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Crystal and molecular structures of $Os_3(CO)_9[\mu_3\text{-}(C_5H_4PR)Fe(C_5H_4)]$ (R = Fc or Ph), two molecules with Fe → Os bonds

William R. Cullen, Steven J. Rettig and Tu Cai Zheng

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C., V6T 1Z1 (Canada)

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Abstract

The thermal reaction between $Os_3(CO)_{12}$ and $Fe(C_5H_4)_2PPh$ affords $Os_3(CO)_9[\mu_3\text{-}(C_5H_4PPh)Fe(C_5H_4)]$ (**5b**) (70%) as the only major product. Heating a solution of $Os_3(CO)_{11}(PFc_2Ph)$ ($FcH = (\eta\text{-}C_5H_5)_2Fe$) in octane for 3 h gives the related molecule $Os_3(CO)_9[\mu_3\text{-}(C_5H_4PFc)Fe(C_5H_4)]$ (**5a**) in low yield (5%). The structures of **5a** and **5b** have been established by X-ray crystallography, revealing in each case that a closed Os_3-triangle is capped on one face by the ferrocenyl phosphido moiety acting as an overall six-electron donor. It is bonded to the cluster via one phosphorus atom, one carbon atom from the C_5H_4 ring, and the iron atom. Two semibridging carbonyls are also present in each structure.

Crystals of $\{\mu_3\text{-}[\eta^5\text{-}C_5H_4)_2Fe]P[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]\text{-}\mathit{Fe,P,P,C}\}Os_3(CO)_9$ (**5a**) are triclinic, *a* 12.304(1), *b* 12.336(2), *c* 10.886(2) Å, *α* 115.38(2), *β* 92.34(1), *γ* 91.76(1)°, $Z = 2$, space group $P\bar{1}$, and those of $\{\mu_3\text{-}\eta^4\text{-}[(\eta^5\text{-}C_5H_4)_2Fe]P(C_6H_5)]\text{-}\mathit{Fe,P,P,C}\}Os_3(CO)_9 \cdot 0.5CH_2Cl_2$ (**5b**) are also triclinic, *a* 12.427(2), *b* 13.061(1), *c* 9.209(1) Å, *α* 96.562(8), *β* 91.25(1), *γ* 76.956(9)°, $Z = 2$, space group $P\bar{1}$. The structures were solved by heavy atom methods and were refined by full-matrix least-squares procedures to $R = 0.036$ and 0.031 for 5884 and 4716 reflections with $I \geqslant 3\sigma(I)$, respectively.

1. Introduction

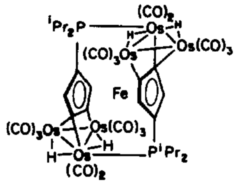
Thermolysis of ferrocenylphosphine derivatives of $Os_3(CO)_{12}$ has afforded a number of novel complexes. $\{Os_3(CO)_{11}\}_2[Fe(C_5H_4P^iPr_2)_2]$ gave complex **1** containing an unsymmetrically bound ferrodicyne moiety [1], $Os_3(CO)_{11}(PFc_2Ph)$ afforded complex **2**, containing a symmetrical ferrocyne moiety [1], and **3a** containing a Fe → Os bond [2]. Four other complexes (**3b**–**3e**) of the latter type have also been characterized [2–4]. $Os_3(CO)_{10}[Fe(C_5H_4P^iPr_2)_2]$ also yielded complex **4** [2] which also shows a Fe → Os interaction.

In the present paper, we describe the synthesis and structural characterization of a new type of complex in which the ferrocenyl moiety is bonded to one osmium center via a C–Os σ bond and a weaker Fe → Os bond. The other Cp ring is attached to a phosphido fragment which bridges the other two osmium atoms.

2. Results and discussion

The previously unidentified complex $Os_3(CO)_9[\mu_3\text{-}(C_5H_4PFc)Fe(C_5H_4)]$ (**5a**) was obtained in low yield from the pyrolysis of $Os_3(CO)_{11}(PFc_2Ph)$, a reaction that afforded **2**, **3a** and a number of other complexes [1,2].

The structure of **5a** was determined (Fig. 1), revealing a ferrocenophane that is bridged by the $P(Fc)Os_3(CO)_9$ unit: there is also a Fe → Os bond. Another way of looking at the structure is to regard it as being formed by the insertion of an Os_3 unit into a P–C_5 ring bond of the unknown [1]ferrocenophane $Fe(C_5H_4)_2PFc$. This suggested that the reaction be-



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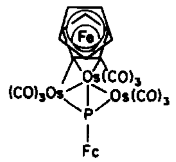

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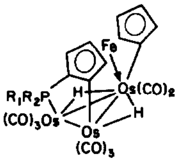

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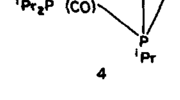
3a, R_1 = Fc, R_2 = Ph
b, $R_1 = R_2$ = Ph
c, $R_1 = R_2 = {}^iPr$
d, R_1 = Fc, R_2 = Et
e, $R_1 = R_2$ = Et



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Correspondence to: Professor W.R. Cullen.

