

## Synthesis of trinuclear mixed-metal clusters $\text{Os}_2\text{Fe}(\text{CO})_{10}\text{L}_2$ ( $\text{L} = \text{OH}, \text{I}, \text{CO}$ ).

### The crystal structures of $\text{Os}_2\text{Fe}(\text{CO})_{10}(\mu\text{-OH})_2$ and $\text{Os}_2\text{Fe}(\text{CO})_{12} \cdot 0.41\text{Os}_3(\text{CO})_{12}$

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#### Abstract

The heterometallic clusters  $\text{Os}_2\text{Fe}(\text{CO})_{10}(\mu\text{-X})_2$  ( $\text{X} = \text{OH}, \text{I}$ ) were obtained from the binuclear osmium complexes  $\text{Os}_2(\text{CO})_6\text{X}_n$  ( $\text{X} = \text{Cl}, n = 4; \text{X} = \text{I}, n = 2$ ). The structure of  $\text{Os}_2\text{Fe}(\text{CO})_{10}(\mu\text{-OH})_2$  was determined by a single-crystal X-ray diffraction analysis. The crystal is triclinic and crystallizes in the space group  $P\bar{1}$  and  $a = 14.009(6)$ ,  $b = 13.330(4)$ ,  $c = 9.511(2)$  Å,  $\alpha = 103.69(2)$ ,  $\beta = 81.83(3)$ ,  $\gamma = 102.22(3)^\circ$ ,  $V = 1699(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 2.969$  g cm<sup>-3</sup>,  $R = 0.093$  for 2359 independent reflections ( $F_o > 6\sigma(F_o)$ ). The cluster consists of an open triangular OsFeOs metal core with no Os–Os bond. The bridging OH groups are coordinated semiaxially and span the Os–Os edge. On heating in the presence of an excess of  $\text{Fe}_2(\text{CO})_9$ , the  $\text{Os}_2\text{Fe}(\text{CO})_{10}(\mu\text{-I})_2$  cluster is converted to  $\text{Os}_2\text{Fe}(\text{CO})_{12}$ . The co-crystallate  $\text{Os}_2\text{Fe}(\text{CO})_{12} \cdot 0.41\text{Os}_3(\text{CO})_{12}$  was isolated from the solution of  $\text{Os}_2\text{Fe}(\text{CO})_{10}(\mu\text{-I})_2$ , as the product of decomposition of the initial cluster. It crystallizes in the monoclinic system, space group  $P2_1/n$ , with  $a = 8.056(2)$ ,  $b = 14.743(2)$ ,  $c = 14.520(2)$  Å,  $\beta = 100.62(1)^\circ$ ,  $V = 1695.0(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 3.179$  g cm<sup>-3</sup> and  $R = 0.0250$  for 1997 independent reflections ( $F_o > 4\sigma(F_o)$ ). © 1997 Elsevier Science S.A.

**Keywords:** Heterometallic clusters; Synthesis; Osmium; Iron; X-ray structure

#### 1. Introduction

One of the most logical suitable methods for the synthesis of heterometallic cluster compounds is to build them up using lower nuclearity fragments [1,2]. This method was used previously [3] for the synthesis of the iron–osmium clusters  $\text{Fe}_2\text{Os}(\text{CO})_{12}$ ,  $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$  and  $\text{FeOs}_2(\text{CO})_{12}$  from  $\text{Fe}_2(\text{CO})_9$  and mono- or bi-nuclear osmium carbonyl hydrides. However the latter heterometallic cluster was obtained only in low yields. This paper reports the preparation of some iron–osmium clusters starting from the binuclear

osmium complexes  $\text{Os}_2(\text{CO})_6\text{X}_n$  ( $\text{X} = \text{Cl}, n = 4; \text{X} = \text{I}, n = 2$ ).

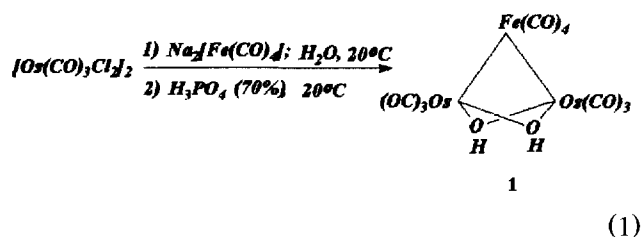
#### 2. Results and discussion

The reaction of  $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$  with  $\text{Na}_2[\text{Fe}(\text{CO})_4]$  was conducted in water because in organic solvents the initial binuclear complex was reduced to  $\text{Os}_2(\text{CO})_n\text{Cl}_2$  ( $n = 6, 8$ ) and  $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-Cl})$ . In aqueous medium,  $[\text{Fe}(\text{CO})_4]^{2-}$  undergoes almost complete hydrolysis to give  $[\text{HFe}(\text{CO})_4]^-$ , a weaker nucleophile and a weaker reducing agent [4].

