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Short Research Article

Synthesis and Crystal Structure of an Air Stable Primary Phosphine-Manganese (+1) Complex; *fac*-Tricarbonyl-tris(*o*-florophenylphosphine)-Manganese(+1)-hexafluorophosphate.

ABSTRACT

The synthesis of an air-stable manganese(+I)-primary phosphine complex from *fac*-$[Mn(CO)_3(CH_3CN)_3]PF_6$ and $(o\text{-}FC_6H_4)PH_2$ is described. The X-ray single crystal structure of the manganese(I) complex is reported.

Keywords: $[\{(o\text{-}FC_6H_4)PH_2\}_3Mn(CO)_3]PF_6$, *crystal structure, synthesis, complex, X-ray.*

1. INTRODUCTION

In comparison with other types of organophosphine metal derivatives, the number of known primary phosphine transition metal complexes is relatively small. This is partially due to some of the chemical and physical properties of primary phosphines. Generally speaking, primary phosphines are easily oxidized by air (in some cases they can ignite spontaneously if not handled under an atmosphere of oxygen free inert gas), and have high toxicity. They are, however, versatile starting materials due to the possibility of functionalising the hydrogen bonds. For this reason, there is increasing interest in the synthesis and coordination chemistry of substituted primary phosphines containing ortho-substituted aryl group [such as $(o\text{-}F\text{-}C_6H_4)PH_2$], particularly for applications in the synthesis of macrocyclic ligands containing three or more phosphorous atoms using the synthetic procedure called a metal template [1] .

In this synthetic method, one of the acidic hydrogen atoms of the metal coordinated-PH_2 group and the ortho-flouro group can easily be activated and then eliminated as a small molecule; HF. As a result, new P-C bonds between the already metal-coordinated phosphine moieties can be formed. This synthetic technique leads to the formation of a metal complex containing a macrocyclic phosphine ligand. For example, a series of triphosphine 9 and 12 membered macrocycles containing a variety of alkyl and aryl phosphine groups have been produced using the metal-template procedure [2].
Generally, the macrocycles–metal complexes produced are kinetically stable. This may explain why the liberation of free macrocyles containing phosphorous (III) is not always achieved [3]. Edwards et al [4-5], showed that the liberation of free phosphorous (III) containing macrocyles can be obtained if the centre of the precursor macrocyclic complex is the ion Mn(+I). For this reason the title complex, $[\{(o\text{-}FC_6H_4)PH_2\}_3Mn(CO)_3]PF_6$, was prepared and characterized by a variety of techniques.

2. EXPERIMENTAL DETAILS

2.1 Synthesis

To a stirred dry methanoic solution (25 ml, 0.001 mol., 0.4gm,) of$[Mn(CO)_3(CH_3CN)_3] PF_6$ (prepared as described in [6-7] kept under a positive pressure of nitrogen gas, a dry methanoic solution of *o*-flourophenylphosphine (25 ml, 0.004 mol.; 0.52gm) was slowly added and then stirred continuously for two days at room temperature. The resulting orange yellow slurry was filtered and the yellow sticky solid

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washed twice with diethyl ether (15 ml each). To the solid obtained, 60 ml of dry methanol was added. The reaction mixture was heated at 50 ℃ with stirring until all solid dissolved and a clear orange yellow solution obtained. The solution was allowed to cool extremely slowly down to room temperature. The very pale yellow cuboid-like crystals obtained were then collected by filtration. A second batch of crystals can be obtained when the filtrate was kept at -25 ℃ for two days. The total mass of the pale yellow crystals was 0.6 gm (yield ≈ 90%), M.P. = 142℃.

Elemental analysis for $[\{(o\text{-}FC_6H_4)PH_2\}_3Mn(CO)_3]PF_6$ calculated M.W.: 668.062; C; 37.76, and H; 2.69. Found: C;37.80, and H; 2.63. The electrospray mass spectrum of the complex shows peaks at *m/z* = 522.9816 (calc.=522.9801), which corresponds to the ion $(M\text{-}PF_6)^+$.

^{31}P NMR (none solvent, 300 MHz, ppm): = -37.8356 (assigned to coordinated PH_2 group).