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tween the readily available [1]ferrocenophane $Fe(C_5H_4)_2PPh$ and $Os_3(CO)_{12}$ might give a product similar to **5a**, and indeed this complex, **5b**, was produced in good yield. The structures of **5a** and **5b** are very similar so metrical remarks will be confined to **5a**.

The structure of **5a** consists of a closed Os_3 triangle capped on one face by the phosphido moiety together with the heteroannular metalated ferrocenyl fragment. The phosphido bridged Os(2)–Os(3) bond at 2.8041(5) Å is shorter than Os(1)–Os(2) at 2.8984(9) and Os(1)–Os(3) at 2.8845(8) Å which are almost of equal length. This asymmetry is probably due to the presence of the PFc group. (In **5b** the two equivalent Os–Os bonds are equal.) Likewise the phosphido bridge of **5a** is almost symmetrical (P(1)–Os(2) 2.337(2), P(1)–Os(3) 2.356(2) Å). Os(1) is σ bonded to the metalated carbon C(6) (2.051(9) Å) and is also bonded to Fe(1) which is situated almost in an axial position with respect to the Os_3-core (Os(2)–Os(1)–Fe(1) 106.20(3), Os(3)–Os(1)–Fe(1) 107.36(3)°). The Fe(1)–Os(1) length (2.994(2) Å) is much longer than the Fe–Os bonds found in complexes **3a** (2.830(1) Å) [2], **3b** (2.826(1) Å) [2], **3c** (2.858(1) Å) [3], **3d** (2.836(1) Å) [3], **3e** (2.826(2) Å) [4], and **4** (2.813(1) Å) [2] indicating a weaker interaction.

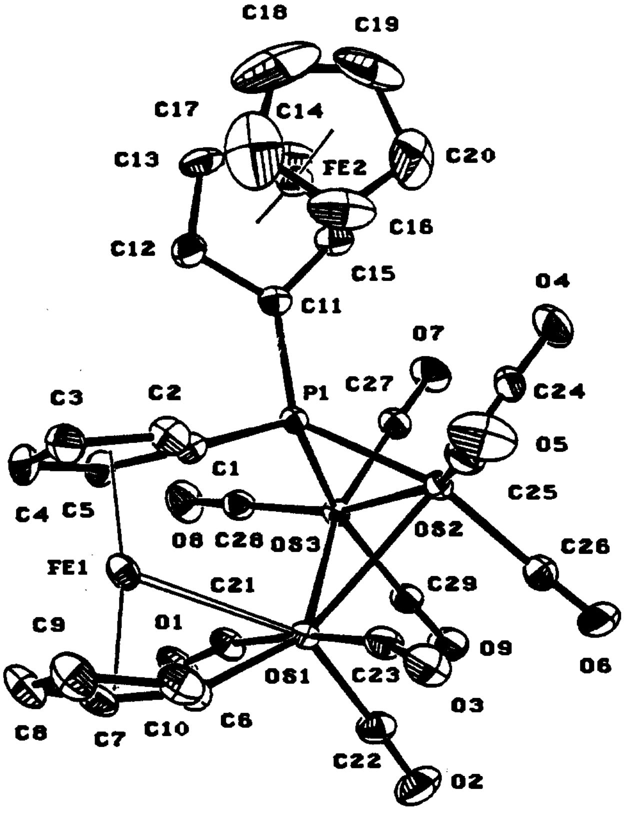


Fig. 1. Perspective view of **5a**; 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.

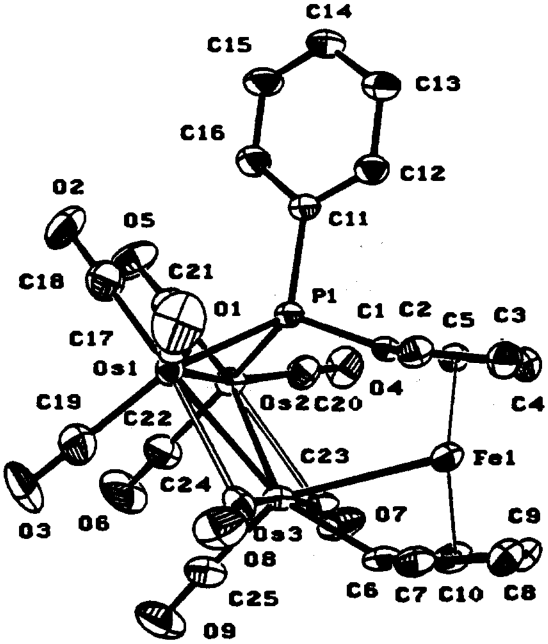
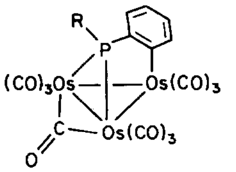


Fig. 2. Perspective view of **5b**; 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.