The binuclear complex  $[\text{Ru}(\text{CO})_3\text{X}_2]_2$  has previously been shown [5] to react with  $\text{Na}_2[\text{Fe}(\text{CO})_4]$  in water with the formation of a number of three- and four-

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nuclear iron–ruthenium cluster complexes. An analogous osmium complex reacts with  $\text{Na}_2[\text{Fe}(\text{CO})_4]$  in a rather different way. The only stable product isolated from the reaction mixture proved to be the heterometallic cluster  $\text{Os}_2\text{Fe}(\text{CO})_{10}(\mu\text{-OH})_2$  (**1**) containing two bridging OH groups:



According to Eq. (1), two chlorides are substituted by  $[\text{Fe}(\text{CO})_4]^{2-}$  and the other two by  $\text{OH}^-$  anions. The bridging hydroxyl groups are not distinguishable in the IR and  $^1\text{H}$  NMR spectra (see Section 3), suggesting their symmetric coordination.

The structure of cluster **1** was determined by X-ray analysis of a single crystal obtained from a  $\text{CHCl}_3$ –hexane solution. Two crystallographically independent molecules occur in the unit cell. The numbering schemes and the crystal packing are shown in Figs. 1 and 2 respectively. Both molecules of **1** possess the idealized point symmetry  $C_{2v}$  and have similar geometric characteristics. Cluster **1** has the opened metal core in accordance with a number of valence electrons ( $N_{\text{val}} = 50$ ), the Os  $\cdots$  Os distance (3.052(4) Å) being close to that found in  $\text{Os}_3(\mu\text{-OCH}_3)_2(\text{CO})_{10}$  (3.078(3) Å) [6]. The Os–Fe bond lengths (mean 2.749 Å) differ slightly from those in  $\text{OsFe}_2(\mu\text{-CO})_2(\text{CO})_{10}$  (2.735 and 2.746 Å) [7]. The bridging OH groups are coordinated semiaxially with respect to the OsFeOs core. There are no short intermolecular contacts in the crystal packing of **1**.

Another way of building a heterometallic cluster core is to add an unsaturated fragment across a metal–metal bond in a low nuclearity complex [8,9]. To prepare an iron–osmium heterometallic cluster by this method,  $\text{Fe}_2(\text{CO})_9$  was used which decomposes in solution to give the coordinatively unsaturated species ‘ $\text{Fe}(\text{CO})_4$ ’. Through its reactivity this species inserts into the Os–Os bond in non-polar solvents under mild conditions with the formation of the heterometallic cluster  $\text{Os}_2\text{Fe}(\text{CO})_{10}(\mu\text{-I})_2$  (**2**):

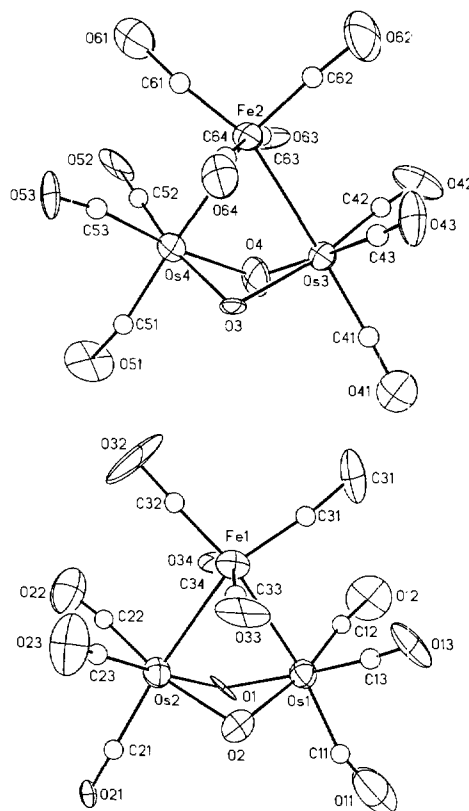
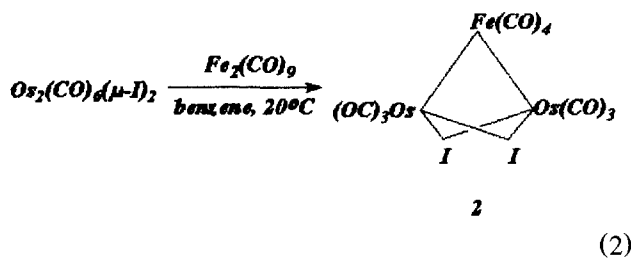


