A new synthetic route to [MF(μ-F)(CO)$_3$]$_4$ (M = Ru, Os) and their reactivity with P(C$_6$H$_4$-4-X)$_3$ (X = OCH$_3$, OH) and P(C$_6$H$_4$-2-OH)$_3$ Crystal structure of [Os(CO)$_3${κ^3-(2-OC$_6$H$_4$)$_2$P(C$_6$H$_4$-2-OH)}]·C$_3$H$_6$O

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Dedicated to Prof. K.O. Christe on the occasion of his 65th birthday

Abstract

The reaction of [M$_3$(CO)$_{12}$] (M = Ru, Os) with elemental fluorine in anhydrous HF offers a clean, convenient route to [MF(μ-F)(CO)$_3$]$_4$. This tetramer reacts with Tris–*ortho*-hydroxyphenyl phosphine, with the elimination of HF, to give a new, metal-bound, trihapto (η^3-P,O,O) ligand. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Recently, there has been renewed interest in fluoride as a ligand in low oxidation state transition metal coordination chemistry [1–4] with groups using a variety of reagents to introduce the fluoride ligand. We have shown [5] that the fluoride-bridged tetrameric complexes, [MF(μ-F)(CO)$_3$]$_4$ (M = Ru, Os), can be used in the synthesis of a range of air- and moisture-stable ruthenium and osmium carbonyl fluoride complexes. However, our synthetic route to these starting materials [6,7] involves the oxidation of the [M$_3$(CO)$_{12}$] (M = Ru, Os) with XeF$_2$ in anhydrous HF which can be both expensive and difficult to control since large quantities of xenon are evolved.

Here, we describe a simpler and easier route to our fluoride-bridged starting materials and their further reactions with hydroxy- and methoxy-derivatised triaryl phosphine ligands that for the former, following elimination of HF, lead to a highly unusual caged ligand.

2. Experimental

Proton, ^{19}F and ^{31}P NMR spectroscopies were carried out on a Bruker ARX250 spectrometer at 250.13, 235.34 and 101.26 MHz or a Bruker DRX 400 spectrometer at 400.13, 376.50 and 161.98 MHz. All chemical shifts are quoted in ppm using the high-frequency positive convention; ^{1}H NMR spectra were referenced to external SiMe$_4$, ^{19}F NMR spectra to external CFCl$_3$ and ^{31}P NMR spectra to external 85% H$_3$PO$_4$. The infrared spectra were recorded on a Digilab FTS40 Fourier-transform spectrometer at 4 cm^{-1} resolution for the complexes as Nujol mulls held between KBr discs. Elemental analyses were performed by Butterworths Laboratories Ltd. Fast atom bombardment (FAB) mass spectra were recorded on a Kratos concept mass spectrometer.

The reactions involving aHF were carried out on a metal vacuum line with facilities to connect Kel-F and FEP reaction vessels. The complexes [M$_3$(CO)$_{12}$] (M = Ru, Os) (Aldrich) were used as supplied and the ligands {P(C$_6$H$_4$-4-X)$_3$ [X = OCH$_3$, OH] and P(C$_6$H$_4$-2-OH)$_3$} were prepared by the literature route [8]. Hydrogen fluoride (Fluorochem Ltd.) was purified by vacuum transfer, dried by repetitive fluorination at room temperature and stored in a Kel-F tube over dry BiF$_5$ [9]. Dichloromethane was dried by heating to reflux over CaH$_2$ and was stored over molecular sieves in a closed ampoule.

2.1. [OsF(μ-F)(CO)$_3$]$_4$ (**1**)

Triosmium-dodecacarbonyl (1 g, 1 mmol) was loaded, in a dry box (<10 ppm water), into a pre-fluorinated FEP

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reactor (10 mm o.d., 1.5 mm wall thickness) fitted with a poly(tetrafluoroethylene) valve (Production Techniques Ltd.) and an industrially-threaded ferrule. After evacuation on the vacuum line, HF (ca. 2 cm^3) was condensed into the reaction tube at $-196\,^{\circ}$C before the reaction mixture was allowed to warm to room temperature and the mixture left for 24 h with occasional agitation to ensure all the metal starting material had dissolved. The solution was cooled to $-78\,^{\circ}$C, fluorine gas (2 atm) was introduced and the mixture allowed to warm to room temperature and to stand at this temperature for a further 12 h, with occasional agitation during which time the deeply orange coloured solution became less intensely coloured. Following re-cooling to $-78\,^{\circ}$C, the uptake of fluorine gas was measured and further cycles of fluorine addition, warming, agitation and re-cooling were carried out until the uptake of fluorine gas stopped. The solvent was then removed in vacuo to give a buff solid (0.3 g, 96%) which was stored in stoppered pre-fluorinated FEP containers in the dry box. The pale yellow [RuF(μ-F)(CO)$_3$]$_4$ (**2**) was prepared similarly in 92% yield.

