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$^{t}Bu_2PF$ as a ligand in tri-osmium clusters ☆

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Abstract

The reaction of (acetonitrile)-undeca(carbonyl)-tri-osmium(0) and bis(*tert*-butyl)fluorophosphine led to the formation of (bis(*tert*-butyl)fluorophosphine) undeca(carbonyl)-tri-osmium(0) (**1**). However, the reaction of bis(acetonitrile)-deca(carbonyl)-tri-osmium(0) and bis(*tert*-butyl)fluorophosphine yielded bis(bis(*tert*-butyl)fluorophosphine)-deca(carbonyl)-*tri*-osmium(0) (**2**) and (*tert*-butyl-difluorophosphine)(bis(*tert*-butyl)fluorophosphine)-deca(carbonyl)-tri-osmium(0) (**3**). Compounds **1** and **2** are the first aliphatic mono-fluorophosphine osmium clusters and were characterized by an X-ray diffraction study. Both compounds show a regular three-membered osmium cycle with equatorially oriented phosphorous atoms. Compound is **3** is the first example of a mixed mono-fluorophosphine–di-fluorophosphine compound and has been characterized by NMR spectra, a mass spectrum and an IR spectrum.

Keywords: Bis(tert.-butyl)fluorophosphine; (Bis(tert.-butyl)fluorophosphine)undeca(carbonyl)-tri-osmium(0); Bis(bis(tert.-butyl)fluorophosphine)-deca(carbonyl)-triosmium(0)

1. Introduction

Some tri-osmium or tri-ruthenium clusters of type $M_3(CO)_{12-n}L_n$ (M = Ru or Os; L = RPF_2; $n = 1$–4, 6) as well as $Os_3(CO)_{12-n}L'_n$ ($L' = R_2PF$; $n = 1, 2$) are known [1]. All these compounds are reasonable stable towards air or moisture. Here we describe the formation of $Os_3(CO)_{11}(PF^{t}Bu_2)$ (**1**) and $Os_3(CO)_{10}(PF^{t}Bu_2)_2$ (**2**). Both are available through the displacement of the labile bonded acetonitrile ligands in $Os_3(CO)_{11}(MeCN)$ (or $Os_3(CO)_{10}(MeCN)_2$) by $^{t}Bu_2PF$:

$$Os_3(CO)_{11}(MeCN) + {}^{t}Bu_2PF \xrightarrow[-MeCN]{66\%} \underset{\mathbf{1}}{Os_3(CO)_{11}(PF^{t}Bu_2)} \qquad (1)$$

$$Os_3(CO)_{10}(MeCN) + {}^{t}Bu_2PF \xrightarrow[-MeCN]{} \underset{\mathbf{2}}{Os_3(CO)_{10}(PF^{t}Bu_2)_2}(26\%) + \underset{\mathbf{3}}{Os_3(CO)_{10}(PF^{t}Bu_2)(PF_2{}^{t}Bu)}(35\%) \qquad (2)$$

In the preparation of **2** the as yet unknown cluster compound **3** was observed and characterized by NMR, IR and mass spectra.

The spectroscopic data for **1** and **2** are exactly in the expected range (Table 1). In particular, coupling constants in the ^{1}H and ^{19}F NMR spectra were found to be smaller than for di-fluorophosphino complexes ($^{3}J(HP) \approx 15$ Hz for mono-fluorophosphine complexes ($^{t}Bu_2PF$) and about 18.5 Hz for di-fluorophosphino clusters ($^{t}BuPF_2$) [1]; $^{1}J(PF) \approx 910$ Hz for mono-fluorophosphine complexes in contrast with $^{1}J(PF) \approx 1150$ Hz for di-fluorophosphine clusters [1]).

In the NMR spectra, **3** shows signals of *mono*-fluorophosphine and di-fluorophosphine as ligands in this cluster. In the proton NMR two groups of signals in a ratio 2 : 1, showing a doublet of doublets and a doublet of triplets, indicate the presence of two different moieties: one $^{t}Bu_2PF$ and one $^{t}BuPF_2$ ligand. The $^{3}J(HP)$ couplings of the two fluorophosphine ligands are different by 3.5 Hz ($^{t}Bu_2PF$; $^{3}J(HP) = 18.4$ Hz (9H) as expected from the proton NMR data of $Os_3(CO)_{11}(PF_2{}^{t}Bu)$ [1], **1** and **2** (see Table 1)). In the ^{19}F NMR spectrum of **3** two sets of signals were also observed: one in the range of di-fluorophosphines ($\delta F = -53.8$ ppm; $J(FP)$ 1154 Hz) and the other in the range of a mono-fluorophosphine ($\delta F = -137.9$; $J(FP) \approx 913$ Hz). Both the coupling constant and the shift value are

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☆ Dedicated to Professor Reinhard Schmutzler on the occasion of his 60th birthday.

