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Reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with *trans*-$[Pd(NH_3)_2I_2]$; molecular structures of $[Os_6Pd(\mu\text{-}H)_8(CO)_{18}]$, $[Os_4Pd(\mu\text{-}H)_4(CO)_{12}(\mu\text{-}I)_2]$, $[Os_4Pd(\mu\text{-}H)_3(CO)_{12}(\mu\text{-}I)_3]$ and $[\{Os_3Pd(\mu\text{-}H)_3(CO)_9(\mu\text{-}I)\}_2]$

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Reaction of the co-ordinatively unsaturated cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with *trans*-$[Pd(NH_3)_2I_2]$ afforded the complexes $[Os_6Pd(\mu\text{-}H)_8(CO)_{18}]$ **1**, $[Os_4Pd(\mu\text{-}H)_4(CO)_{12}(\mu\text{-}I)_2]$ **2**, $[Os_4Pd(\mu\text{-}H)_3(CO)_{12}(\mu\text{-}I)_3]$ **3** and $[Os_3(CO)_{12}]$ in moderate yields. Thermolysis of **2** in refluxing chloroform produced **3** and the linked cluster $[\{Os_3Pd(\mu\text{-}H)_3(CO)_9(\mu\text{-}I)\}_2]$ **4**. Complexes **1**–**4** were fully characterised by IR and ^1H NMR spectroscopy, mass spectrometry, elemental analysis and X-ray crystallography. The structures of **1** and **2** are based on vertex-shared condensed polyhedra with the palladium atoms at the vertex-sharing sites. The molecular structure of complex **1** consists of a central palladium atom sandwiched between two triosmium units. Complexes **2** and **3** possess a similar metal disposition in which an $\{Os_3Pd\}$ tetrahedron bridges to a mononuclear '$Os(CO)_3$' moiety *via* two and three bridging iodide ligands respectively. Complex **4** is dimeric with two $\{Os_3Pd\}$ tetrahedra tied together by two bridging iodide ligands.

Bimetallic clusters of palladium and osmium are of interest as the palladium ion can attain either a 16- or an 18-electron configuration which is an important feature for catalytic processes. On the other hand, osmium clusters display very rich chemistry and are kinetically stable, thus allowing for easy isolation and characterisation. In a different context, polar osmium–palladium bonds make it possible selectively to observe ligands binding to different metal centres. Although the chemistry of osmium–nickel and –platinum hydride clusters is well documented,[1–5] much less attention has been paid to heteronuclear clusters containing palladium–osmium bonds and this has become an ongoing area of research interest in our group.[6–9]

We are interested in the mixed-metal carbonyl cluster chemistry of palladium and osmium. Previously, we reported the reactions of $[Pd(bipy)(O_2CMe)_2]$ (bipy = 2,2′-bipyridine) with the activated triosmium clusters $[Os_3(CO)_{10}(MeCN)_2]$ and $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, which yielded $[Os_6Pd(CO)_{18}(bipy)]$[6] and $[\{(bipy)Pd\}_2Os_3(CO)_{12}]$[7] respectively. Also, the reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with *trans*-$[Pd(py)_2Cl_2]$ (py = pyridine) was found to yield a series of hydrido heterometallic complexes with a common $\{Os_3Pd\}$ tetrahedral unit.[8,9] We believe the presence of a N-donor ligand stabilises these kinds of mixed-metal clusters.

In this paper, we report the reaction of the unsaturated triosmium cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with a palladium reagent containing N-donor ligands, namely, *trans*-$[Pd(NH_3)_2I_2]$, which produces a family of new osmium–palladium hydride clusters.