Fig. 1. Two independent molecules of  $\text{Os}_2\text{Fe}(\text{CO})_{10}(\mu\text{-OH})_2$  (**1**). Some bond distances (Å): Os(1)–Os(2), 3.052(4); Os(1)–Fe(1), 2.75(1); Os(2)–Fe(1), 2.76(1); Os(1)–O(1), 2.08(3); Os(2)–O(1), 2.12(3); Os(1)–O(2), 2.11(4); Os(2)–O(2), 2.14(4); Os(3)–Os(4), 3.041(4); Os(3)–Fe(2), 2.733(9); Os(4)–Fe(2), 2.756(8); Os(3)–O(3), 2.17(4); Os(4)–O(3), 2.11(4); Os(3)–O(4), 2.14(5); Os(4)–O(4), 2.14(5); Os–C(CO), 1.71(8)–2.00(9), av. 1.89(8); Fe–C(CO), 1.70(7)–1.83(7), av. 1.76(5); C–O(CO), 1.03(6)–1.34(8), av. 1.16(8).

The structure of cluster **2** is based on elemental analyses, the mass spectrum, and mainly from the similarity of its infrared spectrum in the carbonyl absorption region to that of **1**. The electron-impact mass spectrum

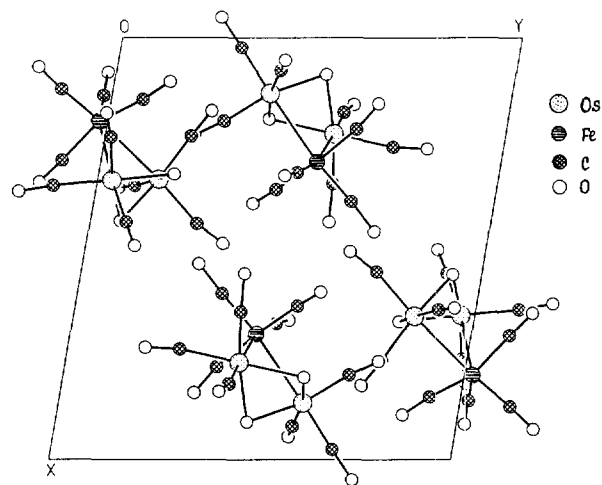


Fig. 2. Crystal packing of  $\text{Os}_2\text{Fe}(\text{CO})_{10}(\mu\text{-OH})_2$  molecules in projection along Z axis.

of this cluster is also reasonably informative. It contains the parent molecular ion with  $m/z$  974 (the intensity about 20%), and a series of ions ( $M^+ - nCO$ ) ( $n = 1, 2, \dots, 10$ ),  $Os_2FeC^+$ ,  $Os_2Fe^+$ ,  $Os_2C^+$ ,  $Os_2^+$ . It is noteworthy that cluster **1** has the same fragmentation pattern under the electron impact as **2**.

Complex **2** is stable in the solid state, but in solution it slowly decomposes, preventing the isolation of a single crystal. Chromatographic analyses and IR spectra showed that the main products of decomposition of **2** are the initial complex  $Os_2(CO)_6(\mu-1)_2$  (ca. 65%) and  $FeOs_2(CO)_{12}$  (ca. 28%) as well as  $Os_3(CO)_{12}$  (ca. 7%). On long standing of **2** in the  $CH_2Cl_2$ –hexane solution, single crystals of the co-crystallate  $Os_2Fe(CO)_{12} \cdot 0.41Os_3(CO)_{12}$  (**3**) were obtained and studied by mass spectroscopy, t.l.c. and X-ray analysis.

The mass spectrum of the co-crystallate **3** displays both the  $Os_2Fe(CO)_{12}$  ( $m/e$  856) and  $Os_3(CO)_{12}$  ( $m/e$  912) molecular peaks as well as the peaks corresponding to a successive loss of 12 CO groups for both clusters. Chromatography on silufol (hexane) displays two spots corresponding to  $Os_2Fe(CO)_{12}$  ( $R_f = 0.32$ ) and  $Os_3(CO)_{12}$  ( $R_f = 0.43$ ), the first being more intensive.