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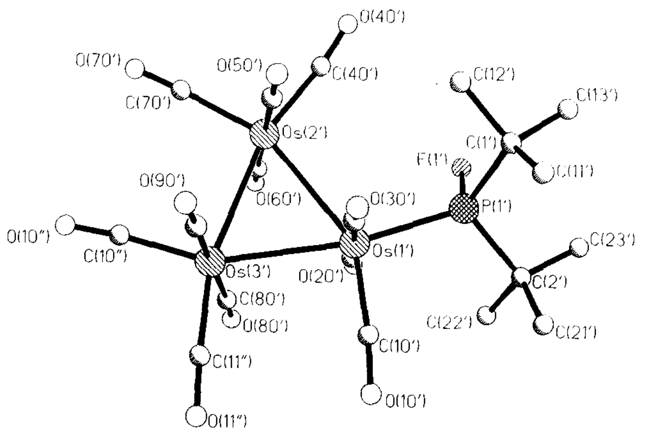

Fig. 1. Molecular structure of compound **1**.

characteristic of each of these fluorophosphine ligands (see Table 1).

For both **2** and **3**, broad signals in the ^{19}F and ^{31}P NMR spectra are observed. This is due to a restricted trigonal twist (a dynamic process) originating from pseudo-*cis* and pseudo-*trans* substitution modes as known for clusters of this type [1,2]. The given data are taken from the major species and represent estimated values only. The ^{19}F and ^{31}P NMR spectra of **2** should be composed from an $[AX_2][BY]$ spectra type ($A \equiv P$; $X, Y \equiv F$).

Compound **1** and **2** were characterized by an X-ray diffraction study. In the literature only very few monofluorophosphine complexes characterized by X-ray studies have been found. Only three structures are known, the most important data of which are compared with the data of **1** and **2** in Table 2.

2. Molecular structure of 1 and 2

The X-ray structure analysis shows that in both compounds the three Os atoms form a three-membered cluster with an Os–Os distance of 288–292 pm and the fluorophosphane ligands coordinated trans to an Os–Os bond (Figs. 1 and 2). The overall molecular structure of **2** is close to C_2 symmetry with the twofold axis through Os(3) and the centre of the Os(1)–Os(2) bond.

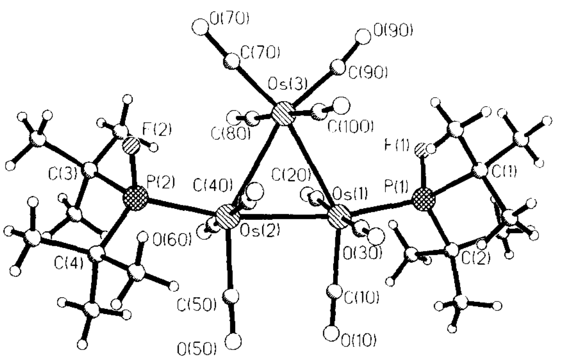

Fig. 2. Molecular structure of compound **2**.

The endocyclic angles at osmium are exactly 60° in **2** and 59.4–60.6° in **1**. In **1** the smallest angle in both crystallographically independent molecules is found at the osmium atom substituted with the phosphorus ligand. Osmium-phosphorus distances are 234–235 pm; the distances between osmium and carbon vary between 192 and 195 pm for **2** and between 185 and 198 pm for **1**. For both compounds the bond angles between the two osmium ligands (carbon or phosphorous) bonds *trans* to the osmium–osmium bonds are significantly larger (C–Os–C, 101–103°; P–Os–C, 100–101°) than those between the ligands *cis* to Os–Os bonds (85–95°). The geometry of the phosphane ligands is very close to that observed in similarly coordinated fluorophosphane groups (P–F, 161–168 pm; P–C, 186–190 pm; F–P–C, 96–101°; C–P–C, 109–111°).

Close non-bonding contacts are found between the carbonyl groups standing perpendicular to the three-membered Os ring and between those carbonyl groups and the methyl groups of the phosphane ligands. No short intermolecular contacts are observed.

Compounds **1**–**3** were also characterized by electron impact (EI) mass spectra. In all mass spectra the parent peak and subsequent loss of CO is observed. All peaks have the typical isotopic distribution and are given with reference to ^{192}Os; intensities given refer to the most intense signal within one peak. The parent peak of **1** is compared with the theoretical pattern in Fig. 3.