Results and Discussion

From the reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with the complex *trans*-$[Pd(NH_3)_2I_2]$ in tetrahydrofuran (thf) at 25 °C, we have isolated three new osmium–palladium carbonyl cluster complexes: $[Os_6Pd(\mu\text{-}H)_8(CO)_{18}]$ **1**, $[Os_4Pd(\mu\text{-}H)_4(CO)_{12}(\mu\text{-}I)_2]$ **2**, $[Os_4Pd(\mu\text{-}H)_3(CO)_{12}(\mu\text{-}I)_3]$ **3** and the known osmium cluster $[Os_3(CO)_{12}]$. Thermolysis of **2** at 61 °C in $CHCl_3$ produced **3** and the linked cluster $[\{Os_3Pd(\mu\text{-}H)_3(CO)_9(\mu\text{-}I)\}_2]$ **4**. The four products **1**–**4** were characterised by both spectroscopic and crystallographic techniques.

Spectroscopic analyses of the complexes 1–4

Table 1 Spectroscopic data for complexes **1**–**4**

Complex	IR Spectra,[a] $\tilde{\nu}(CO)/cm^{-1}$	Mass spectra[b] (*m*/*z*)	^1H NMR spectra[c] (δ)
1	2099w, 2087s, 2069m, 2038w, 2023s	1760 (1759)	−9.44 (s, 3 H) −12.72 (s, 2 H) −16.37 (s, 3 H)
2	2082m, 2068s, 2055m, 2035m, 2021s	1461 (1463)	−9.75 (s, 1 H) −16.12 (s, 3 H)
3	2107m, 2088s, 2069m, 2026s,	1587 (1586)	−16.29 (s, 3 H)
4	2108m, 2088s, 2065m, 2019s	2203 (2202)	−16.01 (s, 6 H)

[a] In CH_2Cl_2. [b] Negative FAB, simulated values in parentheses. [c] In $CDCl_3$.

The spectroscopic (IR, ^1H NMR, mass) (Table 1) and analytical data for the four new compounds are fully consistent with the solid-state structures. The solution IR spectra in the region 1600–2200 cm^{-1} show only terminal carbonyl absorptions. In addition, the negative FAB mass spectra of **1**–**4** show the parent ion peaks at *m*/*z* = 1760, 1461, 1587 and 2203 respectively, with each showing stepwise losses of carbonyls.

The presence of metal hydrides in all the complexes is confirmed by ^1H NMR spectroscopy. Based on results of the structural analyses of the compounds (see below), the signals are assigned to the appropriate protons (see Table 1). They are located in chemically reasonable positions. For complex **1**, three different metal hydride signals are observed with a total integration of eight hydride ligands. The appearance of these three singlets is a consequence of three chemically equivalent environments the ligands are subjected to. Presumably, this is caused by the fluxional processes in solution involving either edge–edge hydride migration or internal rotation of the cluster fragment.[10] The upfield signal at δ −16.37 is assigned to the three hydrides bridging the Os–Os bonds of the $\{Os_3Pd\}$ unit. The signal at δ −12.72 corresponds to the hydrides bridging the Os(4)–Os(5) and Os(4)–Os(6) bonds and lying approximately in the plane of this Os_3 unit. The more downfield signal at δ −9.44 is assigned to the hydrides bridging the Pd–Os bonds. These assignments are based on resonances observed for hydride ligands in other osmium–palladium carbonyl clusters[9] and are also consistent with those in complexes **2**–**4** (see below).

Table 2 Selected bond lengths (Å) and angles (°) for compound **1**

Os(1)–Os(2)	2.873(2)	Os(1)–Os(3)	2.864(2)
Os(2)–Os(3)	2.862(2)	Os(4)–Os(5)	3.039(2)
Os(4)–Os(6)	3.009(2)	Os(5)–Os(6)	2.908(2)
Pd–Os(1)	2.691(3)	Pd–Os(2)	2.704(3)
Pd–Os(3)	2.709(3)	Pd–Os(4)	3.305(3)
Pd–Os(5)	3.003(3)	Pd–Os(6)	2.990(3)
Os(2)–Os(1)–Os(3)	59.85(5)	Os(1)–Os(2)–Os(3)	59.92(5)
Os(1)–Os(3)–Os(2)	60.22(5)	Os(5)–Os(4)–Os(6)	57.49(5)
Os(4)–Os(5)–Os(6)	60.74(5)	Os(4)–Os(6)–Os(5)	61.77(5)
Os(1)–Pd–Os(2)	64.34(7)	Os(1)–Pd–Os(3)	64.06(7)
Os(2)–Pd–Os(3)	63.83(7)	Os(4)–Pd–Os(5)	60.43(6)
Os(4)–Pd–Os(6)	59.92(6)	Os(5)–Pd–Os(6)	58.06(6)