IR (KBr pellet, cm^{-1}): weak, 2367.68; strong sharp, 2051.89; strong sharp, 1995.96; strong sharp, 1978.12; shoulder, 1941; strong medium 1603.04; medium sharp, 1570.25; strong sharp, 1476.24; strong sharp 1448.28; strong sharp, 1269.9; strong sharp 1219.76; small sharp, 1162.38; medium sharp, 1128.74; medium sharp, 1086.69; medium sharp, 1074.64; small sharp, 1028.84; shoulder, 947.84; strong sharp 893.84; shoulder, 874.07; strong broad, 836.47; shoulder, 813.33; strong sharp, 773.797; strong sharp 765.6; strong sharp, 759.8; shoulder, 740.04; medium sharp, 707.26; weak sharp 675.9; strong sharp, 654.7; strong sharp ,621.448; strong sharp, 556.8; shoulder, 543.3; weak sharp ,509.6; weak sharp ,503; weak sharp, 480.2; weak sharp, weak sharp, 456.1; weak sharp, 444.5; weak sharp, 413.4. A single crystal structure analyses confirmed the molecular formula.
The complex is air stable, moderately soluble in methanol and ethanol but very soluble in acetonitrile, THF, and CH_2Cl_2.

2.2 Crystal structure determination

Single-crystal XRD data were collected on an Agilent SuperNova Dual Atlas diffractometer with a mirror monochromator using Cu (λ = 1.5418 Å) radiation and equipped with an Oxford Cryosystems cooling apparatus. Crystal structures were solved and refined using SHELX.[8]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were inserted in idealized positions, and a riding model was used with U_{iso} set at 1.2 times the value of U_{eq} for the atom to which they are bonded. Structure determination and refinement data are shown in Table 1.

Table 1. Crystal data and structure refinement data for $[\{(o\text{-}FC_6H_4)PH_2\}_3Mn(CO)_3]PF_6$.

Empirical formula	$C_{21}H_{18}F_9MnO_3P_4$
Formula weight	668.17
Temperature	150(2) K
λ	1.54184 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 10.4907(3) Å, b = 10.9299(5) Å
	c = 12.2565(5) Å, α= 71.670(4)°
	β= 89.807(3)°, γ = 85.696(3)°.
Volume	1329.99(9) $Å^3$
Z	2
Density (calculated)	1.668 Mg/m^3
Absorption coefficient	7.130 mm^{-1}
F(000)	668
Crystal size	0.260 x 0.230 x 0.160 mm^3
Theta range for data collection	4.227 to 73.411°.
Index ranges	-12<=h<=10, -12<=k<=13, -15<=l<=15
Reflections collected	9171
Independent reflections, R_{int}	5166, 0.0166

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Completeness to theta = 67.684°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.75518
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5166 / 0 / 343
Goodness-of-fit on F2	1.074
Final R indices [I>2sigma(I)]	R_1 = 0.0403, wR_2 = 0.1138
R indices (all data)	R_1 = 0.0418, wR_2 = 0.1153

3. RESULTS AND DISCUSSION

The cationic complex of manganese (I), *fac*-tricarbonyl-tris(*o*-florophenylphosphine)-mangenese(I), was prepared by a single full displacement reaction of the kinetically liable acetonitrile ligands from the *fac*-$[Mn(CO)_3(CH_3CN)_3]$ PF_6 by three groups of $(o\text{-}FC_6H_4)PH_2$. To make sure that all the three acetonitrile ligands were displaced, a 4:1 mole ratio of the phosphine ligand : manganese precursor was used. The insolubility of the new manganese(I) complex in diethyl ether helped to remove any unreacted phosphine, then the yellow solid was extract with hot methanol. The resulting hot yellow filtrate was allowed to cool down slowly to room temperature producing air stable yellow crystals, suitable for single-crystal X-ray structure analysis, in good yield. Elemental microanalysis and the sharpness of the measured melting point confirmed the high purity of the crystalline materials. The observation of the $[\{(o\text{-}FC_6H_4)PH_2\}_3Mn(CO)_3]^+$ ion in the mass spectrum as well as the clear melt obtained when the complex was heated in open air indicate the thermodynamic stability of the complex in both the solid and liquid states.