The molecular structure and the crystal packing of **3** are shown in Figs. 3 and 4 respectively. The analysis of the cell dimensions and atomic coordinates in **3** shows that it is isostructural with  $Os_3(CO)_{12}$  [10]. The average metal–metal distances (2.8382 Å) are shorter than those in  $Os_3(CO)_{12}$  (av. Os–Os bond 2.886 Å) and longer than in  $OsFe_2(\mu-CO)_2(CO)_{10}$  (Os–Fe bonds 2.735 and 2.746 Å) [11]. This means that all metal atom positions are partially occupied by Os and Fe together. The refinement of the Os/Fe occupation factors gives the following results: in M(1) Os = 74.4(7)%, Fe = 25.6(7)%; in M(2) Os = 78.8(7)%, Fe = 21.2(7)%; in M(3) Os = 75.9(7)%, Fe = 24.1(7)%. This means that the crystallographically independent part of the unit cell

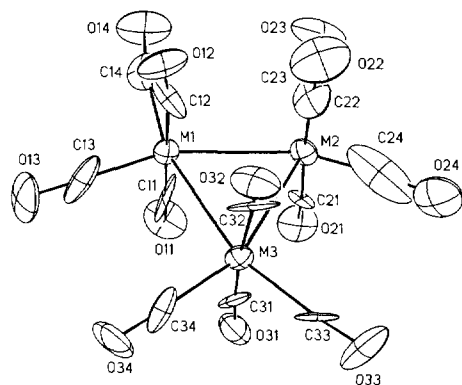


Fig. 3. Molecule of  $Os_2Fe(CO)_{12}$  (50% probability ellipsoids). Some bond distances (Å): M(1)–M(2), 2.8464(8); M(1)–M(3), 2.8351(8); M(2)–M(3), 2.8332(8); M–C(CO), 1.83(1)–1.93(1), av. 1.89(3); C–O(CO), 1.12(1)–1.18(1), av. 1.15(2).

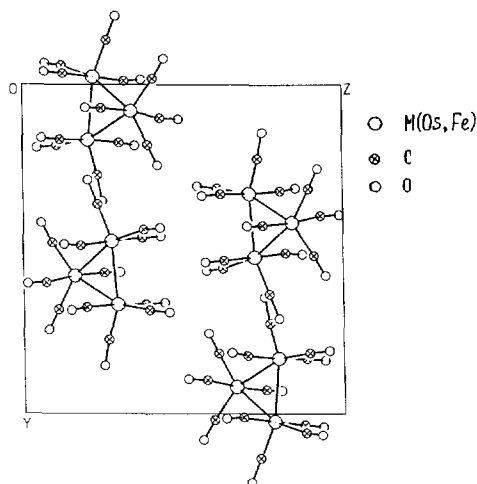


Fig. 4. Crystal packing of  $Os_2Fe(CO)_{12}$  molecules in projection along X axis.

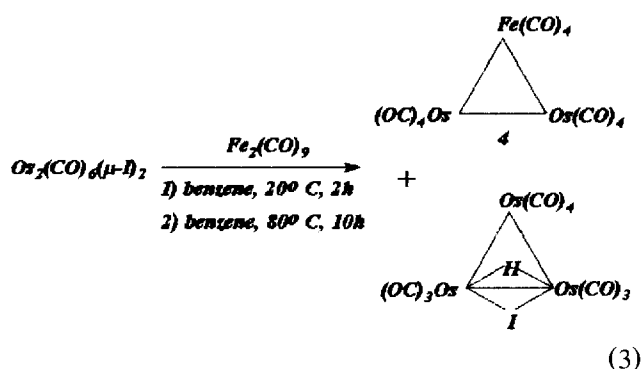
has the formula  $Os_{2.29}Fe_{0.71}(CO)_{12}$ . We propose the following interpretation of this result: the unit cell content can result from either  $[Os_3(CO)_{12}] \cdot 0.41[Fe_3(CO)_{12}]$  or  $[Os_2Fe(CO)_{12}] \cdot 0.41[Os_3(CO)_{12}]$  mixed crystal. However, the first explanation must be rejected because the presence of the heterometallic cluster is clearly visible from t.l.c. data, and in the mass spectrum of the crystals the intensities of the  $Os_3(CO)_{12}$  molecular fragment peaks are about three times lower than those corresponding to  $Os_2Fe(CO)_{12}$ ; the peaks corresponding to  $Fe_3(CO)_{12}$  are absent.

The second explanation means that **3** contains the  $Os_2Fe(CO)_{12}$  cluster disordered with respect to the rotation around the threefold pseudoaxis in such a manner that the carbonyl groups take the same positions in all three orientations, and a portion of the Fe atom can be found in all metal positions. The acceptability of this interpretation is suggested by two facts: first, **3** is isostructural with  $Os_3(CO)_{12}$  and has the cell dimensions slightly larger and M–M bonds shorter than Os–Os in  $Os_3(CO)_{12}$  [10] and longer than those in  $OsFe_2(\mu-CO)_2(CO)_{10}$  [11]; second, the idealized point symmetry of **3** ( $C_{2v}$ ) is consistent with the disorder model proposed.

