

Reactions of  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$  with  $[\text{Rh}(\text{COD})(\text{L})\text{I}]$   
(COD = cycloocta-1,5-diene; L = 2,2'-bipyridine, 1,10-phenanthroline  
and 4,4'-diphenyl-2,2'-dipyridyl): crystal and molecular structures of  
 $[\text{Os}_3\text{Rh}(\mu\text{-H})_3(\text{CO})_{10}(\eta^4\text{-COD})]$ ,  
 $[\text{Os}_3\text{Rh}(\mu\text{-H})_2(\text{CO})_8(\mu\text{-CO})(\mu\text{-I})(\eta^4\text{-COD})]$  and  
 $[\text{Os}_3\text{Rh}(\mu\text{-H})_2(\text{CO})_8(\mu\text{-CO})(\mu\text{-I})(\text{bipy})]$

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**Abstract**

The co-ordinatively unsaturated dihydride cluster  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$  reacts with  $[\text{Rh}(\text{COD})(\text{L})\text{I}]$  (COD = cycloocta-1,5-diene; L = 2,2'-bipyridine, 1,10-phenanthroline and 4,4'-diphenyl-2,2'-dipyridyl) to give a family of hydrido heterometallic clusters  $[\text{Os}_3\text{Rh}(\mu\text{-H})_3(\text{CO})_{10}(\eta^4\text{-COD})]$  **1**,  $[\text{Os}_3\text{Rh}(\mu\text{-H})_2(\text{CO})_8(\mu\text{-CO})(\mu\text{-I})(\eta^4\text{-COD})]$  **2**,  $[\text{Os}_3\text{Rh}(\mu\text{-H})_2(\text{CO})_8(\mu\text{-CO})(\mu\text{-I})(\text{bipy})]$  **3**,  $[\text{Os}_3\text{Rh}(\mu\text{-H})_2(\text{CO})_8(\mu\text{-CO})(\mu\text{-I})(1,10\text{-phen})]$  **4**,  $[\text{Os}_3\text{Rh}(\mu\text{-H})_2(\text{CO})_8(\mu\text{-CO})(\mu\text{-I})(4,4'\text{-diphbipy})]$  **5** and  $[\text{Os}_3(\text{CO})_{12}]$  in moderate yields. The crystal structures of **1–3** were established by X-ray diffraction method; **1** and **2** comprise a saturated tetrahedral  $\text{Os}_3\text{Rh}$  core in which the rhodium atom is  $\eta^4$ -co-ordinated by a COD ligand. In structure **3–5**, a bidentate N-donor ligand chelates to the rhodium metal centre instead of the COD ligand. Clusters **1–5** were fully characterized by IR and  $^1\text{H-NMR}$  spectroscopy, mass spectrometry and elemental analysis. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Osmium; Rhodium; Clusters; Hydrido-clusters

**1. Introduction**

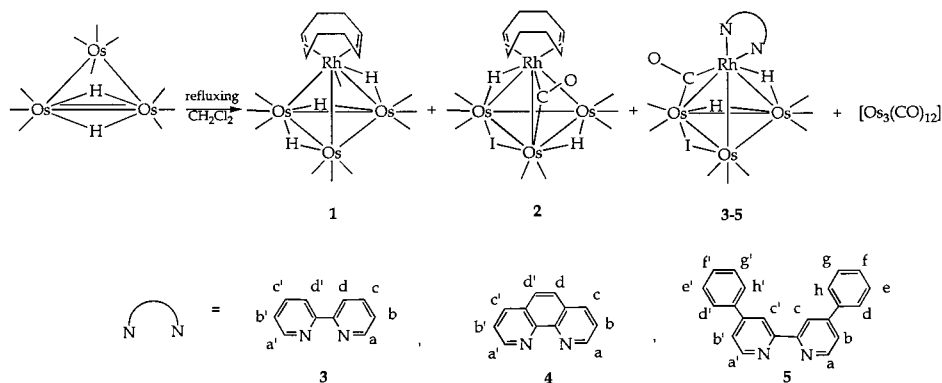
The chemistry of mixed-metal carbonyl clusters remains an active area of research interest [1]. The presence of the inherent polarity in the mixed-metal bonds results in greater reactivity and selectivity in ligands binding than the analogous homometal complexes [2–4]. Besides the osmium–palladium cluster, [5] we are recently interested in the chemistry of mixed-metal clusters containing osmium–rhodium bonds. Rhodium, like palladium ion, can attain either a 16- or 18-electron configuration which is an important feature for cata-

lytic processes while osmium clusters display rich chemistry and are kinetically stable.