Each osmium is bonded to three CO groups, one axial and two equatorial. The Os(1)–C(22) bond *trans* to Fe(1) is short at 1.85(1) Å. The carbonyls C(21) and C(23) are semi-bridging between Os(1)–Os(3) and Os(1)–Os(2) respectively, as shown by the following bonding parameters ($\psi < 70°$) [6]: Os(1)–C(21)–O(1) 162.2(8)°, Os(3)–Os(1)–C(21) 63.1(3)°, Os(3)- - -C(21) 2.65(1) Å, Os(1)–C(23)–O(3) 167.1(9)°, Os(2)–Os(1)–C(23) 66.0(3)°, Os(2)- - -C(23) 2.75(1) Å.

P(1) is displaced 0.383 and 0.112 Å away respectively from the Cp(1) and Cp(3) planes. More remarkably Os(1) is also out of the Cp(2) plane by 0.998 Å. The Cp(1) and Cp(2) rings are slightly opened up (ring tilt angle 8.83°) compared with Cp(3) and Cp(4) (ring tilt angle 3.20°). As a consequence the Cp(1)–Fe(1)–Cp(2) angle is 168.4(3)°, the Fe(1)–C(1) bond (2.105(9) Å) is longer than the other four Fe–C(Cp(1)) bonds (av. 2.05 Å), and Fe(1)–C(6) (1.97(1) Å) is shorter than the other four Fe–C (Cp(2)) bonds (av. 2.07 Å). The Cp(1) and Cp(2) rings make angles of 49.42 and 58.12°, respectively, with the Os_3 plane which is perpendicular (90.14°) to the Os(2)Os(3)P(1) plane.

Complexes **5a** and **5b** may be compared with $Os_3(CO)_{10}(PRC_6H_4)$ (R = Me, Ph) (**6**), products of the pyrolysis of $Os_3(CO)_{11}(PPh_2R)$ [7]. However, there are a number of significant differences. Complex **6** contains an *ortho*-metalated arene moiety, while **5** contains a heteroannular metalated rather than *ortho*-metalated ferrocenyl moiety. This allows the iron atom to form a bond with Os(1) (it should be noted that the doubly metalated compounds **3** also show Fe → Os bonding). In addition, **6** is an intermediate in the formation of the benzyne complexes $Os_3(CO)_9(PR)(C_6H_4)$ (R = Me, Et, Ph) while **5** is rather stable and is unlikely to act as a precursor to ferrocyne complexes such as **2**.



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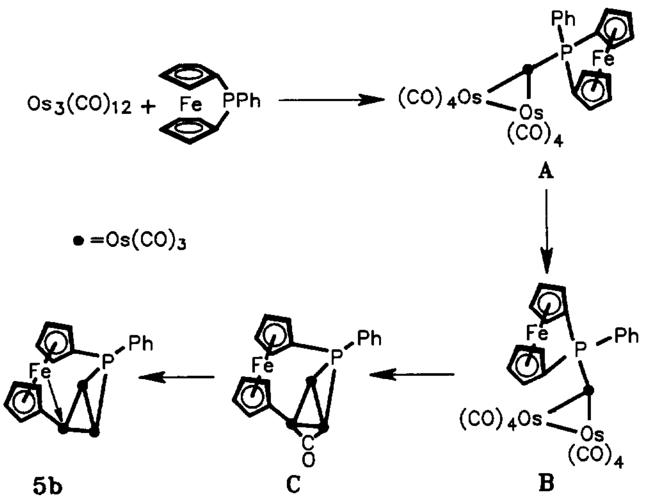
Scheme 1 outlines a proposed reaction sequence for the formation of **5b**. Presumably reaction occurs via the substitution product $Os_3(CO)_{11}[Fe(C_5H_4)_2PPh]$ (**A**). The movement of the ferrocenophane to an axial position leads to **B** and oxidative addition of one P–C_5H_4 bond across an Os–Os bond gives **C**. Establishment of the Fe → Os bond results in **5b**. Similar schemes can be written for the formation of **5a** based on known decomposition pathways for related molecules and an initial step that involves heteroannular C–H activation [5,9].

The P–C bond cleavage reaction B → C presumably involves a strained bond as the tilt angle between the two Cp rings in the ligand is 27° [13]. Such cleavage reactions normally occur at a single metal center [14]; however, there are a few precedents for the involvement of dinuclear centers in the thermolysis reactions of, for example, $Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-}R_2PCH_2PR_2)$ to

TABLE 1. Crystallographic data [a]