The metal complexes [MF$_2$(CO)$_2$L$_2$] {M = Ru, Os; L = P(C$_6$H$_4$-4-X)$_3$ (X = OCH$_3$, OH)} were prepared by the same general synthetic method. A weighed amount of [MF(μ-F)(CO)$_3$]$_4$ (M = Ru, Os) (ca. 0.10 g) was loaded into a Schlenk flask in a dry box along with a slight excess of ligand (8 M equivalents). After connecting the reaction vessel to a vacuum line, freshly distilled dichloromethane was transferred on to the reagents. Reaction ensued immediately with vigorous gas evolution. The reaction mixture was then degassed and stirred under dinitrogen for 3 h to ensure complete reaction. A yellow solution was produced, the solvent removed in vacuo and the pale yellow/white solid recrystallised from dichloromethane and light petroleum (bp 40–60 $^{\circ}$C) to give the products in ca. 90% yields. The [M(CO)$_3${κ^3-(2-OC$_6$H$_4$)$_2$P(C$_6$H$_4$-2-OH)}] (M = Ru, Os) were prepared similarly and recrystallised from acetone (Os) or acetone:hexane (Ru).

2.2. [OsF$_2$(CO)$_2${P(C$_6$H$_4$-4-OCH$_3$)$_3$}$_2$]·2CH$_2$Cl$_2$ (3)

δ ^{1}H NMR (CDCl$_3$) 7.63 (12H, m, o-Ar–H), 7.28 (CHCl$_3$), 6.93 (12H, d, $^3J_{\text{H-H}} = 9$ Hz, m-Ar–H), 5.29 (4H, s, CH$_2$Cl$_2$), 3.80 (18H, s, CH$_3$O–). δ ^{31}P{^{1}H} NMR (CDCl$_3$) -3.1 (t, $^2J_{\text{P-F}} = 30$ Hz). δ ^{19}F{^{1}H} NMR (CDCl$_3$) -153.8 (s), -305.8 (t, $^2J_{\text{P-F}} = 22$ Hz). FAB mass spectrum, m/z 990 ([M]$^+$), 971 ([M–F]$^+$) and 943 ([M– CO– F]$^+$). Found: C 48.41% and H 3.97%. C$_{46}$H$_{44}$Cl$_4$F$_2$O$_8$OsP$_2$ requires C 47.68% and H 4.00%. Infrared (Nujol mull), 2014 s, 1930 s, 1593 s, 1565 s, 1501 s, 1406 w, 1300 s, 1286 s, 1255 s, 1184 s, 1024 s, 829 w, 801 w, 653 w, 535 s, 500 s, 472 w, 453 w, 435 w, 423 w (cm^{-1}).

2.3. [RuF$_2$(CO)$_2${P(C$_6$H$_4$-4-OCH$_3$)$_3$}$_2$]·2CH$_2$Cl$_2$ (4)

δ ^{1}H NMR (CD$_2$Cl$_2$) 7.69 (12H, m, o-Ar–H), 6.98 (12H, d, m-Ar–H), 5.36 (4H, s, CH$_2$Cl$_2$), 3.86 (18H, s, CH$_3$O–).

δ ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) 15.8 (t, $^2J_{\text{P-F}} = 22$ Hz). δ ^{19}F{^{1}H} NMR (CD$_2$Cl$_2$) -339.7 (t, $^2J_{\text{P-F}} = 22$ Hz). FAB mass spectrum, m/z 872 ([M–CO]$^+$), 853 ([M–CO–F]$^+$), 834 ([M–CO–2F]$^+$) and 806 ([M–2CO–2F]$^+$). Found: C 51.24% and H 3.98% C$_{46}$H$_{44}$Cl$_4$F$_2$O$_8$P$_2$Ru requires C 51.64% and H 4.12%. Infrared (Nujol mull), 2035 s, 1962 s, 1592 s, 1568 s, 1501 s, 1406 w, 1290 s, 1255 s, 1183 s, 1026 s, 882 w, 828 s, 799 s, 657 s, 634 w, 626 w, 601 s, 536 s, 506 w, 477 w, 452 w, 430 s (cm^{-1}).