In the IR spectrum of the complex, the weak absorption at about 2368 cm^{-1} is assigned to the stretching of the $-PH_2$ group, whereas absorptions at 2052; 1996 ;1978; 1941 cm^{-1} are attributed to the various modes of carbon monoxide stretching[4].

Atomic coordinates and displacement parameters for $[\{(o\text{-}FC_6H_4)PH_2\}_3Mn(CO)_3]$ PF_6 obtained from structure refinement are shown in Table 2.

Table 2. Atomic coordinates and displacement parameters for $[\{(o\text{-}FC_6H_4)PH_2\}_3Mn(CO)_3]PF_6$. Displacement parameters are in the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$.

	x	y	z	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	0.2587(2)	0.9883(2)	0.3198(2)	0.034(1)	0.022(1)	0.026(1)	-0.007(1)	-0.005(1)	0.002(1)
C(2)	0.1886(3)	0.9801(3)	0.4167(2)	0.038(1)	0.037(1)	0.039(1)	-0.015(1)	0.004(1)	-0.005(1)
C(3)	0.2203(3)	1.0351(3)	0.4985(2)	0.062(2)	0.042(2)	0.032(1)	-0.016(1)	0.008(1)	-0.004(1)
C(4)	0.3293(3)	1.1012(3)	0.4830(2)	0.072(2)	0.029(1)	0.036(1)	-0.014(1)	-0.007(1)	-0.008(1)
C(5)	0.4024(3)	1.1120(3)	0.3879(3)	0.052(2)	0.037(1)	0.049(2)	-0.016(1)	-0.001(1)	-0.017(1)
C(6)	0.3683(3)	1.0566(2)	0.3061(2)	0.044(1)	0.030(1)	0.035(1)	-0.010(1)	0.004(1)	-0.007(1)
C(7)	0.1263(2)	0.5150(2)	0.1190(2)	0.023(1)	0.029(1)	0.027(1)	-0.008(1)	-0.007(1)	-0.002(1)
C(8)	0.0852(2)	0.4059(2)	0.1992(2)	0.024(1)	0.033(1)	0.029(1)	-0.008(1)	-0.005(1)	0.000(1)
C(9)	0.0855(3)	0.2879(3)	0.1814(2)	0.047(2)	0.026(1)	0.043(1)	-0.004(1)	-0.014(1)	0.001(1)
C(10)	0.1330(3)	0.2773(3)	0.0789(3)	0.053(2)	0.039(2)	0.055(2)	-0.026(1)	-0.025(1)	0.019(1)
C(11)	0.1781(3)	0.3826(3)	-0.0018(3)	0.035(1)	0.071(2)	0.040(2)	-0.033(2)	-0.008(1)	0.010(1)
C(12)	0.1739(2)	0.5011(3)	0.0169(2)	0.031(1)	0.054(2)	0.027(1)	-0.012(1)	-0.005(1)	-0.007(1)
C(13)	0.5573(2)	0.5683(3)	0.2220(2)	0.032(1)	0.037(1)	0.035(1)	-0.003(1)	0.001(1)	0.004(1)
C(14)	0.5580(3)	0.4490(3)	0.2056(3)	0.035(1)	0.045(2)	0.049(2)	-0.009(1)	0.004(1)	0.001(1)
C(15)	0.6544(3)	0.3520(3)	0.2492(3)	0.050(2)	0.037(2)	0.063(2)	-0.004(1)	0.020(2)	0.003(1)
C(16)	0.7519(3)	0.3759(3)	0.3119(3)	0.034(1)	0.055(2)	0.052(2)	0.014(1)	0.008(1)	0.010(1)
C(17)	0.7548(3)	0.4936(3)	0.3314(3)	0.030(1)	0.062(2)	0.041(2)	0.006(1)	-0.001(1)	0.002(1)
C(18)	0.6580(3)	0.5904(3)	0.2871(2)	0.031(1)	0.049(2)	0.037(1)	-0.001(1)	0.000(1)	-0.003(1)