In the IR spectra of fluorophosphine cluster compounds, relatively high frequencies for CO were ob-

Table 1
Selected NMR data of **1**–**3**, $Os_3(CO)_{11}(PF_2{}^tBu)$ [1] and $Os_3(CO)_{10}(PF_2{}^tBu)_2$ [1]

Compound	^{1}H NMR δH (ppm)	^{19}F NMR δF (ppm)	^{31}P NMR δP (ppm)
1	1.41 (^3J(HP) = 15.2 Hz)	−141.3 (^1J(HP) = 906.3 Hz)	199.2 (^1J(PF) = 906.2 Hz)
2	1.42 (^3J(HP) = 14.9 Hz)	−141 (J(FP) ≈ 912 Hz)	195.9 (J(PF) ≈ 908 Hz)
3	1.42 (^3J(HP) = 14.9 Hz); 1.28 (^3J(HP) = 18.4 Hz)	−139.7 (J(FP) ≈ 913 Hz); −53.8 (J(FP) ≈ 1154 Hz)	197.2 (J(PF) ≈ 920 Hz); 190.3 (J(PF) ≈ 1157 Hz)
$Os_3(CO)_{11}(PF_2{}^tBu)$	1.27 (^3J(HP) = 18.7 Hz)	–	191.5 (^1J(PF) = 1152 Hz)
$Os_3(CO)_{10}(PF_1{}^tBu)_2$	1.28, 1.26 (^3J(HP) = 18.5,18.6 Hz)	−55.0 (J(PF) = 1142 Hz)	176–189 (^1J(PF) = 1114,1106 Hz)

Table 2
X-ray diffraction data of *mono*-fluorophosphine complexes

Compound	Bond length (pm)			Bond angle
	r(PF)	r(PC)	r(MP)	< CPF (°)
$Os_3(CO)_{11}(PF^tBu_2)$ (**1**)	156, 158	186, 190	235	96, 101
$Os_3(CO)_{10}(PF^tBu_2)_2$ (**2**)	162, 168	186, 190	234	98
trans-$Br_2Ni(PF^tBu_2)_2$ [3]	158	187	223	98
cis-$Cl_2Pt[PF(C_8H_3F_6)_2]_2$ [4]	156	182	222	104
$[Mo(\eta^6-C_6H_6)(dppe)(PFPh_2)H]BF_5$ [5]	164	182, 186	238	97–99

served [1] (Table 3). This is one consequence of the strong d_π–d_π back bond from the osmium atom to the phosphorus atom.

3. Discussion of the formation of 3

Formation of **3**, isolated with 35% yield from the reaction mixture of $^tBu_2PF$ and $Os_3(CO)_{10}(MeCN)$ (see Eq. (2)), was unexpected. Three different explanations might be responsible for the formation of **3**.

First the cleavage of a P–C bond using HF as an reagent which is described in the literature [5,6] was ruled out by treating a solution of about 8 mg of **1** (or **2**) in $CDCl_3$ with one drop of HF–pyridine (70%). After 120 min no reaction was observed in the ^{19}F NMR and almost all the starting material was recovered.

Secondly a scrambling reaction of $^tBu_2PF$ assisted by the metal may be discussed [7–11]. This was ruled out by the observation of a stable compound in solution and no further formation of **3** was observed, not even by treating a solution of **2** for 24 h with an excess of $^tBu_2PF$.

Finally a selective reaction of $Os_3(CO)_{10}(^tBu_2PF)$-(MeCN) and $^tBuPF_2$, the latter found as an impurity of less than 5% (according to the ^{19}F and ^{31}P NMR $\delta P = 227.1$ ppm, $^1J(PF) = 1183.5$ Hz, $\delta F = 109.6$ ppm and $^1J(FP) = 1183, 1$ Hz [10]) in the $^tBu_2PF$ used in excess, may be reason for the observation of **3**. As $^tBuPF_2$ is less bulky, it seems to react much more rapidly with $Os_3(CO)_{10}(^tBu_2PF)(MeCN)$ than a second molecule $^tBu_2PF$, which explains the high yield (35%) of **3** with respect to the yield (26%) of **2**.

Table 3
IR data of **1**–**3**, $Os_3(CO)_{11}L$, $Os_3(CO)_{10}L_2$ (L≡R_2PF (*bis*-(2,4-di(trifluoromethyl)phenyl)-*mono*-fluorophosphine [1])), $Os_3(CO)_{11}(PF_2{}^tBu)$ [1] and $Os_3(CO)_{10}(PF_2{}^tBu)_2$ [1]

Compound	IR (CO region only) ν (cm^{-1})
1	2114 w, 2062 s, 2038 s, 2023 vs, 1992 m, 1975 m, 1965 w
$Os_3(CO)_{11}L$	2115 w, 2064 s, 2043 m, 2029 vs, 2012 m, 2002 m, 1993 m
2	2097 w, 2038 s, 2006 vs, 1995 m
$Os_3(CO)_{10}L_2$	2101 w, 2050 s, 2021 vs, 1996 m
3	2099 w, 2045 s, 2018 vs, 1987 m
$Os_3(CO)_{11}(PF_2{}^tBu)$	2116 w, 2063 s, 2045 s, 2028 vs, 2010 m, 2000 s, 1991 m, 1980 w
$Os_3(CO)_{10}(PF_2{}^tBu)_2$	2103 w, 2063 w, 2049 s, 2033 s, 2021 vs, 1992 s, 1981 m