2.4. [OsF$_2$(CO)$_2${P(C$_6$H$_4$-4-OH)$_3$}$_2$] (5)

δ ^{1}H NMR (d^6-DMSO) 10.40–9.70 (6H, bs, OH–), 7.42–6.83 (24H, m, Ar–H), 5.83 (s, CH$_2$Cl$_2$), 3.46–2.58 (s, HO–). δ ^{31}P{^{1}H} NMR (d^6-DMSO) -3.5 (t, $^2J_{\text{P-F}} = 30$ Hz). δ ^{19}F{^{1}H} NMR (d^6-DMSO) -301.2 (t, $^2J_{\text{P-F}} = 30$ Hz). FAB mass spectrum, m/z 887 ([M–F]$^+$). Infrared (Nujol mull), 2026 s, 1959 s, 1602 s, 1581 s, 1503 s, 1286 s, 1260 s, 1176 s, 1120 s, 1031 w, 947 w, 893 w, 832 s, 676 w, 642 w, 633 w, 525 s, 491 s, 459 s, 432 s, 402 s (cm^{-1}).

2.5. [RuF$_2$(CO)$_2${P(C$_6$H$_4$-4-OH)$_3$}$_2$] (6)

δ ^{1}H NMR (d^6-DMSO) 10.31 (bs, OH–), 9.92 (bs, OH–), 7.23 (dd, $J_{\text{H-H}} = 8$ Hz, o-Ar–H), 7.00 (m, m-Ar–H), 3.39 (s, HO–). δ ^{31}P{^{1}H} NMR (d^6-DMSO) 14.0 (t, $^2J_{\text{P-F}} = 21$ Hz). δ ^{19}F{^{1}H} NMR (d^6-DMSO) -321.1 (t, $^2J_{\text{P-F}} = 21$ Hz). FAB mass spectrum, m/z 769 ([M–CO–F]$^+$). Infrared (Nujol mull), 2055 s, 1982 s, 1600 s, 1578 s, 1504 s, 1294 s, 1253 s, 1176 s, 1120 s, 1010 s, 892 w, 833 s, 677 w, 526 s, 494 s, 456 s, 431 s (cm^{-1}).

2.6. [OC-6-33][Os(CO)$_3${κ^3-(2-OC$_6$H$_4$)$_2$-P(C$_6$H$_4$-2-OH)}]·C$_3$H$_6$O (7)

δ ^{1}H NMR (d^6-DMSO) 11.14 (bs, OH–), 7.58–6.50 (12H, m, Ar–H), 2.01 (6H, s, C$_3$H$_6$O). δ ^{31}P{^{1}H} NMR (d^6-DMSO) 34.5 (s). δ ^{19}F{^{1}H} NMR (d^6-DMSO) -165.2 (s). FAB mass spectrum, m/z 584 ([M]$^+$), 556 ([M–CO)]$^+$, 528 ([M–2CO)]$^+$. Found: C 43.09% and H 2.80% C$_{23}$H$_{19}$O$_7$OsP requires C 43.11% and H 2.97%. Infrared (Nujol mull), 2113 s, 2043 s, 2002 s, 1584 s, 1301 s, 1262 w, 1224 w, 1159 w, 1130 w, 1075 w, 1015 w, 908 w, 850 s, 837 s, 800 w, 751 s, 697 w, 596 s, 575 w, 560 w, 544 w, 526 w, 516 w, 491 w, 481 w, 461 w, 420 w (cm^{-1}).