Table 3 Selected bond lengths (Å) and angles (°) for compound **2**

Os(1)–Os(2)	2.857(3)	Os(1)–Os(3)	2.858(3)
Os(2)–Os(3)	2.876(3)	Os(1)–Pd	2.676(4)
Os(2)–Pd	2.678(4)	Os(3)–Pd	2.674(4)
Os(4)–Pd	2.915(4)	Os(4)–I(1)	2.760(4)
Os(4)–I(2)	2.762(4)	Pd–I(1)	2.829(5)
Pd–I(2)	2.832(5)		
Os(2)–Os(1)–Os(3)	60.44(7)	Os(1)–Os(2)–Os(3)	59.81(7)
Os(1)–Os(3)–Os(2)	59.76(7)	Os(1)–Pd–Os(2)	64.5(1)
Os(1)–Pd–Os(2)	64.6(1)	Os(2)–Pd–Os(3)	65.0(1)
Os(2)–Pd–Os(4)	128.7(2)	Os(3)–Pd–Os(4)	128.5(2)
Os(4)–I(1)–Pd	62.9(1)	Os(4)–I(2)–Pd	62.8(1)

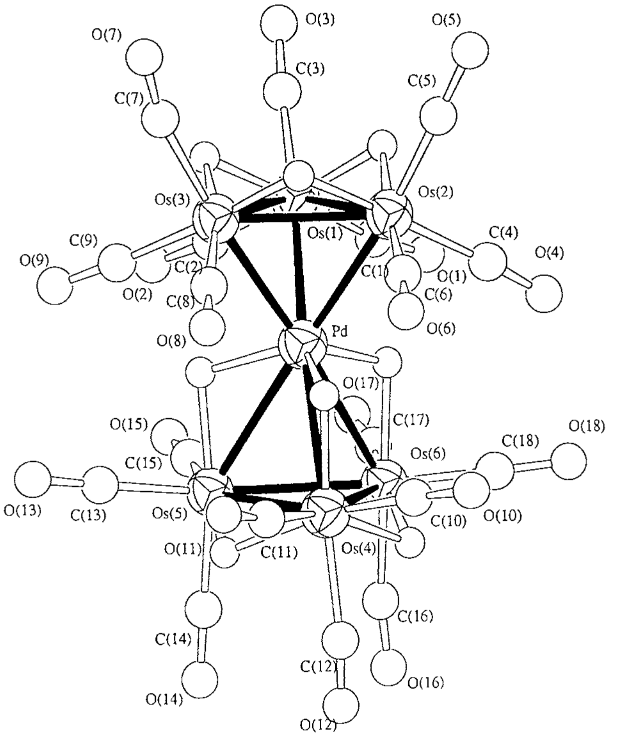


Fig. 1 Molecular structure of complex $[\mathrm{Os_6Pd}(\mu\text{-H})_8(\mathrm{CO})_{18}]$ **1** with the atom numbering scheme