In the course of the investigation, two novel high nuclearity clusters,  $[\text{Os}_{12}\text{Rh}_9(\text{CO})_{44}(\mu_3\text{-Cl})]$  and  $[\text{Os}_4\text{Rh}_3(\mu_3\text{-H})(\text{CO})_{14}(\eta^4\text{-NBD})_2]$  were obtained by the redox condensation of  $[(\text{Ph}_3\text{P})_2\text{N}][\text{Os}_3(\mu\text{-H})(\text{CO})_{11}]$  with  $[\text{Rh}(\text{NBD})\text{Cl}]_2$  (NBD = norbornadiene) in the presence of  $\text{AgPF}_6$  [6].

Although a range of tetranuclear osmium–rhodium mixed-metal clusters have been prepared previously by the reaction of  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$  with some rhodium-cyclopentadienyl reagents, [7–12] there is no example of Os–Rh mixed-metal clusters containing N-donor ligands reported. Herein we describe the preparation of new osmium–rhodium hydrido carbonyl clusters gener-

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Scheme 1.  $[\text{Rh}(\text{COD})(\text{L})\text{I}]$ , reflux,  $\text{CH}_2\text{Cl}_2$ ; (COD = cycloocta-1,5-diene; L = 2,2'-bipyridine, 1,10-phenanthroline and 4,4'-diphenyl-2,2'-dipyridyl).

ated from the reaction of the unsaturated triosmium cluster  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$  with rhodium reagents containing a labile COD group and N-donor ligand, namely  $[\text{Rh}(\text{COD})(\text{L})\text{I}]$  (COD = cycloocta-1,5-diene; L = 2,2'-bipyridine, 1,10-phenanthroline and 4,4'-diphenyl-2,2'-dipyridyl).

## 2. Results and discussion

### 2.1. Synthesis

Attempts to synthesize triosmium-based mixed metal clusters of rhodium were made by employing a rhodium complex comprising a bidentate N-donor ligand together with a labile substituent such as cycloocta-1,5-diene (COD). The bidentate N-donor ligands such as 2,2'-bipyridine (bipy), 1,10-phenanthroline (1,10-phen) and 4,4'-diphenyl-2,2'-dipyridyl (4,4'-diphbipy) were used instead of monodentate ligands so as to stabilise the products and allow ease of characterization [13]. Treatment of  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$  with one equivalent  $[\text{Rh}(\text{COD})(\text{bipy})\text{I}]$  in refluxing  $\text{CH}_2\text{Cl}_2$  gave a series of clusters with a common tetrahedral  $\text{Os}_3\text{Rh}$  core. These complexes were fully characterized by both spectroscopic and crystallographic techniques. The formulae of cluster **1** was first established by FAB MS and  $^1\text{H-NMR}$  to be  $[\text{Os}_3\text{Rh}(\mu\text{-H})_3(\text{CO})_{10}(\eta^4\text{-COD})]$  and confirmed by X-ray crystallography. In fact, **1** had been previously prepared from the substitution reaction of  $[\text{Os}_3\text{Rh}(\mu\text{-H})_3(\text{CO})_{12}]$  with an excess of COD in the presence of  $\text{Me}_3\text{NO}$  [10]. The major products of the title reaction were iodide-bridged clusters  $[\text{Os}_3\text{Rh}(\mu\text{-H})_2(\text{CO})_8(\mu\text{-CO})(\mu\text{-I})(\eta^4\text{-COD})]$  **2** and  $[\text{Os}_3\text{Rh}(\mu\text{-H})_2(\text{CO})_8(\mu\text{-CO})(\mu\text{-I})(\text{bipy})]$  **3**. Similar reactions between  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$  and rhodium cyclooctadiene complexes containing other bidentate N-donor ligands  $[\text{Rh}(\text{COD})(\text{L})\text{I}]$  also resulted in the formation of **1**, **2**,  $[\text{Os}_3\text{Rh}(\mu\text{-H})_2(\text{CO})_8(\mu\text{-CO})(\mu\text{-I})(\text{L})]$  L = 1,10-phenanthroline **4** and 4,4'-diphenyl-2,2'-dipyridyl **5**, see Scheme 1.

### 2.2. Spectroscopic analyses of the complexes 1–5

The spectroscopic (IR,  $^1\text{H-NMR}$  and mass) (Table 1) and analytical data are fully consistent with the observed structures in the solid-state. The solution IR spectra of **2–5** indicate the presence of bridging CO groups in the molecules. Mass spectra of **1–5** obtained from positive FAB techniques show a parent ion envelope and daughter ion envelope corresponding to successive CO losses. The  $^1\text{H-NMR}$  spectrum of **1** shows two multiplets of integration 4:8 which are attributed to the coordinated COD ligand. There are three upfield resonance signals with an integral ratio of 1:1:1. The two broad singlets at  $\delta -18.33$  and  $\delta -19.08$  were assigned to hydrides bridging Os–Os edges and the doublet at  $\delta -15.08$ , due to the coupling with  $^{103}\text{Rh}$  ( $J_{\text{RhH}} = 13$  Hz), was assigned to the hydride bridging an Os–Rh edge. Although such broad signals normally indicate some dynamic processes of the cluster may be occurring in solution, the  $^1\text{H-NMR}$  properties of **1** remains unchanged even at low temperature ( $-50^\circ\text{C}$ ).