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C(19)	0.1174(3)	0.6694(2)	0.3831(2)	0.037(1)	0.030(1)	0.034(1)	-0.002(1)	-0.013(1)	0.000(1)
C(20)	0.2917(2)	0.5067(3)	0.3493(2)	0.031(1)	0.032(1)	0.041(1)	-0.008(1)	-0.013(1)	-0.001(1)
C(21)	0.3682(2)	0.7008(2)	0.3979(2)	0.032(1)	0.029(1)	0.031(1)	-0.006(1)	-0.007(1)	0.000(1)
O(1)	0.0302(2)	0.6546(2)	0.4390(2)	0.041(1)	0.053(1)	0.045(1)	-0.002(1)	0.002(1)	-0.004(1)
O(2)	0.3136(2)	0.3990(2)	0.3907(2)	0.051(1)	0.027(1)	0.067(1)	0.000(1)	-0.019(1)	0.004(1)
O(3)	0.4383(2)	0.7119(2)	0.4639(2)	0.043(1)	0.052(1)	0.037(1)	-0.013(1)	-0.017(1)	-0.005(1)
F(1)	0.0837(2)	0.9131(2)	0.4322(2)	0.052(1)	0.091(2)	0.078(1)	-0.051(1)	0.026(1)	-0.032(1)
F(2)	0.0419(2)	0.4182(2)	0.2996(1)	0.042(1)	0.051(1)	0.033(1)	-0.012(1)	0.008(1)	-0.008(1)
F(3)	0.4610(2)	0.4273(2)	0.1445(2)	0.056(1)	0.055(1)	0.079(1)	-0.031(1)	-0.009(1)	0.000(1)
F(4)	0.1776(4)	0.9263(3)	-0.2107(2)	0.203(4)	0.076(2)	0.067(2)	-0.035(1)	-0.027(2)	-0.036(2)
F(5)	0.1464(2)	1.1348(2)	-0.2414(2)	0.075(1)	0.068(1)	0.066(1)	0.014(1)	-0.014(1)	0.020(1)
F(6)	0.2786(3)	1.1182(3)	-0.0909(2)	0.124(2)	0.084(2)	0.065(1)	-0.036(1)	0.010(1)	-0.048(2)
F(7)	0.3108(3)	0.9067(3)	-0.0616(2)	0.102(2)	0.078(2)	0.058(1)	-0.001(1)	-0.022(1)	0.042(1)
F(8)	0.1166(2)	0.9948(3)	-0.0639(2)	0.059(1)	0.111(2)	0.055(1)	-0.010(1)	0.018(1)	-0.016(1)
F(9)	0.3433(2)	1.0532(3)	-0.2377(2)	0.061(1)	0.160(3)	0.049(1)	-0.021(2)	0.021(1)	0.013(2)
P(1)	0.2190(1)	0.9027(1)	0.2218(1)	0.037(1)	0.024(1)	0.026(1)	-0.007(1)	-0.010(1)	0.003(1)
P(2)	0.1221(1)	0.6660(1)	0.1501(1)	0.041(1)	0.025(1)	0.038(1)	-0.008(1)	-0.020(1)	0.000(1)
P(3)	0.4261(1)	0.6903(1)	0.1685(1)	0.035(1)	0.032(1)	0.033(1)	-0.005(1)	-0.006(1)	0.005(1)
P(4)	0.2296(1)	1.0219(1)	-0.1522(1)	0.040(1)	0.034(1)	0.024(1)	-0.006(1)	0.000(1)	0.004(1)
Mn(1)	0.2576(1)	0.6817(1)	0.2905(1)	0.027(1)	0.022(1)	0.027(1)	-0.006(1)	-0.011(1)	0.001(1)

In the crystal structure of *fac*-tricarbonyl-tris(*o*-florophenylphosphine)-mangenese(I) hexafluorophosphate (Fig 1), the manganese coordination is distorted octahedral with mean Mn-P distances in the range 2.298(1) Å -2.299(1)Å and Mn-C distances in the range 1.827(3) Å - 1.842(1) Å and angles in the range 87.17(8)°– 94.41(11)°. Selected bond lengths and angles are in Table 3.