In this case the independent  $Os_{2.29}Fe_{0.71}(CO)_{12}$  part of the unit cell can be formulated as  $[Os_2Fe(CO)_{12}] \cdot 0.41[Os_3(CO)_{12}]$ . This means that the ratio between the 'pure'  $Os_2Fe(CO)_{12}$  and 'pure'  $Os_3(CO)_{12}$  in the unit cells is equal to 2.45:1.

The similarity of the molecular structures of **3** and  $Os_3(CO)_{12}$  indicates that in both clusters all carbonyl groups occupy terminal positions, whereas in  $OsFe_2(\mu-CO)_2(CO)_{10}$  [7] as well as in  $Fe_3(\mu-CO)_2(CO)_{10}$  [12] there are two bridging carbonyl groups at Fe–Fe bonds. This suggests that once again there is no Fe–Fe bond in **3**.

The formation of  $\text{Os}_2\text{Fe}(\text{CO})_{12}$  when  $\text{Os}_2\text{Fe}(\mu\text{-I})_2(\text{CO})_{10}$  decomposes in solution stimulated us to investigate the reaction in Eq. (2) more thoroughly. With increasing reaction time, two additional products were revealed by t.l.c. The formation of these complexes is increased upon heating the reaction mixture. On stirring of the reaction mixture for 2 h at room temperature followed by refluxing for 10 h the initially formed **2** was converted almost completely to  $\text{Os}_2\text{Fe}(\text{CO})_{12}$  and  $(\mu\text{-H})\text{Os}_3(\mu\text{-I})(\text{CO})_{10}$ :



The reaction in Eq. (3) is a more promising route to prepare the cluster  $\text{Os}_2\text{Fe}(\text{CO})_{12}$  compared to the procedure previously described in Ref. [3] because it employs the more easily handled reagent and results in a rather high (70%) yield of  $\text{Os}_2\text{Fe}(\text{CO})_{12}$ .

Thus we have developed the syntheses of two new heterometallic clusters  $\text{Os}_2\text{Fe}(\text{CO})_{10}(\mu\text{-X})_2$  ( $\text{X} = \text{OH}$ ,  $\text{I}$ ) and improved the preparation method for the known  $\text{Os}_2\text{Fe}(\text{CO})_{12}$  complex. This allows us to start studying the coordination and activation of different ligands on the  $\text{Os}_2\text{Fe}(\text{CO})_{12}$  cluster in comparison with well-studied analogous reactions of  $\text{Os}_3(\text{CO})_{12}$ .

### 3. Experimental section

#### 3.1. General procedures

All reactions were carried out under an argon atmosphere. Before use the solvents were dried and distilled by standard procedures. Water and aqueous  $\text{H}_3\text{PO}_4$  (70%) were deoxygenated by bubbling argon. IR spectra were recorded on a Specord IR-75 spectrometer, mass spectra were recorded on an MX-1310 device (70 eV), whereas the  $^1\text{H}$  NMR spectrum was recorded on a Bruker SXP 4-100 spectrometer.

#### 3.2. Starting compounds

The complexes  $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$  [11],  $\text{Os}_2(\text{CO})_6(\mu\text{-I})_2$  [11],  $\text{Na}_2[\text{Fe}(\text{CO})_4]$  [13] and  $\text{Fe}_2(\text{CO})_9$  [14] were prepared by described procedures.

#### 3.3. Preparation of $\text{Os}_2\text{Fe}(\text{CO})_{10}(\mu\text{-OH})_2$ (**1**)

A suspension of  $\text{Na}_2[\text{Fe}(\text{CO})_4]$  (150 mg,  $7.07 \times 10^{-4}$  mol) in 20 ml of pentane was added to a suspension of  $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$  (141 mg,  $1.89 \times 10^{-4}$  mol) in 10 ml of  $\text{H}_2\text{O}$  and the mixture was stirred at room temperature for 6 h. The brown solution was subsequently filtered and acidified with 70%  $\text{H}_3\text{PO}_4$  in the presence of ether. The ether layer was separated, dried with  $\text{MgSO}_4$ , concentrated and chromatographed on a silica gel column. Hexane elution afforded green  $\text{Fe}_3(\text{CO})_{12}$  and bright-yellow  $\text{Os}_2\text{Fe}(\text{CO})_{10}(\mu\text{-OH})_2$  (**1**). After acidification all manipulations were conducted in air. Yield of **1** 28 mg (20.1%). IR (cyclohexane,  $\text{cm}^{-1}$ ): 2104w, 2077s, 2030s, 2011s, 1982m, 1965m, 1935w ( $\nu_{\text{CO}}$ ); 3518w, 3387vw ( $\nu_{\text{OH}}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ;  $\delta$  ppm): 2.12 s. MS:  $m/z$  754 ( $^{192}\text{Os}$ ,  $\text{M}^+$ ).