However, the  $^1\text{H-NMR}$  spectroscopic properties of **2** are more complicated. Two sets of resonances corresponding to two isomers in an approximate ratio of 1:2 are observed. The multiplets centred at  $\delta 5.43$ ,  $\delta 5.09$ ,  $\delta 4.79$  and  $\delta 4.61$  with integral ratio of 1:1:1:1, are attributed to the olefinic CH of the coordinated COD ligand of the major isomer. The resonances due to methylene hydrogens are observed as three multiplets centred at  $\delta 2.62$ ,  $\delta 2.38$  and  $\delta 1.98$  with a total of integral of 8. The signals due to the minor isomer are found at  $\delta 5.61$  (olefinic CH) and  $\delta 2.86$  (methylene CH). In the upfield region, the resonance signals due to the hydrides in the major isomer are observed at  $\delta -18.2$  as a doublet ( $J_{\text{RhH}} = 21$  Hz) and at  $\delta -19.15$  as a singlet while the minor isomer shows a singlet at  $\delta -17.5$ . The  $^1\text{H-NMR}$  signals due to the major isomer are consistent with the observed solid-state structure of **2** as it contains a hydride bridging an Os–Rh edge. The occurrence of the minor isomer may be due to the rearrangement of the hydride ligands on the cluster

Table 1  
Spectroscopic data for complexes 1–5

Complex	IR spectra, $\nu/\text{cm}^{-1}$	Mass spectra, <sup>b</sup>	<sup>1</sup> H-NMR spectra, <sup>c</sup>
1	2091m, 2070s, 2045s, 2030w, 2012s, 2005s, 1993w, 1979m, 1972w	1065(1065)	5.24 (m, 4H, CH), 2.45 (m, 8H, CH <sub>2</sub> ), –15.18 (d, 1H, $J_{\text{RhH}} = 13$ , RhHOs), –18.33 (s, 1H, OsHOs), –19.08 (s, 1H, OsHOs)
2	2082m, 2064m, 2053m, 2033s, 1997s, 1976m, 1960w, 1933w, 1815w, 1742w	1163(1164)	Isomer A: 5.43 (m, 1H, CH), 5.09 (m, 1H, CH), 4.99 (m, 1H, CH), 4.61 (m, 1H, CH), 2.62 (m, 2H, CH <sub>2</sub> ), 2.38 (m, 4H, CH <sub>2</sub> ), 1.98 (m, 2H, CH <sub>2</sub> ), –18.20 (d, 1H, $J_{\text{RhH}} = 21\text{Hz}$ , RhHOs), –19.5 (s, 1H, OsHOs). Isomer B: 5.61 (m, 4H, CH), 2.86 (m, 8H, CH <sub>2</sub> ), –17.50 (s, 2H, OsHOs)
3	2099w, 2068s, 2030s, 2015s, 1966m, 1916w, 1781m	1210(1213)	8.89 (d, 1H, $J_{\text{HH}} = 6$ , H <sup>d</sup> /H <sup>d'</sup> ), 8.76 (d, 1H, $J_{\text{HH}} = 6$ , H <sup>d</sup> /H <sup>d'</sup> ), 8.09 (m, 4H, H <sup>a</sup> , H <sup>a'</sup> , H <sup>c</sup> & H <sup>c'</sup> ), 7.59 (m, 1H, H <sup>b</sup> /H <sup>b'</sup> ), 7.34 (m, 1H, H <sup>b</sup> /H <sup>b'</sup> ), –19.43 (s, 1H, OsHOs), –22.56 (d, 1H, $J_{\text{RhH}} = 34$ , RhHOs)
4	2070s, 2030s, 2015s, 1991m, 1966m, 1918w, 1783m	1234(1235)	9.18 (d, 1H, $J_{\text{HH}} = 5$ , H <sup>a</sup> /H <sup>a'</sup> ), 9.01 (d, 1H, $J_{\text{HH}} = 5$ , H <sup>a</sup> /H <sup>a'</sup> ), 8.64 (d, 1H, $J_{\text{HH}} = 5$ , H <sup>b</sup> /H <sup>b'</sup> ), 8.49 (d, 1H, $J_{\text{HH}} = 6$ , H <sup>b</sup> /H <sup>b'</sup> ), 8.03 (m, 2H, H <sup>c</sup> & H <sup>c'</sup> ), 7.91 (m, 1H, H <sup>d</sup> /H <sup>d'</sup> ), 7.67 (m, 1H, H <sup>d</sup> /H <sup>d'</sup> ), –19.42 (s, 1H, OsHOs), –22.18 (d, 1H, $J_{\text{RhH}} = 25$ , RhHOs)
5	2070s, 2029s, 2015s, 1991m, 1966m, 1916w, 1781m	1362(1363)	8.82 (d, 1H, $J_{\text{HH}} = 5$ , H <sup>a</sup> /H <sup>a'</sup> ), 8.67 (d, 1H, $J_{\text{HH}} = 5$ , H <sup>a</sup> /H <sup>a'</sup> ), 8.27 (m, 4H, H <sup>b</sup> , H <sup>b'</sup> , H <sup>c</sup> & H <sup>c'</sup> ), 7.66 (m, 4H, H <sup>d</sup> , H <sup>d'</sup> , H <sup>e</sup> & H <sup>e'</sup> ), 7.53 (m, 4H, H <sup>c</sup> , H <sup>c'</sup> , H <sup>e</sup> & H <sup>e'</sup> ), 7.42 (m, 2H, H <sup>f</sup> /H <sup>f'</sup> ), –19.50 (s, 1H, OsHOs), –22.39 (d, 1H, $J_{\text{RhH}} = 24$ , RhHOs)