2.7. [OC-6-33][Ru(CO)$_3${κ^3-(2-OC$_6$H$_4$)$_2$P(C$_6$H$_4$-2-OH)}] (8)

δ ^{1}H NMR (MeOD) 7.58–6.50 (12H, m, Ar–H), 4.80 (s, HO–). δ ^{31}P{^{1}H} NMR (MeOD) 30.2 (s). δ ^{19}F{^{1}H} NMR (MeOD) -176.1 (s). FAB mass spectrum, m/z 438 ([M–2CO]$^+$) and 410 ([M–3CO]$^+$). Infrared (Nujol mull), 2059 s, 2001 s, 1585 s, 1558 s, 1407 w, 1302 s, 1264 s, 1245 w, 1232 w, 1158 w, 1152 w, 1130 s, 1077 w, 1064 w, 1030 w, 1023 w, 854 s, 797 w, 755 s, 697 w, 685 w, 667 w, 648 w,

630 w, 597 w, 570 s, 536 w, 521 w, 506 w, 500 w, 491 s, 467 s, 435 s, 421 s, 327 w (cm^{-1}).

2.8. Crystal structure of [Os(CO)$_3${κ^3-(2-OC$_6$H$_4$)$_2$-P(C$_6$H$_4$-2-OH)}]·C$_3$H$_6$O

Crystals were grown by slow evaporation from a solution of the complex in acetone.

2.9. Crystal data

C$_{24}$H$_{19}$O$_7$OsP, $M = 640.56$, monoclinic, space group $P2_1/c$, $a = 15.981(3)$, $b = 9.503(2)$, $c = 15.802(4)$ Å, $\beta = 102.13(2)^\circ$, $U = 2346.3(8)$ Å^3 (by least-squares refinement of the setting angles of 44 reflections in the range $\theta = 5.38$–11.92°), $T = 190(2)$ K, graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, $Z = 4$, $D_c = 1.813$ g cm^{-3}, F(000) = 1240, dimensions 0.24 mm × 0.20 mm × 0.09 mm, μ (Mo Kα) = 5.545 mm^{-1}, semi-empirical absorption correction based on ψ scans, maximum and minimum transmission factors of 0.69 and 0.39 respectively Siemens P4 diffractometer, ω scans, data collection range $\theta = 2.5$–27.0°, $-19 \le h \le 20$, $-12 \le k \le 1$, $-20 \le l \le 1$, no crystal decay was detected from periodically measured check reflections; 5757 reflections were measured and 5111 were unique ($R_{int} = 0.055$). The data were corrected for Lorentz and polarisation effects.

2.10. Structure solution and refinement

Structure solution by Patterson methods and structure refinement on F^2 employed SHELXTL/PC Version 5.0 [10]. The hydroxy H atom was located from a difference Fourier map and fixed to ride on O4, all other hydrogen atoms were included in calculated positions (C–H = 0.96 Å) with isotropic displacement parameters of the methyl and hydroxy H atoms set to 1.5 U$_{eq}$ of the bonded atom and 1.2 U$_{eq}$ (C) for all other H atoms. All non-H atoms were refined with anisotropic displacement parameters. Final, $R_1 = 0.0453$, $wR_2 = 0.0875$ (0.1015 and 0.1057, respectively for all data) for 263 variables. The final residual

Fourier map showed peaks of 1.132 and -1.885 e Å^{-3} at <1 Å from the osmium atom.

3. Results and discussion

Previously, the versatile fluoride-bridged ruthenium and osmium complexes (**1**, **2**) had been prepared either by oxidation of the binary metal carbonyls with xenon difluoride [6,7] or, for ruthenium, by carbonylation of ruthenium pentafluoride [11]. Neither of these synthetic routes are particularly attractive, and we have now found that these complexes can be prepared on a large scale using elemental fluorine as an oxidant; the products have been characterised by a comparison of their infrared spectroscopic data with those in the literature and by their reactivity with phosphine ligands (see following sections). During the reactions, there are no side products generated; we have previously shown by NMR spectroscopy that the main products obtained in the fluorination of the binary metal carbonyls are the monomeric [MF$_2$(CO)$_4$] (M = Ru, Os) compounds [6,7]. Consequently, it is straightforward to monitor the reactions by the uptake of fluorine gas and to establish when the reactions have finished since, at room temperature in anhydrous HF solution, the products do not undergo further reactions even under prolonged exposure (weeks) to fluorine gas. This, therefore, represents a very clean, straightforward, synthetic route to these low-valent metal fluoride starting materials.