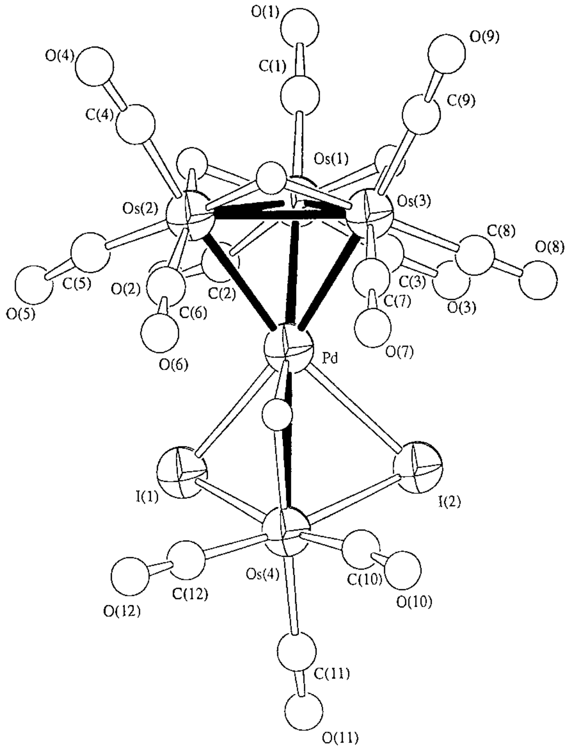


Fig. 2 Molecular structure of complex $[\mathrm{Os_4Pd}(\mu\text{-H})_4(\mathrm{CO})_{12}(\mu\text{-I})_2]$ **2** with the atom numbering scheme

Two hydride signals are observed in the spectrum of **2**. As in **1**, the upfield singlet (δ −16.12) originates from the bridging hydrides in the $\mathrm{Os_3}$ triangle. The signal due to the bridging hydride across the Os–Pd bond appears at δ −9.75. Again, the upfield hydride signals of **3** and **4** are ascribed to those bridging the edges of the $\mathrm{Os_3}$ triangle. However, the spectroscopic evidence discussed so far does not allow definitive assignment of the structures of these compounds; thus X-ray crystallographic analyses were carried out in each case.

Crystallographic analyses of complexes 1–3 and 4·$\mathrm{CH_2Cl_2}$

Dark red crystals of **1** of good X-ray quality were grown from a $\mathrm{CH_2Cl_2}$–*n*-hexane solution of the complex. A perspective view of the molecular structure of **1** is shown in Fig. 1. Selected interatomic distances and angles are listed in Table 2. The cluster can be viewed as a combination of two $\{\mathrm{Os_3Pd}\}$ tetrahedra sharing a common Pd vertex with the two osmium triangles arranged in a staggered conformation. The corresponding platinum analogue $[\mathrm{Os_6Pt}(\mu\text{-H})_8(\mathrm{CO})_{18}]$ has been synthesised by Adams *et al.*[11] from hydrogenation of $[\mathrm{Os_4Pt_2(CO)_{18}}]$, whilst a similar 'sandwich-type' arrangement is also observed in $[\mathrm{Hg\{Pt_3(2,6\text{-}Me_2C_6H_3NC)_6\}_2}]$[12] and $[\mathrm{M\{Pt}(\mu\text{-CO})_3\mathrm{L_3\}_2}]^+$ (M = Cu,[10] Ag[13] or Au;[14] L = tertiary phosphine). The Os–Os bond lengths for complex **1** range from 2.862(2) to 3.039(2) Å {*cf.* 2.877(3) Å in $[\mathrm{Os_3(CO)_{12}}]$[15]}. In addition to the Os–Os bonds, there are two types of heterometallic Os–Pd bonds in compound **1**: (*i*) non-bridging Os(1)–Pd, Os(2)–Pd and Os(3)–Pd with an average bond distance of 2.701(3) Å and (*ii*) singly hydrido-bridged Os(4)–Pd, Os(5)–Pd and Os(6)–Pd with an average bond distance of 3.099(3) Å. As expected, the non-bridging bonds are the shortest of the two types.[16,17] In addition to the hydride ligands, there are 18 terminal carbonyl ligands, three on each osmium atom. Thus, compound **1** contains 102 valence electrons, and obeys Mingos' theory of condensed polyhedra.[18]