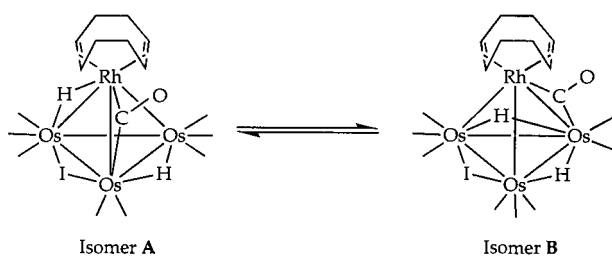
<sup>a</sup> **1,2** in *n*-hexane, **3–5** in CH<sub>2</sub>Cl<sub>2</sub>.

<sup>b</sup> Positive FAB, simulated values in parentheses.

<sup>c</sup> in CDCl<sub>3</sub>, *J* values in Hz.

core. A process is proposed in Scheme 2 which may account for the observed spectroscopic data. The suggested isomer **B** contains a mirror symmetry so that two hydride ligands are equivalent.

The profile of the IR spectra of cluster **3**, **4** and **5** in the region 1600–2200 cm<sup>–1</sup> ( $\nu_{\text{CO}}$ ) are almost identical and suggests that their structures are similar (Table 1). Their <sup>1</sup>H-NMR spectra contain a set of multiplets arising from the bidentate N-donor ligands and two resonances due to hydride ligands. As in the case of **2**, the singlet should be due to the hydride bridging Os–Os bond while the doublet is assigned to the hydride bridging Os–Rh bond.



Scheme 2.

### 2.3. Crystallographic analyses of complexes 1–3·0.5 C<sub>6</sub>H<sub>6</sub>

Single crystals suitable for X-ray analysis of **1** and **2** were obtained from pure *n*-hexane solutions at room temperature (r.t.) whereas crystals of **3** were grown in a CH<sub>2</sub>Cl<sub>2</sub> and benzene solution at room temperature. Perspective drawings of complexes **1** and **2** are shown in Fig. 1 and Fig. 2, respectively, with selected bond lengths and angles given in Table 2 and Table 3. X-ray analyses of **1** and **2** revealed that the metal frameworks constitute distorted Os<sub>3</sub>Rh tetrahedra with COD ligands coordinated to the rhodium atoms in a  $\eta^4$ -co-ordination mode; the co-ordinating double bonds in COD are situated in a plane parallel to the basal plane defined by three osmium metals of the tetrahedron. Similar mixed-metal clusters have been found in the platinum analogues [Os<sub>3</sub>Pt( $\mu$ -H)<sub>2</sub>( $\mu$ -CO)(CO)<sub>9</sub>(COD)] [14] and [Os<sub>3</sub>Pt( $\mu$ -H)<sub>2</sub>(CH<sub>2</sub>)(CO)<sub>9</sub>(COD)] [15]. All carbonyl ligands in **1** are coordinated in a terminal mode. For cluster **1**, three hydrides are believed to bridge Os(1)–Os(3), Os(2)–Os(3) and Os(1)–Rh(1) based on the spectroscopic data (<sup>1</sup>H-NMR) and further supported by the elongated metal–metal bonds. For complex **2**, the Os(1)–Rh(1) bond is coordinated by an asymmetrically bridging carbonyl ligand [Rh(1)–C(3) = 2.30(3) Å, Os(1)–C(3) = 1.89(3) Å] and Os(3)–Rh(1) is bridged by a hydride with the Os(2)–Rh(1)