4. Experimental details

All reactions were carried out in dry solvents under an atmosphere of dry nitrogen. NMR spectra were recorded on a Bruker AC 200 and are given with reference to the following conditions and references: $CDCl_3$, ^1H (tetramethylsilane; 200.1 MHz); ^{13}C ($CDCl_3$, 50.3 MHz); ^{19}F ($CFCl_3$; 188.3 MHz); ^{31}P (H_3PO_4; 81.0 MHz). Low field shifts were allocated positive signs. Mass spectra were recorded on a Finnigan MAT 8430 under EI conditions. All peaks have the typical isotopic distribution and are given with reference to ^{192}Os; intensities refer to the most intense signal within one peak. IR spectra were recorded on a Beckman 4260 in methyl cyclohexane as a solvent. Preparative thin layer chromatography (TLC) has been conducted using plates of Schleicher & Schüll (G 1510, KG 60; 20 × 20 cm). Melting points were recorded on a Büchi 530 using 0.5 mm capillaries. $^tBu_2PF$ was prepared according to literature [10].

4.1. *Preparation of undeca(carbonyl)(bis(tert-butyl)fluorophosphine)tri*-osmium(0), (**1**)

A mixture of 65 mg (0.07 mmol) of $Os_3(CO)_{11}(MeCN)$ and three drops of $^tBu_2PF$ in 5 ml of CH_2Cl_2 was stirred at 25°C for 50 min. Distributed onto six TLC plates the mixture was chromatographed using petrol ether (PE 60/70) as a solvent and the plates were dried and restarted twice. The deep-yellow band at $R_f \approx 50$ was scraped off and afterwards eluted using CH_2Cl_2 (about 30 ml) (yield (**1**); 48.8 mg (66%)).

Mass spectrum (70 eV): m/z (%) $[M]^+$ 1048 (24), $[M-CO]^+$ 1020 (8), $[M-2CO]^+$ 992 (2), $[M-3CO]^+$ 964 (7), $[M-4CO]^+$ 936 (38), $[M-5CO]^+$ 908 (40), $[M-6CO]^+$ 880 (54), $[M-7CO]^+$ 852 (42),

$[M-8CO]^+$ 824 (21), $[^t\text{Bu}]^+$ 57 (100). Some further peaks between mass units 600 and 800 (2–30) were observed. Their assignment was impossible owing to a complicated isotopic pattern.

^{1}H NMR: δH 1.41 (dd, ^3J(HP) = 15.2 Hz, ^4J(HF) = 1.3 Hz) ppm. ^{13}C NMR: δC 28.7 (dd, $J \approx 1$ Hz, 4 Hz; C-CH_3); 44.2 (dd, $J = 11.5$ Hz, 17.5 Hz; C-CH_3) ppm; resonances not observed for CO. ^{19}F NMR: δF-141.3 (d, ^1J(FP) = 906.3 Hz) ppm. ^{31}P NMR: δP 199.2 (d, ^1J(PF) = 906.2 Hz) ppm.

Crystals of **1** suitable for an X-ray diffraction study were grown at room temperature using a 1 : 1 mixture of methylcyclohexane: dichloromethane (melting point (m.p.), 139°C). Crystalline **1** is air stable for at least 5 weeks.

4.1.1. X-ray analysis

Crystals of **1** have triclinic symmetry and space group $P\bar{1}$. The unit cell which has the parameters $a = 869.9(4)$, $b = 1564.6(7)$, $c = 1932.5(8)$ pm, $\alpha = 95.78(4)°$, $\beta = 95.17(4)°$ and $\gamma = 93.98(4)°$ contains four molecules, yielding a calculated density of 2.666 g cm^{-3}. The data were collected at 293 K on a Siemens P3F diffractometer using graphite-monochromated Cu Kα radiation ($\lambda = 154.184$ pm) in the θ–2θ mode in the range $3° \leqslant 2\theta \leqslant 135°$ at a scan speed between 2.93 and 29.3° min^{-1} depending on the intensity of the reflection.

The data were corrected for Lorentz, polarization and absorption effects ($\mu = 21.80$ mm^{-1}). The structure was solved by direct methods and difference Fourier syntheses. The refinement using all 8718 measured independent reflections converged at $R = 0.105$ (R value based on 7771 reflections with $I \geqslant 2.0\sigma(I)$). A final difference map displayed no electron density higher than 5.22×10^{-6} electrons pm^{-3} (near Os atoms). The program SHELXL-93 [12] and our own programs were used. Complex atom scattering factors [13] were employed. Table 4 contains bond distances and angles for **1**.