Bright red crystals of **2** suitable for structural analysis were grown by slow evaporation of a $\mathrm{CH_2Cl_2}$–*n*-hexane solution. The molecular structure of **2** is shown in Fig. 2, with selected bond lengths and angles given in Table 3. The metal core of **2** consists of an $\{\mathrm{Os_3Pd}\}$ tetrahedron with the palladium atom bonded to an additional osmium atom through two bridging iodide and one bridging hydride ligands. Of the four mixed-metal bonds found in the structure, three of them are non-bridging with distances only slightly shorter than those found in **1** [2.674(4)–2.678(4) Å]. The Os(4)–Pd bond is triply bridged by a hydride and two iodide ligands, this results in a lengthening of the bond [2.915(4) Å]. The Os–Os bond lengths fall in the range 2.857(3)–2.876(3) Å which are comparable to those found in **1**. Complex **2** is electron deficient and contains a total of 76

Table 4 Selected bond lengths (Å) and angles (°) for compound **3**

Os(1)–Os(2)	2.866(2)	Os(1)–Os(3)	2.872(2)
Os(2)–Os(3)	2.871(2)	Os(1)–Pd	2.683(3)
Os(2)–Pd	2.690(3)	Os(3)–Pd	2.675(3)
Os(4)–I(1)	2.732(3)	Os(4)–I(2)	2.734(3)
Os(4)–I(3)	2.746(3)	Pd–I(1)	2.866(4)
Pd–I(2)	2.845(4)	Pd–I(3)	2.956(4)
Os(4) ··· Pd	3.52(1)		
Os(2)–Os(1)–Os(3)	60.05(5)	Os(1)–Os(2)–Os(3)	60.08(5)
Os(1)–Os(3)–Os(2)	59.87(5)	Os(3)–Os(1)–Pd	57.46(7)
Os(1)–Os(2)–Pd	57.64(8)	Os(3)–Os(2)–Pd	57.40(7)
Os(1)–Os(3)–Pd	57.71(7)	I(1)–Os(4)–I(2)	87.57(10)
I(1)–Os(4)–I(3)	88.20(9)	I(2)–Os(4)–I(3)	87.80(9)
Os(4)–I(1)–Pd	77.85(9)	Os(4)–I(2)–Pd	78.18(10)
Os(4)–I(3)–Pd	76.10(9)	Os(1)–Pd–Os(2)	64.47(8)
Os(1)–Pd–Os(3)	64.82(8)	Os(2)–Pd–Os(3)	64.70(8)

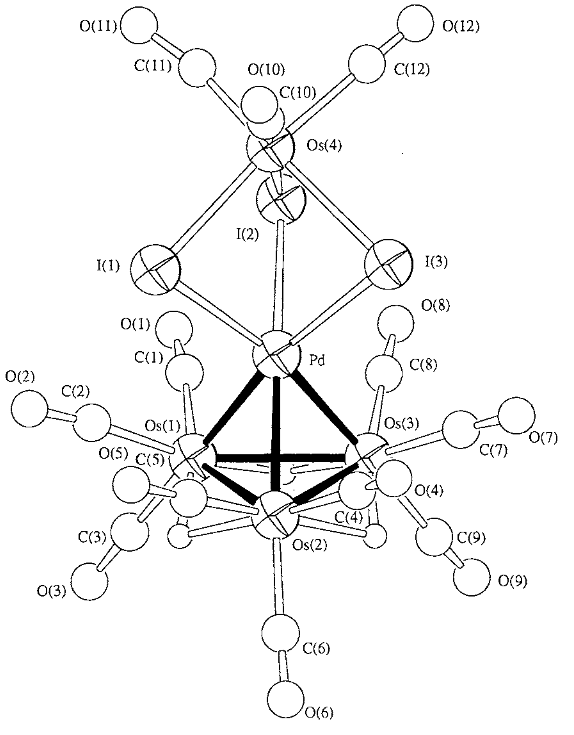


Fig. 3 Molecular structure of complex [Os$_4$Pd(μ-H)$_3$(CO)$_{12}$(μ-I)$_3$] **3** with the atom numbering scheme