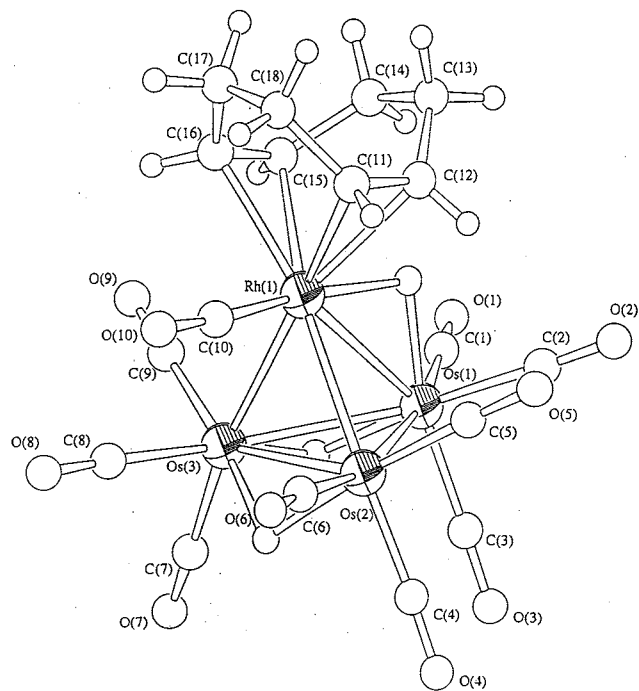


Fig. 1. Molecular structure of cluster **1** showing the atomic labelling scheme for non-hydrogen atoms.

vector being unsupported. Besides, there is an iodide bridge across the Os(1)–Os(3) bond and a hydride ligand bridging the Os(1)–Os(2) edge.

Complex **3** is the only bipyridine-containing product from the reaction as confirmed by both spectroscopic

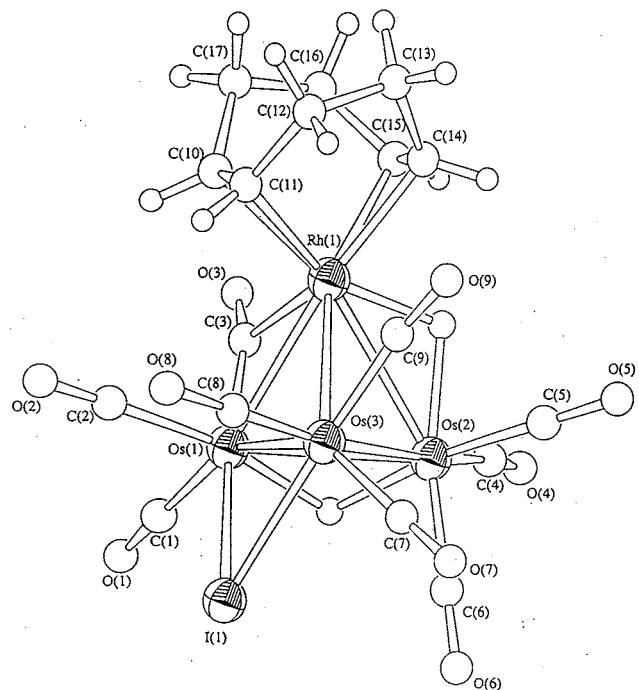


Fig. 2. Molecular structure of cluster **2** showing the atomic labelling scheme for non-hydrogen atoms.

Table 2

Selected bond distances (Å) and angles (°) for cluster **1**

Bond length (Å)			
Os(1)–Os(2)	2.7951(8)	Os(1)–Os(3)	2.9735(8)
Os(2)–Os(3)	2.9189(8)	Os(1)–Rh(1)	2.920(1)
Os(2)–Rh(1)	2.733(1)	Os(3)–Rh(1)	2.739(1)
Os(1)–C(1)	1.92(2)	Os(3)–C(3)	1.92(2)
Rh(1)–C(11)	2.36(1)	Rh(1)–C(12)	2.39(1)
Rh(1)–C(15)	2.39(2)	Rh(1)–C(16)	2.39(2)
C(11)–C(12)	1.35(2)	C(11)–C(18)	1.49(2)
C(12)–C(13)	1.52(2)	C(13)–C(14)	1.51(3)
C(14)–C(15)	1.49(2)	C(15)–C(16)	1.34(2)
C(16)–C(17)	1.52(3)	C(17)–C(18)	1.49(3)
Bond angle (°)			
Os(2)–Os(1)–Os(3)	60.70(2)	Os(1)–Rh(1)–Os(3)	63.30(3)
Os(2)–Rh(1)–C(10)	82.9(5)	C(10)–Rh(1)–C(15)	117.3(7)

and structural analyses. The molecular geometry with atomic labelling of **3** is depicted in Fig. 3 and selected bonding parameters in Table 4. Complex **3** also contains a rhodium atom face capping on the triangular osmium metal framework with the bidentate bipyridine group chelating to the rhodium apex of the tetrahedron. A bridging iodide and carbonyl ligand are found to coordinate across the Os(1)–Os(2) and Os(2)–Rh(1) bonds, respectively. The structures of **2** and **3** are very similar except the chelating ligands on the rhodium atom are different.