The cation is structurally related to *fac*-tricarbonyl-tris(phenylphosphine)-molybdenum(0) (but with a different metal, oxidation state and contains fluoro substituents)[9]. Similar cation coordination is observed in fac-tris(1-methylethenylphosphine)-tricarbonyl-chromium(0) and fac-tris(1-methylethenylphosphine)-tricarbonyl-molybdenum(0) [10].

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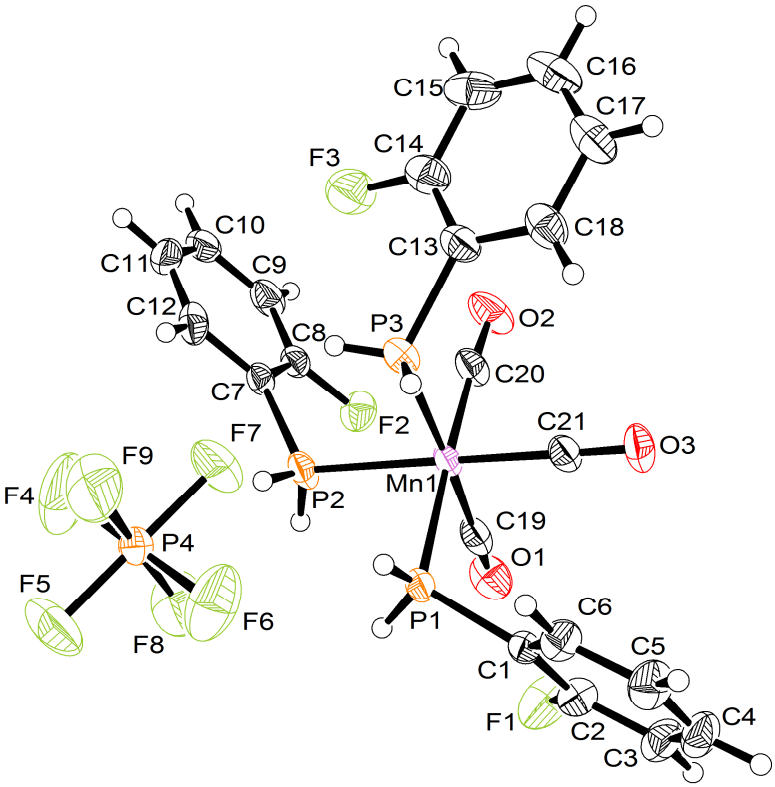

Fig. 1. The asymmetric unit showing 50% thermal ellipsoids for non-hydrogen atoms in [{(*o*-FC$_6$H$_4$)PH$_2$}$_3$Mn(CO)$_3$]PF$_6$.

Table 3. Selected bond lengths [Å] and angles [°] f or [{(*o*-FC$_6$H$_4$)PH$_2$}$_3$Mn(CO)$_3$]PF$_6$.

C(1)-P(1)	1.806(2)	C(2)-F(1)	1.347(3)
C(7)-P(2)	1.804(2)	C(13)-P(3)	1.813(3)
C(14)-F(3)	1.344(4)	C(19)-O(1)	1.132(4)
C(19)-Mn(1)	1.842(3)	C(20)-O(2)	1.131(3)
C(20)-Mn(1)	1.827(3)	C(21)-O(3)	1.136(3)
C(21)-Mn(1)	1.828(2)	P(1)-Mn(1)	2.2985(7)
P(2)-Mn(1)	2.2912(7)	P(3)-Mn(1)	2.2991(8)
C(2)-C(1)-P(1)	121.42(19)	C(6)-C(1)-P(1)	121.48(19)
C(14)-C(13)-P(3)	121.2(2)	C(18)-C(13)-P(3)	120.6(2)
C(20)-Mn(1)-C(21)	88.89(11)	C(20)-Mn(1)-C(19)	89.27(12)
C(21)-Mn(1)-C(19)	94.41(11)	C(20)-Mn(1)-P(2)	93.17(8)
C(21)-Mn(1)-P(2)	177.42(8)	C(19)-Mn(1)-P(2)	87.17(8)
C(20)-Mn(1)-P(1)	177.93(8)	C(21)-Mn(1)-P(1)	89.05(8)
C(19)-Mn(1)-P(3)	176.42(8)	P(2)-Mn(1)-P(3)	89.59(3)