	5a	5b
Formula	$C_{29}H_{17}Fe_2O_9Os_3P$	$C_{25}H_{13}FeO_9Os_3P \cdot 0.5CH_2Cl_2$
FW	1222.71	1157.26
Color, habit	Red-brown, plate	Red-orange, plate
Crystal size (mm)	0.04 × 0.15 × 0.37	0.05 × 0.15 × 0.25
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	12.304(1)	12.427(2)
b (Å)	12.336(2)	13.061(1)
c (Å)	10.886(2)	9.209(3)
α (°)	115.38(2)	96.562(8)
β (°)	92.34(1)	91.25(1)
γ (°)	91.76(1)	76.956(9)
V (Å³)	1489.5(5)	1446.5(3)
Z	2	2
ρ_{calc} (g cm^{-3})	2.726	2.657
$F(000)$	1116	1050
μ(Mo $K\alpha$) (cm^{-1})	138.20	138.36
Trans. factors (relative)	0.32–1.00	0.26–1.00
Scan type	ω–2θ	ω–2θ
Scan range (deg in ω)	1.37 + 0.35 tan θ	1.15 + 0.35 tan θ
Scan rate (deg/min)	16	16
Data collected	$+h, \pm k, \pm l$	$+h, \pm k, \pm l$
$2\theta_{max}$ (°)	60	60
Crystal decay (%)	negligible	11.0
Total no. of reflections	9072	8772
No. of unique reflections	8693	8411
R_{merge}	0.041	0.039
Reflections with $I \geqslant 3\sigma(I)$	5884	4716
No. of variables	398	371
R	0.036	0.031
R_w	0.038	0.027
GOF	2.14	1.55
Max Δ/σ (final cycle)	0.005	0.10
Residual density (e/Å³)	−1.86 to 2.46 (near Os)	−1.12 to 1.22 (near Os)

[a] Temperature 294 K, Rigaku AFC6S diffractometer, Mo Kα radiation (λ 0.71069 Å), graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2/1, up to 8 rescans), $\sigma^2(F^2) = [S^2(C + 4B) + (pF^2)^2]/Lp^2$ (S = scan rate, C = scan count, B = normalized background count, $p = 0.01$ for **5a** and 0.00 for **5b**), function minimized $\Sigma w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$, $R_w = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2)^{1/2}$, and $GOF = [\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Values given for R, R_w, and GOF are based on those reflections with $I \geqslant 3\sigma(I)$.



Scheme 1. Reaction pathway leading to **5b**.

give $Fe_2(CO)_6(\mu\text{-}PR_2)(\mu\text{-}PR_2CH_2)$ [15]. Complexes of fluorocarbon bridged ligands also seem to decompose in this manner [16,17].

It is apparent that a range of compounds related to **5b** should be available from the reaction of $Os_3(CO)_{12}$ with appropriate ferrocenophanes or ruthenocenophanes. We intend to explore these reactions further.

3. Experimental details

All reactions were carried out under an argon atmosphere. Solvents were distilled prior to use. $^{31}P\{^1H\}$ and ^1H NMR chemical shifts are given in ppm from 85% H_3PO_4 and TMS, respectively, and they were recorded in $CDCl_3$ at room temperature by using a Varian XL-300 spectrometer. Elemental analyses were performed by Mr. Peter Borda of this department. Mass spectra (fast atom bombardment) were obtained by using an AEI MS-9 spectrometer with 3-nitrobenzyl alcohol as the matrix and argon as exciting gas. The ferrocenophane $Fe(C_5H_4)_2PPh$ was synthesized according to the literature method [10].

3.1. Preparation of ***5a***

The preparation of $Os_3(CO)_{11}(PFc_2Ph)$ and its pyrolytic reaction in octane for 3 h has been described previously [1]. Complex **5a** was eluted as the last (fifteenth) band from a silica chromatographic column by using 4/1 (v/v) petroleum ether/CH_2Cl_2 as eluant (5% yield). It is a red-brown solid, $^{31}P\{^1H\}$ NMR δ: 39.3. ^1H NMR δ: 4.91 (t, 2H, C_5H_4); 4.79 (t, 2H, C_5H_4); 4.67 (t, 2H, C_5H_4); 4.22 (m, 2H, C_5H_4); 4.07 (s, 5H, C_5H_5); 3.78 (q, 2H, C_5H_4); 3.12 (q, 2H, C_5H_4). Mass spectrum (FAB): *m/e* 1222 (M^+, base peak), 1194, 1166, 1138, 1110, 1082, 1054, 1026, 998, 970. Anal. Found: C, 28.66; H, 1.53. $C_{29}H_{17}Fe_2O_9Os_3P$ calc.: C, 28.49; H, 1.40%.

3.2. Preparation of ***5b***

A solution of $Os_3(CO)_{12}$ (190 mg, 0.21 mmol) and $Fe(C_5H_4)_2PPh$ (65 mg, 0.22 mmol) in octane (100 ml) was refluxed for 7 h. The solvent was removed *in vacuo* and the residue was chromatographed on a silica column with 3/1 (v/v) petroleum ether/CH_2Cl_2 as eluant. The only major band (the third) contained pure complex **5b** (180 mg, 70%). It is a red-orange solid,

TABLE 2. Final atomic coordinates (fractional) and B_{eq} (Å^2) for **5a** [a]