We have not been able to obtain suitable single crystals of **4** and **5** for X-ray analysis. However, they are proposed to be isostructural to **3** according to the spectroscopic and elemental analyses. As far as the electron counting rule is concerned, all the clusters **1**–**5** possess 60 cluster valence electrons (c.v.e.) count which is consistent with the tetranuclear clusters with six metal-metal bonds. Hence the rhodium atoms in these clusters adopt 18-electron configuration.

This work showed that nitrogen donor ligands can be incorporated on the cluster core by simple coupling

Table 3

Selected bond distances (Å) and angles (°) for cluster **2**

Bond length (Å)			
Os(1)–Os(2)	2.963(2)	Os(1)–Os(3)	2.842(2)
Os(2)–Os(3)	2.714(2)	Os(1)–Rh(1)	2.778(2)
Os(2)–Rh(1)	2.908(2)	Os(3)–Rh(1)	2.902(2)
Os(1)–I(1)	2.714(2)	Os(3)–I(1)	2.744(2)
Os(1)–C(3)	1.91(3)	Rh(1)–C(3)	2.32(3)
Rh(1)–C(10)	2.22(3)	Rh(1)–C(11)	2.19(3)
Rh(1)–C(14)	2.11(3)	Rh(1)–C(15)	2.17(3)
C(10)–C(11)	1.31(4)	C(10)–C(17)	1.54(4)
C(11)–C(12)	1.54(5)	C(12)–C(13)	1.51(5)
C(13)–C(14)	1.54(5)	C(14)–C(15)	1.34(4)
C(15)–C(16)	1.53(4)	C(16)–C(17)	1.48(4)
Bond angle (°)			
Os(2)–Os(1)–Os(3)	57.31(4)	Os(1)–Rh(1)–Os(3)	59.99(5)
Os(1)–I(1)–Os(3)	62.75(5)	Os(1)–C(3)–Rh(1)	81(1)

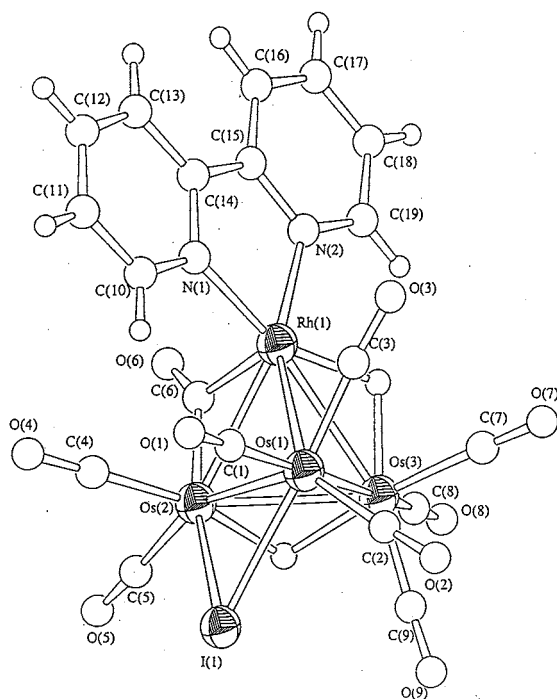


Fig. 3. Molecular structure of cluster **3** showing the atomic labelling scheme for non-hydrogen atoms.

reaction from a metal reagent containing the nitrogen donors although the yields are not high.

### 3. Experimental

#### 3.1. Materials

All reactions and manipulations were carried out under an inert atmosphere of dinitrogen using standard Schlenk techniques. Solvents were purified by standard procedures and freshly distilled prior to use. All chemicals, except where stated, were purchased commercially and used as received. The complexes  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$