A single crystal of **1** was obtained from a 1:3  $\text{CHCl}_3$ -hexane solution.

#### 3.4. Preparation of $\text{Os}_2\text{Fe}(\text{CO})_{10}(\mu\text{-I})_2$ (**2**)

$\text{Fe}_2(\text{CO})_9$  (100 mg,  $2.75 \times 10^{-4}$  mol) was added to 10 ml of benzene solution of  $\text{Os}_2(\text{CO})_6(\mu\text{-I})_2$  (46 mg,  $5.73 \times 10^{-5}$  mol). The initial yellow solution turned red after 5 h stirring at room temperature. The solution was filtered, evaporated to dryness and the residue was chromatographed on thin-layer silica plates using hexane as the eluent. The fractions resulted in the following

Table 1  
Crystallographic data for  $\text{Os}_2\text{Fe}(\text{CO})_{10}(\mu\text{-OH})_2$  (**1**) and  $\text{Os}_2\text{Fe}(\text{CO})_{12} \cdot 0.41\text{Os}_3(\text{CO})_{12}$  (**3**)

	<b>1</b>	<b>3</b>
Formula	$\text{C}_{10}\text{H}_2\text{FeO}_{12}\text{Os}_2$	$\text{C}_{12}\text{O}_{12}\text{Fe}_{0.71}\text{Os}_{2.29}$
Molecular weight	750.4	811.3
Crystal system	triclinic	monoclinic
Space group, Z	$P\bar{1}$ , 4	$P2_1/n$ , 4
$a$ (Å)	14.009(6)	8.056(2)
$b$ (Å)	13.330(4)	14.743(2)
$c$ (Å)	9.511(2)	14.520(2)
$\alpha$ (deg)	103.69(2)	
$\beta$ (deg)	81.83(3)	100.62(1)
$\gamma$ (deg)	102.22(3)	
$V$ (Å <sup>3</sup> )	1699(1)	1695(05)
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	2.969	3.179
Crystal dimensions (mm <sup>3</sup> )	0.01 × 0.09 × 0.15	0.10 × 0.20 × 0.22
Crystal colour	yellow	red-orange
Diffractometer	Syntex P2 <sub>1</sub>	CAD-4
Radiation	Mo K $\alpha$	Mo K $\alpha$
$\mu$ ( $\text{cm}^{-1}$ )	160.1	177.9
Absorption correction	none	2 $\psi$ -curves
Total reflections	4525, $2\theta < 45^\circ$	2857, $2\theta < 45^\circ$
Reflections used	2399 $F_{hkl} > 6\sigma(F)$	2667
$R_F$	0.0930	0.0250 for 1997 $F > 4\sigma(F)$ 0.0435 for all data

order: unreacted  $\text{Os}_2(\text{CO})_6(\mu\text{-I})_2$  (yellow);  $\text{Os}_2\text{Fe}(\text{CO})_{10}(\mu\text{-I})_2$  (orange) (**2**). Yield of **2** 34 mg (66.6% of reacted  $\text{Os}_2(\text{CO})_6(\mu\text{-I})_2$ ). Anal.: calcd for  $\text{C}_{10}\text{FeI}_2\text{O}_{10}\text{Os}_2 \cdot \frac{1}{3}\text{C}_6\text{H}_{14}$ : C, 14.43; H, 0.43 Os, 38.08; Fe, 5.52; I, 25.44. Found: C, 14.11; H, 0.44; Fe, 5.83; I, 25.06; Os, 38.51%. IR (cyclohexane,  $\text{cm}^{-1}$ ): 2104w,

Table 2  
Atomic coordinates and equivalent thermal parameters ( $\text{\AA}^2$ ) for  $\text{Os}_2\text{Fe}(\text{CO})_{10}(\mu\text{-OH})_2$  (**1**)