In the crystal, o-fluorophenylphosphine groups of neighbouring cations are involved in both edge-to-face and π-π interactions. Two edge-to-face interactions with a centroid-to-centroid distance of 4.87(1)Å link pairs of molecules as shown in Fig. 2. A similar arrangement is observed in the crystal structure of *fac*-tricarbonyl-tris(phenylphosphine)-molybdenum(0).[9] For each cation in the Mn complex (**I**), one of the o-fluorophenyl phosphine groups already involved in edge-to-face contact also participates in π-π contact

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(centroid-to-centroid contact of 3.77(1) Å) with an inversion related ring from a neighbouring molecule leading to the formation of ribbons parallel to the *a*-axis.

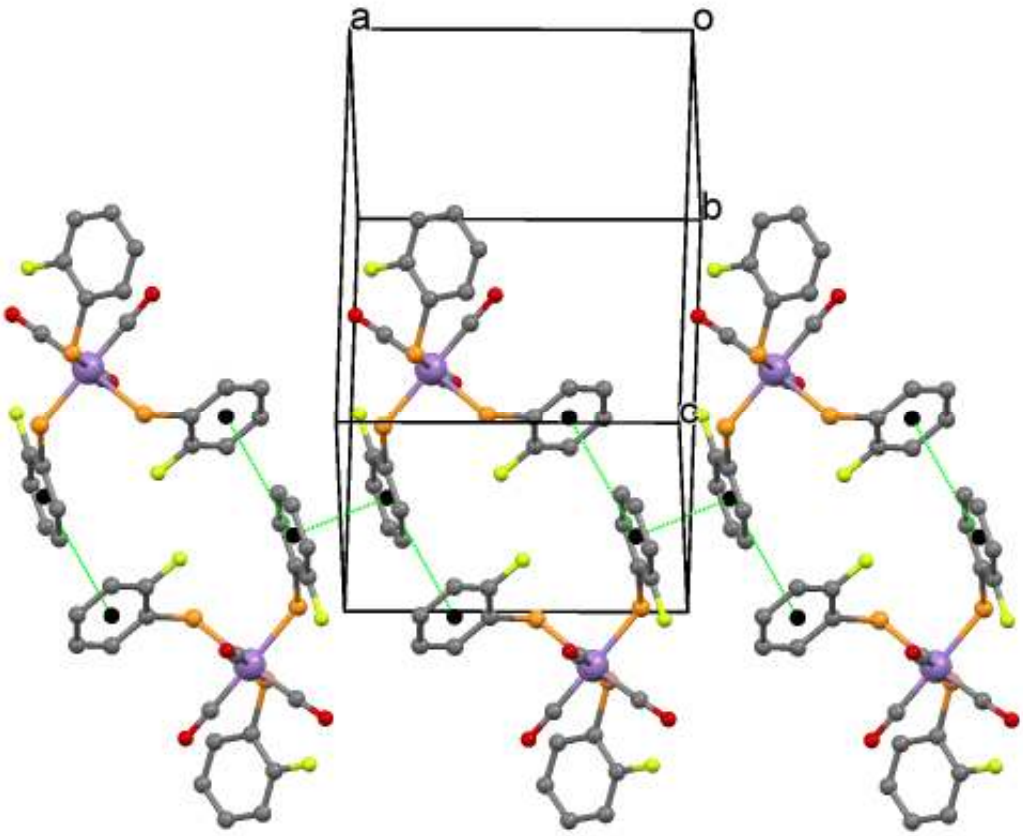

Fig. 2. The crystal structure of $[\{(o\text{-}FC_6H_4)PH_2\}_3Mn(CO)_3]PF_6$ showing edge-to-face and π-π contacts as dotted lines. The PF_6^- counterions and hydrogen atoms have been omitted for clarity.

4. CONCLUSION

The kinetic trans effect of carbon monoxide ligands has facilitated the full displacement of all three acetonitrile groups in one reaction. As a result, the entering ligands (namely, *o*-fluorophenylphosphine) have taken a facial arrangement which is an essential requirement for any successful template cyclisation attempt of the coordinated *o*-florophenylphosphine ligands.

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