Table 4  
Selected bond distances (Å) and angles (°) for cluster **3**

Bond length (Å)			
Os(1)–Os(2)	2.8833(7)	Os(1)–Os(3)	2.7947(7)
Os(2)–Os(3)	2.9870(7)	Os(1)–Rh(1)	2.897(1)
Os(2)–Rh(1)	2.788(1)	Os(3)–Rh(1)	2.899(1)
Os(1)–I(1)	2.803(1)	Os(2)–I(1)	2.7840(9)
Os(2)–C(6)	1.99(1)	Rh(1)–C(6)	1.99(1)
Rh(1)–N(1)	1.074(10)	Rh(1)–N(2)	2.081(9)
N(1)–C(10)	1.32(2)	N(1)–C(14)	1.37(1)
N(2)–C(15)	1.35(2)	N(2)–C(19)	1.33(2)
C(10)–C(11)	1.39(2)	C(11)–C(12)	1.36(2)
Bond angle (°)			
Os(2)–Os(1)–Os(3)	63.46(2)	Os(1)–Rh(1)–Os(2)	60.91(2)
Os(1)–I(1)–Os(2)	62.14(2)	Os(2)–C(6)–Rh(1)	89.0(5)
N(1)–Rh(1)–N(2)	78.8(4)	C(10)–N(1)–C(14)	117(1)

[16] and  $[\text{Rh}(\text{COD})(\text{L})\text{I}]^{13}$ ; L = 2,2'-bipyridine, 1,10-phenanthroline and 4,4'-diphenyl-2,2'-dipyridyl) were prepared using the method from the literature. IR spectra were recorded on Bio-Rad FTS-7 IR spectrometer, using 0.5 mm calcium fluoride solution cells. Proton NMR spectra were recorded on a Bruker DPX 300 NMR spectrometer using  $\text{CDCl}_3$  and referenced to  $\text{SiMe}_4$  ( $\delta$  0). Mass spectra were recorded on a Finnigan MAT 95 instrument by the fast atom bombardment technique, using *m*-nitrobenzyl alcohol or  $\alpha$ -thioglycerol as the matrix solvents. Microanalyses were performed by Butterworth Laboratories, UK. Routine purification of products was carried out in air by thin-layer chromatography (TLC) on plates coated with Merck Kieselgel 60  $\text{GF}_{254}$ .

#### 3.2. Reaction of $[\text{Rh}(\text{COD})(\text{bipy})\text{I}]$ (COD = cycloocta-1,5-diene); bipy = 2,2'-bipyridine with $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$

A solution of  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$  (30 mg, 0.035 mmol) and  $[\text{Rh}(\text{COD})(\text{bipy})\text{I}]$  (17 mg, 0.035 mmol) in  $\text{CH}_2\text{Cl}_2$  (20  $\text{cm}^3$ ) was refluxed under an dinitrogen atmosphere for 1 h (TLC monitoring). The solution gradually turned from bright-red to brown. The solvent was removed in vacuo and the residue was chromatographed on silica gel using *n*-hexane- $\text{CH}_2\text{Cl}_2$  (1:3) as eluent. The first yellow band was found to be  $[\text{Os}_3(\text{CO})_{12}]$  (as confirmed by IR spectroscopy). Three consecutive bands were then eluted, namely complex, **1** ( $R_f$  0.70; 10, 0.010, 22), **2** ( $R_f$  0.55; 16, 0.014, 38), **3** ( $R_f$  0.30; 12 mg, 0.009 mmol, 24%) (Found: C, 20.2; H, 1.4. Calc. for  $\text{C}_{18}\text{H}_{15}\text{IO}_{10}\text{Os}_3\text{Rh}$  **1**: C, 20.3; H, 1.4. Found: C, 17.4; H, 1.2. Calc. for  $\text{C}_{17}\text{H}_{15}\text{IO}_9\text{Os}_3\text{Rh}$  **2**: C, 17.6; H, 1.3. Found: C, 18.8; H, 0.8; N, 2.1. Calc. for  $\text{C}_{19}\text{H}_{10}\text{IO}_9\text{N}_2\text{Os}_3\text{Rh}$  **3**: C, 18.8; H, 0.8; N, 2.2%).

#### 3.3. Reaction of $[\text{Rh}(\text{COD})(\text{L})\text{I}]$ ; L = 1,10-phen or 4,4'-diphbipy with $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$

The same treatment with  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$  using equal molar  $[\text{Rh}(\text{COD})(1,10\text{-phen})\text{I}]$  or  $[\text{Rh}(\text{COD})(4,4'\text{-diphbipy})\text{I}]$  afforded same products, **1**, **2** and  $[\text{Os}_3(\text{CO})_{12}]$  (confirmed by IR and  $^1\text{H-NMR}$  spectroscopy); however, instead of **3**, cluster **4** (ca. 20%) and **5** (ca. 25%) were isolated, respectively. (Found: C, 20.5; H, 0.9; N 2.2. Calc. for  $\text{C}_{21}\text{H}_{11}\text{IO}_9\text{N}_2\text{Os}_3\text{Rh}$  **4**: C, 20.4; H, 0.8; N, 2.3. Found: C, 27.4; H, 1.2; N, 2.0. Calc. for  $\text{C}_{31}\text{H}_{19}\text{IO}_9\text{N}_2\text{Os}_3\text{Rh}$  **5**: C, 27.3; H, 1.3; N, 2.1%).