*4.2. Preparation of deca(carbonyl)-bis(bis(tert-*butyl)-fluorophosphine) tri-osmium(0) (2) and deca(carbonyl)-(bis(tert-butyl)fluorophosphine) (*tert*-butyldifluorophosphine) *tri*-osmium(0) (3)

As described in the preceding experiment, 74 mg (0.08 mmol) of $Os_3(CO)_{10}(MeCN)_2$ and five drops of $^t\text{Bu}_2\text{PF}$ in 5 ml of CH_2Cl_2 were stirred at 25°C for 50 min. Compounds **2** and **3** were separated using TLC techniques (PE 60/70; twice restarted R_f (**3**) ≈ 25, R_f (**2**) ≈ 15) (yield (**2**), 23.7 mg (26%); yield (**3**), 32.9 mg (35%)).

2: Mass spectrum (70 eV): m/z (%) $[M]^+$ 1184 (14), $[M-CO]^+$ 1156 (6) $[M-2CO]^+$ 1128 (10), $[M-3CO]^+$ 1100 (16), $[M-4CO]^+$ 1072 (24), $[M-5CO]^+$ 1044 (20), $[M-6CO]^+$ 1016 (18), $[M-7CO]^+$ 988 (16), $[M-8CO]^+$ 960 (18), $[^t\text{Bu}]^+$ 57 (100). Some further peaks between mass units 300 and 470 (2–6) and between 600 and 850 (2–20) were observed. Their assignment was impossible owing to a complicated isotopic pattern.

2: ^{1}H NMR: δH 1.42 (dd, ^3J(HP) = 14.9 Hz, ^4J(HF) = 1.1 Hz, 18H; $((CH_3)_3C)_2PF$)/ppm. ^{13}C NMR: δC = 44.5 (dd, $J = 11.6$ Hz; 17.1 Hz; $C(CH_3)_3$); 28.8 (d, $J = 4.1$ Hz; $C(CH_3)_3$) ppm; resonances not observed for CO: ^{19}F NMR: δF = −141 ("d", J(FP) ≈ ^1J(PF) ≈ 912 Hz, R_2PF) ppm. ^{31}P NMR: δP = 195.9 ("d", J(PF) ≈ ^1J(PF) ≈ 908 Hz; R_2PF) ppm.

Crystals of **2** suitable for an X-ray diffraction study were grown at room temperature using a 1 : 1 mixture of methylcyclohexane:dichloromethane (m.p., 191°C (decomposition)). Crystalline **2** is air stable for at least 5 weeks.

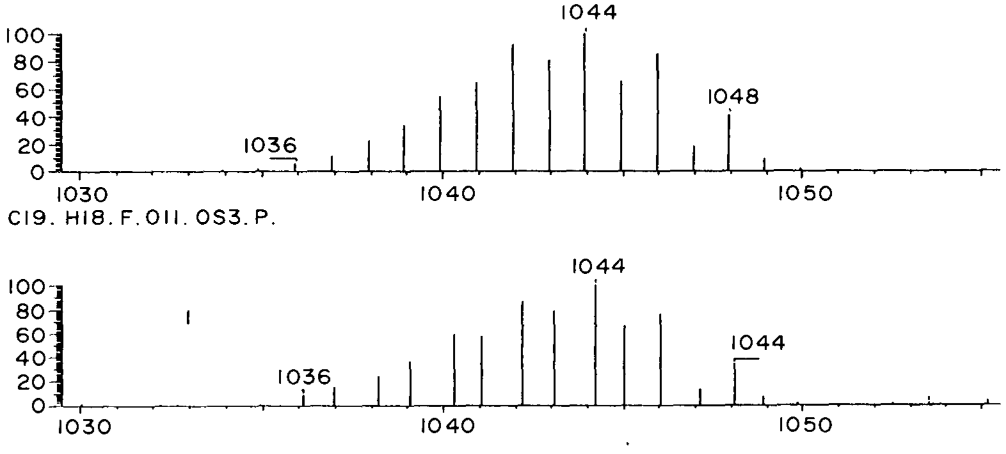

Fig. 3. E1-MS spectra of compound **1**. Parent peak 1 and theoretical pattern.