Atom	*x*	*y*	*z*	B_{eq}
Os(1)	0.25473(3)	0.13830(3)	−0.00006(3)	2.18(1)
Os(2)	0.15772(3)	0.29899(3)	0.24641(3)	2.17(1)
Os(3)	0.38299(3)	0.27142(3)	0.25150(3)	2.03(1)
Fe(1)	0.2768(1)	0.2733(1)	−0.1708(1)	2.69(5)
Fe(2)	0.2246(1)	0.7143(1)	0.3514(1)	2.73(5)
P(1)	0.2912(2)	0.4134(2)	0.2006(2)	1.87(7)
O(1)	0.4977(5)	0.0988(7)	−0.0441(7)	4.4(3)
O(2)	0.2395(6)	−0.0984(7)	0.015(1)	5.4(4)
O(3)	0.0060(5)	0.1070(7)	−0.0446(8)	4.4(3)
O(4)	0.1390(7)	0.4732(8)	0.5419(8)	5.5(4)
O(5)	−0.0585(7)	0.3669(8)	0.157(1)	6.1(4)
O(6)	0.0881(8)	0.0856(7)	0.3059(8)	5.3(4)
O(7)	0.4088(7)	0.4309(7)	0.5548(7)	4.5(3)
O(8)	0.6223(6)	0.3117(8)	0.2059(8)	5.1(3)
O(9)	0.3872(8)	0.0474(7)	0.3054(8)	5.5(4)
C(1)	0.2929(6)	0.4050(8)	0.0322(8)	2.1(3)
C(2)	0.2096(8)	0.430(1)	−0.045(1)	3.2(4)
C(3)	0.254(1)	0.444(1)	−0.153(1)	4.0(4)
C(4)	0.366(1)	0.423(1)	−0.152(1)	3.8(4)
C(5)	0.3912(7)	0.398(1)	−0.040(1)	2.9(3)
C(6)	0.2489(6)	0.105(1)	−0.202(1)	2.7(3)
C(7)	0.343(1)	0.112(1)	−0.273(1)	3.8(4)
C(8)	0.310(1)	0.157(1)	−0.368(1)	4.2(4)
C(9)	0.199(1)	0.173(1)	−0.364(1)	4.3(5)
C(10)	0.1604(8)	0.136(1)	−0.266(1)	3.9(4)
C(11)	0.3210(6)	0.5713(8)	0.3015(9)	2.2(3)
C(12)	0.3625(8)	0.656(1)	0.253(1)	3.3(4)
C(13)	0.3826(8)	0.768(1)	0.365(1)	4.1(4)
C(14)	0.3577(9)	0.758(1)	0.483(1)	4.1(4)
C(15)	0.3217(8)	0.638(1)	0.445(1)	3.2(4)
C(16)	0.073(1)	0.661(1)	0.261(2)	5.9(6)
C(17)	0.119(1)	0.748(3)	0.227(2)	9(1)
C(18)	0.138(2)	0.846(2)	0.341(4)	10(1)
C(19)	0.111(1)	0.828(2)	0.449(2)	7.6(7)
C(20)	0.071(1)	0.708(2)	0.400(2)	6.6(7)
C(21)	0.4133(7)	0.126(1)	−0.006(1)	2.9(3)
C(22)	0.2457(8)	−0.007(1)	0.012(1)	3.4(4)
C(23)	0.0979(8)	0.130(1)	−0.014(1)	3.3(4)
C(24)	0.1466(8)	0.409(1)	0.430(1)	3.3(4)
C(25)	0.0226(8)	0.341(1)	0.190(1)	3.5(4)
C(26)	0.1132(8)	0.162(1)	0.282(1)	3.3(4)
C(27)	0.3993(7)	0.374(1)	0.441(1)	3.0(3)
C(28)	0.5307(8)	0.298(1)	0.221(1)	3.1(4)
C(29)	0.3852(8)	0.129(1)	0.283(1)	3.1(4)

[a] $B_{eq} = (8/3)\eta^2\Sigma\Sigma U_{ij}a_i * a_j * (\mathbf{a}_i \cdot \mathbf{a}_j)$.

$^{31}P\{^1H\}$ NMR δ: 59.9. ^1H NMR δ: 7.55–7.15 (bm, 5H, C_6H_5); 4.77 (m, 2H, C_5H_4); 4.70 (m, 2H, C_5H_4); 4.62 (m, 2H, C_5H_4); 3.00 (m, 2H, C_5H_4). Mass spectrum (FAB): m/e 1114 (M^+, base peak), 1086, 1058, 1030, 1002, 974, 946, 918, 890, 862. Anal. Found: C, 26.53; H, 1.30. $C_{25.5}H_{14}ClFeO_9Os_3P$ $0.5CH_2Cl_2$ (**5b** · $0.5CH_2Cl_2$) calc.: C, 26.47; H, 1.22%.