#### 3.4. X-ray data collection and structural determination of complexes **1–3**

All pertinent crystallographic data and other experimental details are summarised in Table 5. Data were collected at ambient temperature either on a Rigaku

Table 5  
Crystallographic data and data collection parameters for compounds **1**–**3**

Compound	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	Os <sub>3</sub> RhC <sub>18</sub> H <sub>15</sub> O <sub>10</sub>	Os <sub>3</sub> RhC <sub>17</sub> O <sub>9</sub> H <sub>14</sub> I	Os <sub>3</sub> RhC <sub>19</sub> N <sub>2</sub> O <sub>9</sub> H <sub>10</sub> I·0.5C <sub>6</sub> H <sub>6</sub>
<i>M</i>	1064.82	1162.70	1210 (1249.76 with solvent)
Crystal colour, habit	Red, block	Brown, cubic	Orange, block
Crystal size/mm	0.14 × 0.18 × 0.21	0.12 × 0.14 × 0.18	0.19 × 0.23 × 0.24
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	C2/c (no. 15)	P <sub>2</sub> /c (no. 14)	P $\bar{1}$ (no. 2)
<i>a</i> (Å)	32.311(2)	9.200(6)	10.825(1)
<i>b</i> (Å)	10.111(1)	10.915(5)	12.253(1)
<i>c</i> (Å)	–15.997(1)	23.057(6)	12.318(1)
$\alpha$ (°)	—	—	74.97(2)
$\beta$ (°)	116.32(2)	92.02(4)	71.18(2)
$\gamma$ (°)	—	—	70.26(2)
<i>U</i> /Å <sup>3</sup>	4684.4(9)	2314(1)	1434.8(4)
<i>Z</i>	8	4	2
<i>D</i> <sub>calc.</sub> /g cm <sup>–3</sup>	3.019	3.337	2.893
<i>F</i> (000)	3808	2056	1114
$\mu$ (Mo–K $\alpha$ )/cm <sup>–1</sup>	169.52	184.88	149.22
$\omega$ -Scan width/°	—	0.94 + 0.35 tan $\theta$	—
2 $\theta$ Range collected/°	51.1	2–45	51.2
Scan speed/° min <sup>–1</sup>	0.0	16.0	0.0
Reflections collected	19887	3450	20542
No. unique reflections	4598	3218	4774
Reflections observed [ <i>I</i> > 3 $\sigma$ ( <i>I</i> )]	3021	2416	3134
<i>p</i> in weighting scheme $w = [\sigma_c^2(F_o) + p^2/4(F_o^2)]^{-1}$	0.024	0.020	0.028
<i>R</i> indices (observed data)	<i>R</i> = 0.042, <i>R'</i> = 0.052	<i>R</i> = 0.065, <i>R'</i> = 0.081	<i>R</i> = 0.035, <i>R'</i> = 0.042
Goodness of fit <i>S</i>	1.70	2.23	1.05
Maximum $\Delta/\sigma$	0.02	1.45	0.09
No. of parameters	289	195	328
Maximum, minimum density in $\Delta F$ map/eÅ <sup>–3</sup> , close to Os or Rh	1.32 to –1.83	1.45 to –1.51	0.89 to –1.29

AFC7R diffractometer (complex **2**) or a MAR research image plate scanner (complex **1** and **3**), using Mo–K $\alpha$  radiation ( $\lambda = 0.71073$  Å) with a graphite-crystal monochromator in the incident beam. For **2**, the data were collected using the ( $\omega$ -2 $\theta$ ) scan technique with an exposure time of 5 min per frame used. The diffracted intensities were corrected for Lorentz and polarization effects. The  $\psi$ -scan method was employed for semi-empirical absorption corrections for **2** [17], while an approximation to absorption correction by inter-image scaling was made for **1** and **3**. Scattering factors were taken from reference ([18]a) and anomalous dispersion effects ([18]b) were included in *F<sub>c</sub>*.

The space group of all structures were determined from their systematic absences and the Laue symmetry check. We realized that **3** can be transformed into a C-centered cell. However, the required 2/*m* Laue symmetry is not observed. Therefore, the triclinic cell is used for structure solution and refinement. All structures were solved by direct methods (SIR 88) [19] and expanded by Fourier-difference techniques. The solutions were refined on *F* by full-matrix least-squares analysis with all non-hydrogen atoms refined anisotropically except carbon atoms in **2**. The hydrogen atoms of all the organic moieties were generated in their idealised

positions whilst all the metal hydrides were estimated by potential energy calculations [20]. All the hydrogen atoms were included in the structure factors but the parameters were not refined. Calculations were performed on a Silicon-Graphics computer, using the program package TEXSAN [21].

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

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