On reaction of **1** or **2** with a slight excess of the *para*-substituted aryl phosphine ligands, carbon monoxide is evolved and the new air- and moisture-stable ruthenium(II) and osmium(II) carbonyl fluoride phosphine complexes **3–6** are formed in high yield. The complexes are readily characterised in solution by NMR spectroscopy and show mutually-coupled triplets in both their ^{19}F{^{1}H} and ^{31}P{^{1}H} NMR spectra (Table 1). As expected, the *para*-aryl substituents have little influence on the $^2J_{PF}$ values and cause a slight reduction in Δ_P (the coordination shift). Of greater interest are the unusually high frequency ^{19}F NMR chemical shifts for the metal complexes with the tris–*para*-hydroxyphenyl phosphine ligands. It is likely that

Table 1
Spectroscopic data for [OC-6-13][MF$_2$(CO)$_2$\{P(C$_6$H$_4$-4-X)$_3$\}$_2$] (M = Ru, Os; X = H, F, Me, OMe, OH)

X	v(CO)[a] (cm^{-1})		δ(P) (ppm)		δ(F) (ppm)		$^2J_{PF}$ (Hz)	
	Ru	Os	Ru[b]	Os[c]	Ru[b]	Os[c]	Ru[b]	Os[c]
H[d]	2045, 1973	2017, 1937	21.6	1.0	−324.3	−303.3	20	30
OCH$_3$	2035, 1962	2014, 1930	15.8	−3.1	−339.7	−305.8	22	30
CH$_3$[d]	2045, 1975	2021, 1942	15.7	−3.0	−327.5	−302.7	22	32
F[d]	2047, 1974	2035, 1962	14.9	−4.0	−333.1	−308.8	23	32
OH	2055, 1982	2026, 1959	14.0[e]	−3.5[e]	−321.1[e]	−301.2[e]	21[e]	30[e]

[a] Recorded as Nujol mulls; ±2 cm^{-1}.
[b] Spectra recorded in d^6-acetone unless otherwise stated.
[c] Spectra recorded in CD$_2$Cl$_2$ unless otherwise stated.
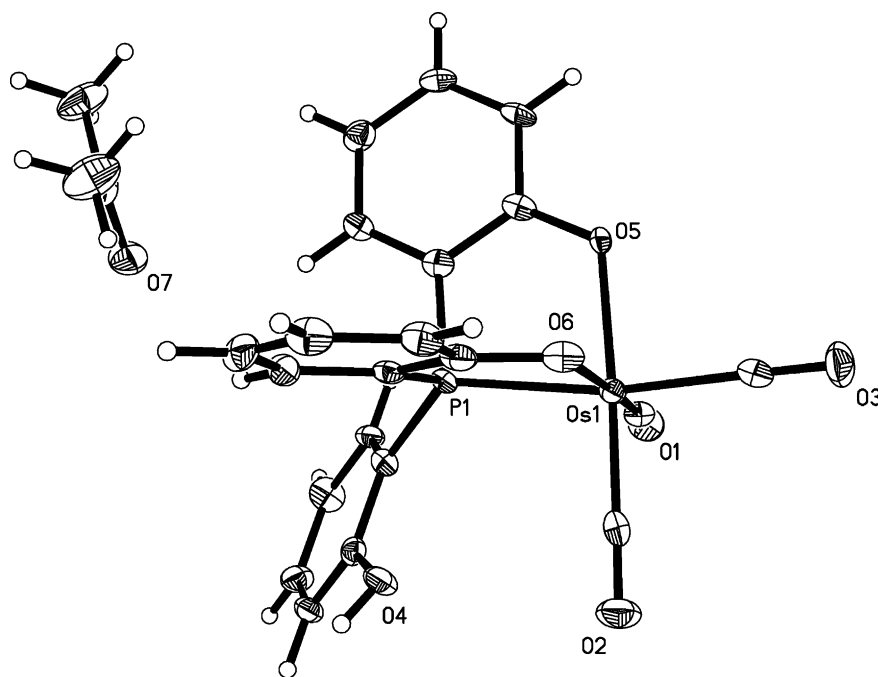[d] Data taken from [5].
[e] Spectra recorded in d^6-DMSO.