Atom	x	y	z	$U_{\text{eq}}^a$
Os(1)	0.6632(2)	0.8482(2)	0.4645(3)	0.0353(7)
Os(2)	0.6610(2)	0.9645(2)	0.2247(3)	0.0372(7)
Fe(1)	0.8016(7)	1.0206(7)	0.418(1)	0.038(2)
O(1)	0.676(2)	0.812(3)	0.238(3)	0.025(9)
O(2)	0.564(3)	0.927(3)	0.408(4)	0.03(1)
O(11)	0.509(9)	0.660(6)	0.513(8)	0.13(3)
O(12)	0.826(3)	0.746(4)	0.505(6)	0.08(2)
O(13)	0.644(4)	0.945(4)	0.781(5)	0.07(2)
O(21)	0.505(3)	0.879(4)	0.020(6)	0.07(2)
O(22)	0.821(4)	1.006(4)	-0.009(6)	0.08(2)
O(23)	0.635(4)	1.191(3)	0.268(5)	0.07(2)
O(31)	0.917(5)	1.020(6)	0.664(5)	0.12(2)
O(32)	0.930(4)	1.195(4)	0.317(6)	0.13(2)
O(33)	0.657(3)	1.143(4)	0.590(6)	0.08(2)
O(34)	0.895(3)	0.861(3)	0.204(5)	0.06(1)
C(11)	0.557(4)	0.735(4)	0.481(6)	0.03(1)
C(12)	0.767(5)	0.787(5)	0.482(7)	0.05(2)
C(13)	0.648(5)	0.906(5)	0.664(8)	0.05(2)
C(21)	0.561(4)	0.912(4)	0.097(6)	0.02(1)
C(22)	0.764(7)	0.986(7)	0.08(1)	0.08(3)
C(23)	0.648(6)	1.108(7)	0.235(9)	0.06(2)
C(31)	0.862(4)	1.021(4)	0.571(6)	0.03(1)
C(32)	0.876(6)	1.127(6)	0.361(8)	0.07(2)
C(33)	0.709(5)	1.096(5)	0.518(6)	0.04(1)
C(34)	0.853(5)	0.921(5)	0.291(7)	0.04(2)
Os(3)	0.1333(2)	0.3928(2)	0.1142(3)	0.0302(7)
Os(4)	0.2283(2)	0.5685(2)	-0.0425(3)	0.0357(7)
Fe(2)	0.2953(6)	0.5377(6)	0.200(1)	0.033(2)
O(3)	0.088(2)	0.524(3)	0.062(4)	0.026(9)
O(4)	0.193(3)	0.401(3)	-0.104(6)	0.07(1)
O(41)	-0.049(3)	0.238(3)	0.006(5)	0.06(1)
O(42)	0.231(4)	0.221(4)	0.146(5)	0.07(2)
O(43)	0.054(4)	0.415(3)	0.425(5)	0.06(1)
O(51)	0.160(3)	0.606(4)	-0.315(4)	0.07(1)
O(52)	0.439(3)	0.594(4)	-0.188(6)	0.08(2)
O(53)	0.264(4)	0.808(3)	0.095(6)	0.07(2)
O(61)	0.462(4)	0.711(3)	0.205(5)	0.06(1)
O(62)	0.328(4)	0.463(4)	0.456(5)	0.08(2)
O(63)	0.394(3)	0.396(3)	-0.013(4)	0.05(1)
O(64)	0.157(3)	0.668(3)	0.365(4)	0.05(1)
C(41)	0.024(5)	0.300(5)	0.054(7)	0.04(2)
C(42)	0.198(4)	0.289(4)	0.133(5)	0.02(1)
C(43)	0.078(5)	0.409(5)	0.315(7)	0.03(1)
C(51)	0.178(4)	0.585(5)	-0.218(7)	0.04(2)
C(52)	0.347(6)	0.587(6)	-0.120(8)	0.05(2)
C(53)	0.260(6)	0.722(7)	0.047(9)	0.07(2)
C(61)	0.390(5)	0.640(5)	0.197(7)	0.04(2)
C(62)	0.320(6)	0.493(6)	0.344(9)	0.08(2)
C(63)	0.361(4)	0.448(5)	0.067(7)	0.03(1)
C(64)	0.218(5)	0.623(5)	0.294(7)	0.05(2)

<sup>a</sup> Equivalent isotropic  $U$  defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 3  
Atomic coordinates ( $\times 10^4$ ) and equivalent thermal parameters ( $\text{\AA}^2 \times 10^2$ ) for  $\text{Os}_{2.29}\text{Fe}_{0.71}(\text{CO})_{12}$

