:** Conceptualization, Writing – review & editing.

Acknowledgments

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Supplementary materials

Contains the supplementary crystallographic data for this paper. CCDC reference numbers for the crystallographic information files in cif format are: 2161481 ([Mn(CO)$_3$(**1**)][OTf]) and 2161482 ([Mn(CO)$_3${H$_2$P(CH$_2$)$_2$PH$_2$}(PAr$_3$)][OTf]). These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ UK. Other SI includes the IR, ^{1}H, ^{19}F{^{1}H}, ^{31}P{^{1}H} and ^{55}Mn NMR spectra for [Mn(CO)$_3$(**1**)][OTf].

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