Table 4
Bond distances (pm) and bond angles (°) for **1**

Bond distances			
Os(1)–C(10)	186(2)	Os(1)–C(20)	195(2)
Os(1)–C(30)	197(2)	Os(1)–P(1)	235.1(6)
Os(1)–Os(2)	289.5(2)	Os(1)–Os(3)	292.2(2)
Os(2)–C(40)	191(2)	Os(2)–C(60)	194(2)
Os(2)–C(50)	195(2)	Os(2)–C(70)	197(2)
Os(2)–Os(3)	288.4(2)	Os(3)–C(90)	191(2)
Os(3)–C(80)	192(2)	Os(3)–C(110)	198(2)
Os(3)–C(100)	198(2)	P(1)–F(1)	161(2)
P(1)–C(2)	189(2)	P(1)–C(1)	189(2)
Os(1′)–C(10′)	185(2)	Os(1′)–C(30′)	194(2)
Os(1′)–C(20′)	197(2)	Os(1′)–P(1′)	234.4(5)
Os(1′)–Os(3′)	289.6(2)	Os(1′)–Os(2′)	292.4(2)
Os(2′)–C(40′)	193(2)	Os(2′)–C(70′)	194(2)
Os(2′)–C(60′)	195(2)	Os(2′)–C(50′)	198(2)
Os(2′)–Os(3′)	288.2(2)	Os(3′)–C(11″)	192(2)
Os(3′)–C(10″)	194(2)	Os(3′)–C(90′)	198(2)
Os(3′)–C(80′)	200(2)	P(1′)–F(1′)	163.4(13)
P(1′)–C(1′)	188(2)	P(1′)–C(2′)	189(2)
Bond angles			
C(10)–Os(1)–C(20)	89.5(9)	C(10)–Os(1)–C(30)	91.9(10)
C(20)–Os(1)–C(30)	177.5(9)	C(10)–Os(1)–P(1)	100.9(7)
C(20)–Os(1)–P(1)	95.2(7)	C(30)–Os(1)–P(1)	86.6(9)
C(10)–Os(1)–Os(2)	91.5(7)	C(20)–Os(1)–Os(2)	87.9(7)
C(30)–Os(1)–Os(2)	89.9(9)	P(1)–Os(1)–Os(2)	167.3(2)
C(10)–Os(1)–Os(3)	150.4(7)	C(20)–Os(1)–Os(3)	94.2(6)
C(30)–Os(1)–Os(3)	83.6(7)	P(1)–Os(1)–Os(3)	108.0(2)
Os(2)–Os(1)–Os(3)	59.44(4)	C(40)–Os(2)–C(60)	101.4(10)
C(40)–Os(2)–C(50)	89.2(11)	C(60)–Os(2)–C(50)	87.9(13)
C(40)–Os(2)–C(70)	92.1(11)	C(60)–Os(2)–C(70)	91.9(13)
C(50)–Os(2)–C(70)	178.6(9)	C(40)–Os(2)–Os(3)	99.7(6)
C(60)–Os(2)–Os(3)	158.9(8)	C(50)–Os(2)–Os(3)	92.2(8)
C(70)–Os(2)–Os(3)	87.4(8)	C(40)–Os(2)–Os(1)	160.3(6)
C(60)–Os(2)–Os(1)	98.2(8)	C(50)–Os(2)–Os(1)	89.4(6)
C(70)–Os(2)–Os(1)	89.3(6)	Os(3)–Os(2)–Os(1)	60.75(4)
C(90)–Os(3)–C(80)	101.8(12)	C(90)–Os(3)–C(110)	92.5(10)
C(80)–Os(3)–C(110)	86.6(12)	C(90)–Os(3)–C(100)	91.7(10)
C(80)–Os(3)–C(100)	91.8(12)	C(110)–Os(3)–C(100)	175.8(10)
C(90)–Os(3)–Os(2)	91.1(9)	C(80)–Os(3)–Os(2)	166.9(9)
C(110)–Os(3)–Os(2)	90.6(8)	C(100)–Os(3)–Os(2)	90.1(7)
C(90)–Os(3)–Os(1)	150.5(8)	C(80)–Os(3)–Os(1)	107.5(9)
C(110)–Os(3)–Os(1)	92.4(7)	C(100)–Os(3)–Os(1)	84.4(6)
Os(2)–Os(3)–Os(1)	59.81(4)	F(1)–P(1)–C(2)	96.3(11)
F(1)–P(1)–C(1)	101.4(11)	C(2)–P(1)–C(1)	110.2(9)
F(1)–P(1)–Os(1)	108.2(6)	C(2)–P(1)–Os(1)	122.3(8)
C(1)–P(1)–Os(1)	114.6(7)	C(10′)–Os(1′)–C(30′)	90.8(10)
C(10′)–Os(1′)–C(20′)	92.4(10)	C(30′)–Os(1′)–C(20′)	176.3(10)
C(10′)–Os(1′)–P(1′)	100.4(6)	C(30′)–Os(1′)–P(1′)	96.0(7)
C(20′)–Os(1′)–P(1′)	85.3(6)	C(10′)–Os(1′)–Os(3′)	90.1(6)
C(30′)–Os(1′)–Os(3′)	86.9(7)	C(20′)–Os(1′)–Os(3′)	91.2(6)
P(1′)–Os(1′)–Os(3′)	169.05(14)	C(10′)–Os(1′)–Os(2′)	149.2(7)
C(30′)–Os(1′)–Os(2′)	91.8(7)	C(20′)–Os(1′)–Os(2′)	84.5(7)
P(1′)–Os(1′)–Os(2′)	109.89(14)	Os(3′)–Os(1′)–Os(2′)	59.37(4)
C(40′)–Os(2′)–C(70′)	100.0(14)	C(40′)–Os(2′)–C(60′)	91.6(9)
C(70′)–Os(2′)–C(60′)	88.9(12)	C(40′)–Os(2′)–C(50′)	90.5(11)
C(70′)–Os(2′)–C(50′)	91.5(12)	C(60′)–Os(2′)–C(50′)	177.7(10)
C(40′)–Os(2′)–Os(3′)	163.9(11)	C(70′)–Os(2′)–Os(3′)	95.9(10)
C(60′)–Os(2′)–Os(3′)	86.4(6)	C(50′)–Os(2′)–Os(3′)	91.4(8)
C(40′)–Os(2′)–Os(1′)	104.4(10)	C(70′)–Os(2′)–Os(1′)	155.5(9)
C(60′)–Os(2′)–Os(1′)	92.6(7)	C(50′)–Os(2′)–Os(1′)	86.1(7)
Os(3′)–Os(2′)–Os(1′)	59.83(4)	C(11″)–Os(3′)–C(10″)	102.7(14)
C(11″)–Os(3′)–C(90′)	88.1(11)	C(10″)–Os(3′)–C(90′)	88.7(10)
C(11″)–Os(3′)–C(80′)	87.9(11)	C(10″)–Os(3′)–C(80′)	94.7(9)
C(90′)–Os(3′)–C(80′)	175.2(10)	C(11″)–Os(3′)–Os(2′)	162.8(8)