3.3. X-Ray crystallographic analyses

Crystallographic data for $\{\mu_3\text{-}\eta^4\text{-}[(\mu^5\text{-}C_5H_4)_2Fe]P[\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]\text{-}Fe,P,P,C\}Os_3(CO)_9$ (**5a**) and $\{\mu_3\text{-}\eta^4\text{-}[(\eta^5\text{-}C_5H_4)_2Fe]P(C_6H_5)]\text{-}Fe,P,P,C\}Os_3(CO)_9 \cdot 0.5CH_2Cl_2$ (**5b** · $0.5CH_2Cl_2$) appear in Table 1. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with 2θ = 39.8–48.4° for **5a** and 31.8–35.5 for **5b**. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, remained constant for **5a** and decreased uniformly by 11.0% for **5b**. The data were processed [11] and corrected for Lorentz and polarization effects, decay (for **5b**), and absorption (empirical, based on azimuthal scans for three reflections).

TABLE 3. Final atomic coordinates (fractional) and B_{eq} (Å^2) for **5b** [a]

Atom	x	y	z	B_{eq}
Os(1)	0.33159(3)	0.17557(2)	0.20976(4)	2.98(2)
Os(2)	0.25285(3)	0.19622(2)	0.49661(3)	3.06(2)
Os(3)	0.13146(3)	0.10860(2)	0.26233(4)	3.15(2)
Fe(1)	−0.0586(1)	0.27827(9)	0.1900(1)	3.48(6)
P(1)	0.2073(2)	0.3213(1)	0.3285(2)	2.6(1)
O(1)	0.3313(6)	0.2431(7)	−0.0958(8)	7.6(5)
O(2)	0.5365(5)	0.2557(6)	0.295(1)	7.5(5)
O(3)	0.4614(7)	−0.0571(6)	0.175(1)	9.5(6)
O(4)	0.0988(6)	0.2985(6)	0.7521(7)	6.0(4)
O(5)	0.4539(6)	0.2621(6)	0.6314(8)	6.9(5)
O(6)	0.3469(8)	−0.0275(6)	0.581(1)	9.0(6)
O(7)	0.0249(6)	0.1077(6)	0.5618(8)	6.3(5)
O(8)	0.1940(6)	0.0582(6)	−0.0639(7)	6.3(4)
O(9)	0.2259(7)	−0.1220(5)	0.2809(8)	7.4(5)
C(1)	0.0671(6)	0.3533(5)	0.2605(8)	2.8(4)
C(2)	0.0354(7)	0.3696(6)	0.1125(8)	3.5(4)
C(3)	−0.0767(8)	0.4222(7)	0.114(1)	4.6(5)
C(4)	−0.1162(7)	0.4357(7)	0.258(1)	4.6(5)
C(5)	−0.0291(7)	0.3935(6)	0.3483(9)	3.5(4)
C(6)	−0.0267(8)	0.1201(6)	0.186(1)	4.6(5)
C(7)	−0.0586(8)	0.1478(7)	0.043(1)	4.7(5)
C(8)	−0.1666(8)	0.2146(8)	0.051(1)	5.0(6)
C(9)	−0.2040(7)	0.2259(7)	0.194(1)	5.4(6)
C(10)	−0.1234(8)	0.1675(8)	0.278(1)	5.0(6)
C(11)	0.2392(6)	0.4525(6)	0.3576(8)	3.0(4)
C(12)	0.1703(7)	0.5405(6)	0.3024(9)	3.7(4)
C(13)	0.1977(7)	0.6386(6)	0.323(1)	4.5(5)
C(14)	0.2898(8)	0.6509(7)	0.401(1)	5.9(6)
C(15)	0.3552(8)	0.5668(7)	0.457(1)	6.4(6)
C(16)	0.3296(8)	0.4698(7)	0.433(1)	5.5(6)
C(17)	0.3319(8)	0.2145(7)	0.018(1)	4.5(5)
C(18)	0.4581(8)	0.2262(8)	0.264(1)	5.4(6)
C(19)	0.4140(9)	0.0282(9)	0.187(1)	5.6(6)
C(20)	0.1568(8)	0.2603(8)	0.659(1)	4.4(5)
C(21)	0.3753(8)	0.2400(7)	0.5819(9)	4.4(5)
C(22)	0.3114(8)	0.0555(7)	0.552(1)	5.1(6)
C(23)	0.0723(8)	0.1178(7)	0.462(1)	4.7(5)
C(24)	0.1818(7)	0.0876(6)	0.054(1)	3.5(4)
C(25)	0.1905(8)	−0.0318(7)	0.276(1)	4.8(5)
Cl(1)	0.6004(6)	0.4830(8)	0.057(1)	25.6(9)
C(26)	0.520(3)	0.430(4)	−0.037(6)	21 (4)

[a] $B_{eq} = (8/3)\pi^2\Sigma\Sigma U_{ij}a_i * a_j * (\mathbf{a}_1 \cdot \mathbf{a}_j)$. Atom C(26) has a site occupancy of 0.50.