Atom	x	y	z	$U_{\text{eq}}^a$
M(1) <sup>b</sup>	4429(1)	-237(1)	2229(1)	29(1)
M(2) <sup>c</sup>	4427(1)	1687(1)	2069(1)	31(1)
M(3) <sup>d</sup>	6951(1)	805(1)	3381(1)	27(1)
C(1)	5809(14)	-304(7)	1303(8)	40(3)
O(1)	6591(11)	-411(6)	713(5)	59(3)
C(2)	3046(16)	-154(8)	3175(8)	45(3)
O(2)	2197(12)	-170(7)	3709(6)	66(3)
C(3)	5171(14)	-1355(8)	2673(8)	42(3)
O(3)	5663(12)	-2070(6)	2965(6)	65(3)
C(4)	2495(16)	-497(8)	1313(8)	46(3)
O(4)	1311(11)	-655(8)	769(6)	84(3)
C(5)	5852(14)	1623(8)	1171(8)	41(3)
O(5)	6668(11)	1641(6)	590(5)	58(2)
C(6)	2993(15)	1768(9)	2982(8)	51(3)
O(6)	2075(12)	1854(7)	3489(6)	73(3)
C(7)	2538(15)	1827(8)	1101(8)	42(3)
O(7)	1395(12)	1927(7)	510(6)	77(3)
C(8)	5158(15)	2860(9)	2369(8)	46(3)
O(8)	5625(13)	3580(6)	2567(7)	71(3)
C(9)	8364(13)	713(7)	2466(7)	35(2)
O(9)	9330(10)	677(6)	1964(5)	52(2)
C(10)	5548(13)	951(7)	4296(7)	35(3)
O(10)	4809(11)	1058(6)	4884(5)	55(2)
C(11)	8204(14)	1813(8)	3907(7)	38(3)
O(11)	8960(11)	2431(6)	4220(6)	63(3)
C(12)	8104(16)	-196(7)	4051(7)	39(3)
O(12)	8752(10)	-791(6)	4447(5)	56(2)

<sup>a</sup> Equivalent isotropic  $U$  defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

<sup>b</sup> Content: 0.744(7)Os + 0.256(7)Fe.

<sup>c</sup> Content: 0.788(7)Os + 0.212(7)Fe.

<sup>d</sup> Content: 0.759(7)Os + 0.241(7)Fe.

2077s, 2042s, 2017s, 1998m, 1979m, 1975m ( $\nu_{\text{CO}}$ ). MS:  $m/z$  974 ( $^{192}\text{Os}$ ,  $\text{M}^+$ ).

On long standing of a 1:3  $\text{CH}_2\text{Cl}_2$ -hexane solution of **2** the co-crystallate  $\text{Os}_2\text{Fe}(\text{CO})_{12} \cdot 0.41\text{Os}_3(\text{CO})_{12}$  (**3**) was obtained. IR (cyclohexane,  $\text{cm}^{-1}$ ): 2099w, 2079m, 2070s, 2046vs, 2020s, 2010m, 2003m, 1982m, 1991w ( $\nu_{\text{CO}}$ ). MS:  $m/z$  912 and 776 ( $^{192}\text{Os}$ ,  $\text{M}^+$ ).

### 3.5. Preparation of $\text{Os}_2\text{Fe}(\text{CO})_{12}$ (**4**)

$\text{Fe}_2(\text{CO})_9$  (200 mg,  $5.49 \times 10^{-4}$  mol) was added to 35 ml of benzene solution of  $\text{Os}_2(\text{CO})_6(\mu\text{-I})_2$  (56 mg,  $6.98 \times 10^{-5}$  mol). The solution was stirred at room temperature for 2 h and then refluxed for 10 h, the initially yellow solution turning red-brown. The solution was filtered, evaporated to dryness and the residue was chromatographed on a silica gel column using hexane as eluent. The fractions resulted in the following order: unreacted  $\text{Os}_2(\text{CO})_6(\mu\text{-I})_2$  (yellow, 10 mg);  $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-I})$  (dark-yellow, 13 mg, 23.2%);  $\text{Os}_3(\text{CO})_{12}$  (yellow, 4 mg);  $\text{Fe}_3(\text{CO})_{12}$  (green);  $\text{Os}_2\text{Fe}(\text{CO})_{10}(\mu\text{-I})_2$  (orange, trace);  $\text{Os}_2\text{Fe}(\text{CO})_{12}$  (**4**) (red, 28.6 mg, 69.6%). The  $R_f$  value and IR data of **4**

(in  $C_6H_{14}$ ) were similar to those resulting from another preparation [3].

### 3.6. X-ray diffraction measurements

The structures of  $Os_2Fe(CO)_{10}(\mu-OH)_2$  (**1**) and  $Os_2Fe(CO)_{12} \cdot 0.41 Os_3(CO)_{12} \equiv Os_{2.29}Fe_{0.71}(CO)_{12}$  (**3**) were determined by X-ray structural analysis. The unit cell parameters and reflection intensities were obtained by the standard procedure (see Table 1). The structures were solved by direct methods using the SHELX-86 program [15] and refined by block-diagonal (**1**) and full-matrix (**3**) least squares methods in an anisotropic approximation for Os, Fe, O atoms in **1** and for all non-hydrogen atoms in **3** using the SHELX-93 program [16]. Hydrogen atoms were not located. Atomic coordinates are given in Tables 2 and 3. The high value of *R*-factor for **1** might be explained by insufficient crystal quality. The selected bond lengths are given in the captions for Figs. 1 and 3.

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