Table 4 (continued)

Bond angles			
C(10″)–Os(3′)–Os(2′)	94.1(12)	C(90′)–Os(3′)–Os(2′)	88.6(7)
C(80′)–Os(3′)–Os(2′)	94.5(6)	C(11″)–Os(3′)–Os(1′)	102.6(8)
C(10″)–Os(3′)–Os(I′)	154.6(12)	C(90′)–Os(3′)–Os(1′)	93.9(7)
C(80′)–Os(3′)–Os(1′)	84.5(6)	Os(2′)–Os(3′)–Os(1′)	60.80(4)
F(1′)–P(1′)–C(1′)	98.3(8)	F(1′)–P(1′)–C(2′)	99.4(8)
C(1′)–P(1′)–C(2′)	110.9(8)	F(1′)–P(1′)–Os(1′)	108.7(5)
C(1′)–P(1′)–Os(1′)	120.4(6)	C(2′)–P(1′)–Os(1′)	115.4(7)

4.2.1. X-ray analysis

Crystals of **2** have monoclinic symmetry and space group $P2_1$. The unit cell which has the parameters $a = 1003.2(2)$, $b = 1165.9(3)$, $c = 1544.9(4)$ pm and $\beta = 107.20(2)°$ contains two molecules, yielding a calculated density of 2.269 g cm^{-3}. The data were collected at 293 K on a Siemens P3F diffractometer using graphite-monochromated Cu Kα radiation ($\lambda = 154.184$ pm) in the θ–2θ mode in the range $3° \leqslant 2\theta \leqslant 135°$ at a scan speed between 2.93 and 29.30° min^{-1} depending on the intensity of the reflection.