Fig. 1. Molecular structure of $[Os(CO)_3\{\kappa^3\text{-}(2\text{-}OC_6H_4)_2P(C_6H_4\text{-}2\text{-}OH)\}]\cdot C_3H_6O$ showing the atom labelling scheme with 30% probability ellipsoids. H atoms are shown as spheres of arbitrary radii.

these arise from intermolecular hydrogen bonding interactions between the fluoride ligands and the hydroxyl protons, although we were unable to prove this unequivocally using 2D NMR experiments. However, circumstantial evidence is available from the unusual, for this class of complex, solution instability of **5** and **6**. For the ruthenium complex **6**, after 24 h the $^{19}F\{^1H\}$ NMR spectrum showed the presence of HF and the intensity of the triplet in the $^{31}P\{^1H\}$ NMR spectrum had decreased to be replaced by a new doublet at δ 19.1 ($^2J_{PF} = 18$ Hz). Unfortunately, we were unable to resolve a related new resonance in the ^{19}F NMR spectrum. This data suggests that, following elimination of HF, the phosphine ligand is bridging between two metal centres. This mirrors the behaviour of metal chloride complexes of this and the related tris–*ortho*-hydroxyphenyl phosphine ligand [12].

Additional support for this elimination of HF arises from the reactions of the fluoride-bridged tetramers with tris–*ortho*-hydroxyphenyl phosphine. Regardless of the ligand:metal ratio, these reactions give a single air- and moisture-stable species which, following slow recrystallisation from acetone (Os) or acetone:hexane (Ru), are characterised by the complete absence of signals in their $^{19}F\{^1H\}$ NMR and singlets in their $^{31}P\{^1H\}$ NMR solution spectra at unusually high frequencies; 30.2 ppm (Ru) and 34.5 ppm (Os). These data are suggestive of a phosphorus atom in a chelating ligand system and support for this assignment comes from a single crystal X-ray structural characterisation of the product from the osmium reaction which reveals a single η^3-P,O,O trihapto ligand coordinated to a *fac*-Os-(CO)$_3$ metal fragment. Although this trihapto coordination

with this ligand has not been reported previously, it has been structurally confirmed for the closely related P(2,6-CH$_3$O)$_2$-C$_6$H$_3$)$_3$ ligand in [(η^6-arene)Ru{P(2-OC$_6$H$_3$-6-OCH$_3$)$_2$(2,6-[CH$_3$O]$_2$C$_6$H$_3$)}] [13] and [Cp*IrCl{P(2-OC$_6$H$_3$-6-OCH$_3$)$_2$-(2,6-[CH$_3$O]$_2$C$_6$H$_3$)}] [14] in which the caged ligands form following elimination of CH$_3$Cl. The molecular structure of $[Os(CO)_3\{\kappa^3\text{-}(2\text{-}OC_6H_4)_2P(C_6H_4\text{-}2\text{-}OH)\}]\cdot C_3H_6O$ is shown in Fig. 1 and selected bond lengths and angles are given in Table 2. The complex is pseudo-octahedral with the three carbonyl ligands in a facial arrangement. One carbonyl is *trans* to the phosphorus ligand and the other two are *trans* to deprotonated aryloxide ligands in chelating five-membered rings. The difference in *trans*-influence between the aryloxy

Table 2
Selected bond distances (Å) and angles (°) for $[Os(CO)_3\{\kappa^3\text{-}(2\text{-}OC_6H_4)_2P(C_6H_4\text{-}2\text{-}OH)\}]\cdot C_3H_6O$