TABLE 4. Selected bond lengths (Å) with estimated standard deviations for **5a** [a] and **5b** [b]

5a			
Os(1)–Os(2)	2.8984(9)	Fe(1)–C(4)	2.05(1)
Os(1)–Os(3)	2.8845(8)	Fe(1)–C(5)	2.05(1)
Os(1)–Fe(1)	2.994(2)	Fe(1)–C(6)	1.97(1)
Os(1)–C(6)	2.051(9)	Fe(1)–C(7)	2.04(1)
Os(1)–C(21)	1.963(9)	Fe(1)–C(8)	2.07(1)
Os(1)–C(22)	1.85(1)	Fe(1)–C(9)	2.10(1)
Os(1)–C(23)	1.93(1)	Fe(1)–C(10)	2.05(1)
Os(2)–Os(3)	2.8041(5)	Fe(1)–Cp(1)	1.673(5)
Os(2)–P(1)	2.337(2)	Fe(1)–Cp(2)	1.653(5)
Os(2)–C(23)	2.75(1)	Fe(2)–C(11)	2.044(8)
Os(2)–C(24)	1.89(1)	Fe(2)–C(12)	2.03(1)
Os(2)–C(25)	1.91(1)	Fe(2)–C(13)	2.02(1)
Os(2)–C(26)	1.95(1)	Fe(2)–C(14)	2.03(1)
Os(3)–P(1)	2.356(2)	Fe(2)–C(15)	2.04(1)
Os(3)–C(21)	2.65(1)	Fe(2)–C(16)	2.02(1)
Os(3)–C(27)	1.90(1)	Fe(2)–C(17)	2.01(1)
Os(3)–C(28)	1.90(1)	Fe(2)–C(18)	2.01(1)
Os(3)–C(29)	1.94(1)	Fe(2)–C(19)	2.00(1)
Fe(1)–C(1)	2.105(9)	Fe(2)–C(20)	1.99(1)
Fe(1)–C(2)	2.05(1)	Fe(2)–Cp(3)	1.635(5)
Fe(1)–C(3)	2.05(1)	Fe(2)–Cp(4)	1.638(8)
5b			
Os(1)–Os(2)	2.7997(6)	Os(3)–C(6)	2.050(8)
Os(1)–Os(3)	2.8838(6)	Os(3)–C(23)	1.98(1)
Os(1)–P(1)	2.340(2)	Os(3)–C(24)	1.997(8)
Os(1)–C(17)	1.89(1)	Os(3)–C(25)	1.83(1)
Os(1)–C(18)	1.87(1)	Fe(1)–C(1)	2.080(6)
Os(1)–C(19)	1.96(1)	Fe(1)–C(2)	2.040(8)
Os(1)–C(24)	2.703(8)	Fe(1)–C(3)	2.044(9)
Os(2)–Os(3)	2.8832(5)	Fe(1)–C(4)	2.047(9)
Os(2)–P(1)	2.347(2)	Fe(1)–C(5)	2.061(7)
Os(2)–C(20)	1.92(1)	Fe(1)–C(6)	2.011(8)
Os(2)–C(21)	1.870(9)	Fe(1)–C(7)	2.054(8)
Os(2)–C(22)	1.94(1)	Fe(1)–C(8)	2.077(8)
Os(2)–C(23)	2.667(8)	Fe(1)–C(9)	2.073(8)
Os(3)–Fe(1)	2.974(1)	Fe(1)–C(10)	2.054(9)

[a] Here and elsewhere Cp(1–4) refer to the unweighted centroids of the C(1–5), C(6–10), C(11–15) and C(16–20) cyclopentadienyl rings, respectively. [b] Here and elsewhere, Cp(1) and Cp(2) are the unweighted centroids of the C(1–5) and C(6–10) cyclopentadienyl rings.

Both structures were solved by heavy-atom methods, the coordinates of the Os and Fe atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. Both structure analyses were initiated in the centrosymmetric space group $P\bar{1}$, these choices being confirmed by the subsequent successful solutions and refinements of the structures. The dichloromethane solvent in **5b** was 1:1 disordered about the centre of symmetry at (1/2, 1/2, 0). The Cl atom was refined at full occupancy while the carbon atom was refined with the site occupancy fixed at 0.50. All non-hydrogen atoms of both complexes were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in idealized positions (C–H = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$). Corrections for secondary extinction were applied for both structures, the final values of the extinction coefficient being $5.3(2) \times 10^{-6}$ for **5a** and $1.37(9) \times 10^{-7}$ for **5b**. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the *International Tables for X-Ray Crystallography* [12]. Final atomic coordinates and equivalent isotropic thermal parameters, selected bond lengths, and selected bond angles appear in Tables 2–5, respectively. Hydrogen atom parameters, anisotropic thermal parameters, complete tables of bond lengths and bond angles, torsion angles, intermolecular contacts, least-squares planes, and measured and calculated structure factor amplitudes are included as supplementary material.