The data were corrected for Lorentz, polarization and

Table 5
Bond distances (pm) and bond angles (°) for **2**

Bond distances			
Os(1)–C(10)	192.2(10)	Os(1)–C(30)	194.8(12)
Os(1)–C(20)	194.7(11)	Os(1)–P(1)	233.8(5)
Os(1)–Os(3)	292.27(12)	Os(1)–Os(2)	292.44(12)
Os(2)–C(50)	192.6(12)	Os(2)–C(40)	194.0(12)
Os(2)–C(60)	194.8(12)	Os(2)–P(2)	233.6(5)
Os(2)–Os(3)	292.32(11)	Os(3)–C(70)	191.7(13)
Os(3)–C(100)	193.7(12)	Os(3)–C(90)	193.1(10)
Os(3)–C(80)	194.3(13)	P(1)–F(1)	168.4(12)
P(1)–C(2)	188(3)	P(1)–C(1)	190(2)
P(2)–F(2)	161.8(12)	P(2)–C(4)	186(2)
P(2)–C(3)	189(2)		
Bond angles			
C(10)–Os(1)–C(30)	93.5(8)	C(10)–Os(1)–C(20)	92.1(10)
C(30)–Os(1)–C(20)	173.6(9)	C(10)–Os(1)–P(1)	101.3(6)
C(30)–Os(1)–P(1)	94.8(6)	C(20)–Os(1)–P(1)	87.1(6)
C(10)–Os(1)–Os(3)	148.5(7)	C(30)–Os(1)–Os(3)	93.5(5)
C(20)–Os(1)–Os(3)	80.1(7)	P(1)–Os(1)–Os(3)	108.71(12)
C(10)–Os(1)–Os(2)	90.3(6)	C(30)–Os(1)–Os(2)	83.9(6)
C(20)–Os(1)–Os(2)	93.0(6)	P(1)–Os(1)–Os(2)	168.41(13)
Os(3)–Os(1)–Os(2)	59.99(3)	C(50)–Os(2)–C(40)	94.5(11)
C(50)–Os(2)–C(60)	90.1(10)	C(40)–Os(2)–C(60)	174.5(8)
C(50)–Os(2)–P(2)	101.3(8)	C(40)–Os(2)–P(2)	86.7(7)
C(60)–Os(2)–P(2)	95.4(6)	C(50)–Os(2)–Os(3)	149.2(8)
C(40)–Os(2)–Os(3)	81.7(6)	C(60)–Os(2)–Os(3)	92.8(5)
P(2)–Os(2)–Os(3)	108.93(12)	C(50)–Os(2)–Os(1)	89.9(8)
C(40)–Os(2)–Os(1)	92.8(7)	C(60)–Os(2)–Os(1)	84.2(6)
P(2)–Os(2)–Os(1)	168.80(12)	Os(3)–Os(2)–Os(1)	59.98(3)
C(70)–Os(3)–C(100)	89.1(8)	C(70)–Os(3)–C(90)	101.5(8)
C(100)–Os(3)–C(90)	91.8(9)	C(70)–Os(3)–C(80)	92.7(9)
C(100)–Os(3)–C(80)	177.5(8)	C(90)–Os(3)–C(80)	89.6(8)
C(70)–Os(3)–Os(1)	159.2(5)	C(100)–Os(3)–Os(1)	85.4(6)
C(90)–Os(3)–Os(1)	98.7(6)	C(80)–Os(3)–Os(1)	92.3(6)
C(70)–Os(3)–Os(2)	100.2(5)	C(100)–Os(3)–Os(2)	91.3(7)
C(90)–Os(3)–Os(2)	158.2(6)	C(80)–Os(3)–Os(2)	86.7(5)
Os(1)–Os(3)–Os(2)	60.03(3)	F(1)–P(1)–C(2)	98.4(9)
F(1)–P(1)–C(1)	97.9(8)	C(2)–P(1)–C(1)	109.0(11)
F(1)–P(1)–Os(1)	111.5(5)	C(2)–P(1)–Os(1)	115.6(8)
C(1)–P(1)–Os(1)	120.7(7)	F(2)–P(2)–C(4)	97.9(13)
F(2)–P(2)–C(3)	98.4(10)	C(4)–P(2)–C(3)	109.7(11)
F(2)–P(2)–Os(2)	109.7(5)	C(4)–P(2)–Os(2)	116.1(10)
C(3)–P(2)–Os(2)	121.0(8)		

absorption effects ($\mu = 21.80$ mm^{-1}). The structure was solved by direct methods and difference Fourier syntheses. The refinement using all 5437 measured independent reflections converged at $R = 0.065$ (the R value based on 5124 reflections with $I \geqslant 2.0\sigma(I)$). A final difference map displayed no electron density higher than 0.89×10^{-6} electrons pm^{-3} (near Os atoms). The program SHELXL-93 [12] and our own programs were used. Complex atom scattering factors [13] were employed.

3: Mass spectrum (70 eV): m/z (%) [M]$^+$ 1146 (10) [1M − CO]$^+$ 1118 (3), [M − 2CO]$^+$ 1090 (2), [M − 3CO]$^+$ 1062 (5), [M − 4CO]$^+$ 1034 (12), [M − 5CO]$^+$ 1006 (10), [M − 6CO]$^+$ 978 (10), [M − 7CO]$^+$ 950 (12), [^{t}Bu]$^+$ 57(100). Some further peaks between mass units 250 and 470 (2–4) and between 600 and 850 (2–8) were observed. Their assignment was impossible owing to a complicated isotopic pattern.

3: ^{1}H NMR: δH 1.42 (dd, ^3J(HP) = 14.9 Hz, ^4J(HF) = 1.1 Hz, 18H; ((CH$_3$)$_3$C)$_2$PF); 1.28 (dt, ^3J(HP) = 18.4 Hz, ^4J(HF) = 1.1 Hz, 9H; (CH$_3$)$_3$CPF$_2$) ppm. ^{19}F NMR: δF = −53.8 (dd(br), J(FP) ≈ ^1J(PF) ≈ 1154 Hz, J(FP) ≈ 238 Hz; RPF$_2$); −139.7 (dd(br), J(FP) ≈ ^1J(PF) ≈ 913 Hz, J(FP) ≈ 328 Hz; R$_2$PF) ppm. ^{31}P NMR: δP 1900.3 ("t" m(br), J(PF) ≈ ^1J(PF) ≈ 1157 Hz; RPF$_2$); 197.2 ("d" m(br), J(PF) ≈ ^1J(PF) ≈ 920 Hz, R$_2$PF) ppm.

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