Os(1)–C(1)	1.890(9)	O(1)–C(1)	1.140(10)
Os(1)–C(2)	1.891(10)	O(2)–C(2)	1.143(11)
Os(1)–C(3)	1.984(10)	O(3)–C(3)	1.130(11)
Os(1)–O(5)	2.106(5)	O(5)–C(21)	1.367(6)
Os(1)–O(6)	2.083(6)	O(6)–C(36)	1.360(7)
Os(1)–P(1)	2.345(2)	O(4)–C(16)	1.344(10)
		O(4)···H···O(5′)	2.620(8)
C(1)–Os(1)–C(2)	92.7(4)	C(1)–Os(1)–C(3)	95.6(4)
C(1)–Os(1)–O(6)	173.5(3)	C(1)–Os(1)–O(5)	90.5(3)
C(1)–Os(1)–P(1)	92.5(3)	C(2)–Os(1)–C(3)	91.4(4)
C(2)–Os(1)–O(6)	90.0(3)	C(2)–Os(1)–O(5)	176.2(3)
C(3)–Os(1)–O(6)	90.3(3)	C(3)–Os(1)–O(5)	90.4(3)
O(6)–Os(1)–O(5)	86.7(2)	O(6)–Os(1)–P(1)	81.26(18)
O(5)–Os(1)–P(1)	80.69(15)		
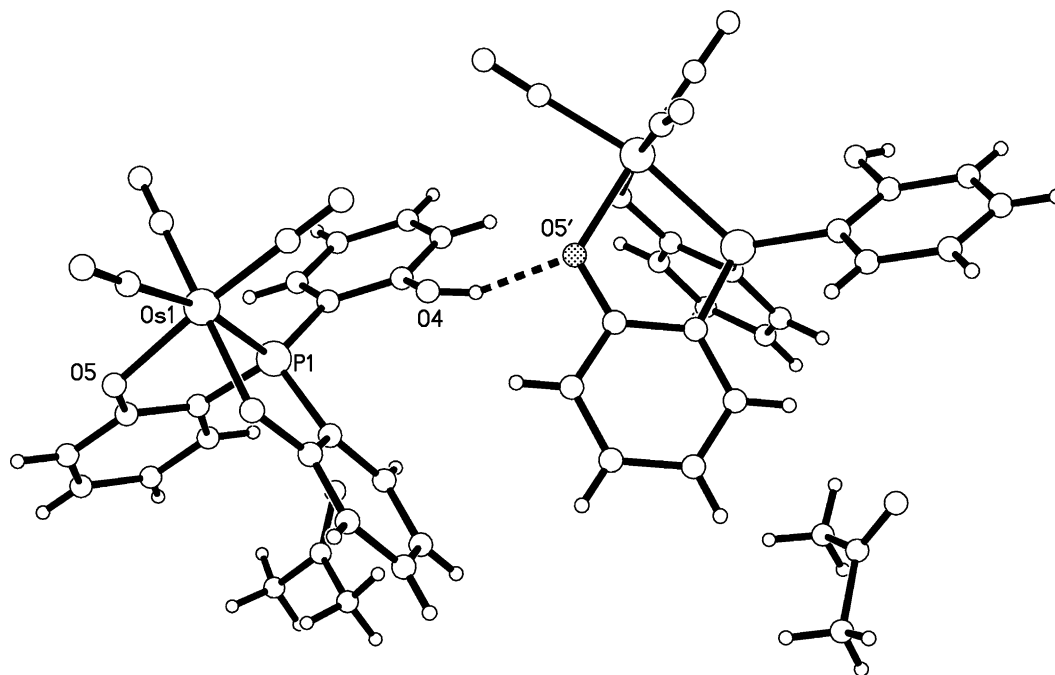
Fig. 2. Extended view of the structure of $[Os(CO)_3\{\kappa^3\text{-}(2\text{-}OC_6H_4)_2P(C_6H_4\text{-}2\text{-}OH)\}]\cdot C_3H_6O$ showing the short hydrogen bonding interaction.

and phosphine ligands is reflected in the Os-C bond lengths where Os-$C_{trans\text{-}P}$ is significantly longer than either Os-$C_{trans\text{-}O}$, although it should be noted that all the osmium-carbon bond lengths are longer than those observed for other osmium(II) carbonyl compounds (1.873–1.880 Å) [15]. Within the trihapto ligand, the P-Os–O and O–Os–O bond angles are similar to those in the related ruthenium–arene [13] and Cp*–iridium [14] complexes. However, in contrast to the observations for these crystal structures where coordination of the aryloxy groups causes a reduction in the C–O bond lengths (ca. 1.32 Å cf. ca. 1.36 Å) [13,14], in this osmium complex the C–O bond lengths in the coordinated aryloxy groups are longer than that for the free phenol. An extended view of the crystal structure (Fig. 2) reveals a relatively short hydrogen bonding interaction between this remaining, unreacted, *ortho*-hydroxy group on the ligand and one of the chelating aryloxide groups on a neighbouring molecule generating both the asymmetry in the osmium-oxygen bond lengths and a hydrogen-bonded chain of molecules in the solid state.

4. Conclusions

The direct reaction of triruthenium- or triosmium-dode-cacarbonyl with elemental fluorine in anhydrous HF solution represents a clean, efficient, route to the fluoride-bridged $[MF(\mu\text{-}F)(CO)_3]_4$ (M = Ru, Os). In contrast to the reaction of these metal fluorocomplexes with many phosphine ligands, their reactions with $P(C_6H_4\text{-}2\text{-}OH)_3$ generate, following elimination of HF, a highly unusual, metal-bound, trihapto ligand.

Acknowledgements

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