TABLE 5. Selected bond angles (°) with estimated standard deviations for **5a** and **5b**

5a			
Os(2)–Os(1)–Os(3)	58.01(2)	Os(3)–Os(2)–P(1)	53.62(5)
Os(2)–Os(1)–Fe(1)	106.20(3)	Os(3)–Os(2)–C(24)	98.8(3)
Os(2)–Os(1)–C(6)	137.5(3)	Os(3)–Os(2)–C(25)	156.5(3)
Os(2)–Os(1)–C(21)	120.9(3)	Os(3)–Os(2)–C(26)	97.7(3)
Os(2)–Os(1)–C(22)	102.5(3)	P(1)–Os(2)–C(24)	95.6(3)
Os(2)–Os(1)–C(23)	66.0(3)	P(1)–Os(2)–C(25)	105.1(3)
Os(3)–Os(1)–Fe(1)	107.36(3)	P(1)–Os(2)–C(26)	151.1(3)
Os(3)–Os(1)–C(6)	141.0(2)	C(24)–Os(2)–C(25)	92.9(4)
Os(3)–Os(1)–C(21)	63.1(3)	C(24)–Os(2)–C(26)	92.3(4)
Os(3)–Os(1)–C(22)	97.1(3)	C(25)–Os(2)–C(26)	102.2(4)
Os(3)–Os(1)–C(23)	123.5(3)	Os(1)–Os(3)–Os(2)	61.24(2)
Fe(1)–Os(1)–C(6)	40.8(3)	Os(1)–Os(3)–P(1)	73.28(6)
Fe(1)–Os(1)–C(21)	86.3(3)	Os(1)–Os(3)–C(27)	153.0(3)
Fe(1)–Os(1)–C(22)	149.2(3)	Os(1)–Os(3)–C(28)	112.1(3)
Fe(1)–Os(1)–C(23)	94.2(3)	Os(1)–Os(3)–C(29)	89.7(3)
C(6)–Os(1)–C(21)	88.4(3)	Os(2)–Os(3)–P(1)	53.01(5)
C(6)–Os(1)–C(22)	108.8(4)	Os(2)–Os(3)–C(27)	91.9(3)
C(6)–Os(1)–C(23)	87.2(4)	Os(2)–Os(3)–C(28)	156.1(3)
C(21)–Os(1)–C(22)	88.4(4)	Os(2)–Os(3)–C(29)	99.5(3)
C(21)–Os(1)–C(23)	172.6(4)	P(1)–Os(3)–C(27)	93.6(3)
C(22)–Os(1)–C(23)	87.4(4)	P(1)–Os(3)–C(28)	103.4(3)
Os(1)–Os(2)–Os(3)	60.75(2)	P(1)–Os(3)–C(29)	152.1(3)
Os(1)–Os(2)–P(1)	73.26(6)	C(27)–Os(3)–C(28)	93.7(4)
Os(1)–Os(2)–C(24)	159.5(3)	C(27)–Os(3)–C(29)	92.0(4)
Os(1)–Os(2)–C(25)	106.5(3)	C(28)–Os(3)–C(29)	103.5(4)
Os(1)–Os(2)–C(26)	90.1(3)	Os(1)–Fe(1)–Cp(1)	110.4(2)
		Os(1)–Fe(1)–Cp(2)	81.2(2)
		Cp(1)–Fe(1)–Cp(2)	168.4(3)
		Cp(3)–Fe(2)–Cp(4)	176.7(5)
5b			
Os(2)–Os(1)–Os(3)	60.95(1)	Os(1)–Os(2)–Os(3)	60.97(1)
Os(2)–Os(1)–P(1)	53.43(5)	Os(1)–Os(2)–P(1)	53.20(5)
Os(2)–Os(1)–C(17)	154.4(3)	Os(1)–Os(2)–C(20)	155.1(3)
Os(2)–Os(1)–C(18)	94.3(3)	Os(1)–Os(2)–C(21)	94.8(3)
Os(2)–Os(1)–C(19)	101.1(3)	Os(1)–Os(2)–C(22)	101.7(3)
Os(3)–Os(1)–P(1)	72.56(5)	Os(3)–Os(2)–P(1)	72.48(4)
Os(3)–Os(1)–C(17)	110.3(3)	Os(3)–Os(2)–C(20)	110.7(2)
Os(3)–Os(1)–C(18)	155.1(3)	Os(3)–Os(2)–C(21)	155.1(3)
Os(3)–Os(1)–C(19)	90.2(3)	Os(3)–Os(2)–C(22)	90.0(2)
P(1)–Os(1)–C(17)	101.5(3)	P(1)–Os(2)–C(20)	102.4(3)
P(1)–Os(1)–C(18)	95.1(3)	P(1)–Os(2)–C(21)	98.4(3)
P(1)–Os(1)–C(19)	153.8(3)	P(1)–Os(2)–C(22)	154.0(3)
C(17)–Os(1)–C(18)	93.1(4)	C(6)–Os(3)–C(24)	87.9(4)
C(17)–Os(1)–C(19)	103.0(4)	C(6)–Os(3)–C(25)	107.0(3)
C(18)–Os(1)–C(19)	92.7(4)	C(23)–Os(3)–C(24)	173.9(3)
		C(23)–Os(3)–C(25)	87.7(4)
		C(24)–Os(3)–C(25)	89.1(4)
		Os(3)–Fe(1)–Cp(1)	109.5
		Os(3)–Fe(1)–Cp(2)	81.4
		Cp(1)–Fe(1)–Cp(2)	169.1

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