valence electrons, but should contain 78 if the effective atomic number rule is to be complied with. The unsaturation may be localised on Pd which adopts a 16-electron configuration instead of the anticipated 18-electron configuration.[19] In most cases, the associated metal–metal bonds would be expected to show a shortening effect caused by such electron deficiency. However, in this case, such shortening is not observed, which may be due to the counterbalancing effect of two bridging iodide and one hydride ligands across this bond. In addition to the hydride and iodide ligands, there are 12 terminal carbonyl groups, three on each osmium atom.

An X-ray crystallographic study was undertaken on a red single crystal obtained from a CH$_2$Cl$_2$–*n*-hexane solution of **3**. The molecular structure of **3** is shown in Fig. 3, together with some important bond parameters in Table 4. The crystal structure of complex **3** has a metal disposition similar to that of complex **2**. It contains a basic {Os$_3$Pd} unit with the fourth osmium clamped to the palladium by three iodide ligands, with no formal Os–Pd bond expected between Os(4) and the palladium atom [Os(4) ··· Pd 3.52(1) Å]. All the Os–Os bonds are bridged by hydride ligands in the tetrahedron, with three terminal carbonyls on each osmium atom. Complex **3** is also electron deficient with a total of 76 valence electrons. We believe that this electron deficiency may be again associated with the Os–Pd bond, which is relatively short [average 2.683(6) Å] as compared with those unsupported bonds found in **1** [average 2.701(3) Å].

Table 5 Selected bond lengths (Å) and angles (°) for compound **4**

Os(1)–Os(2)	2.889(1)	Os(1)–Os(3)	2.839(2)
Os(1)–Pd(1)	2.675(2)	Os(2)–Os(3)	2.814(1)
Os(2)–Pd(1)	2.673(2)	Os(3)–Pd(1)	2.681(3)
Os(4)–Os(5)	2.796(2)	Os(4)–Os(6)	2.883(2)
Os(4)–Pd(2)	2.699(2)	Os(5)–Pd(2)	2.691(3)
Os(5)–Os(6)	2.859(1)	Os(6)–Pd(2)	2.659(2)
I(1)–Pd(1)	2.699(3)	I(1)–Pd(2)	2.708(3)
I(2)–Pd(1)	2.706(3)	I(2)–Pd(2)	2.684(3)
Os(2)–Os(1)–Os(3)	58.84(4)	Os(2)–Os(1)–Pd(1)	57.26(5)
Os(3)–Os(1)–Pd(1)	58.09(6)	Os(1)–Os(2)–Os(3)	59.70(3)
Os(1)–Os(2)–Pd(1)	57.35(5)	Os(3)–Os(2)–Pd(1)	58.44(6)
Os(1)–Os(3)–Os(2)	61.46(4)	Os(1)–Os(3)–Pd(1)	57.90(5)
Os(2)–Os(3)–Pd(1)	58.15(5)	Os(5)–Os(4)–Os(6)	60.42(4)
Os(5)–Os(4)–Pd(2)	58.60(6)	Os(6)–Os(4)–Pd(2)	56.78(5)
Os(4)–Os(5)–Os(6)	61.29(4)	Os(4)–Os(5)–Pd(2)	58.90(5)
Os(6)–Os(5)–Pd(2)	57.16(5)	Os(4)–Os(6)–Pd(2)	58.13(5)
Os(5)–Os(6)–Pd(2)	58.24(6)		

The reactivity studies of complexes **1** and **3** are hampered because of their relatively low yields. However, thermolysis of **2** in refluxing CHCl$_3$ produced **3**, [{Os$_3$Pd(μ-H)$_3$(CO)$_9$(μ-I)}$_2$] **4** and the known complex [Os$_4$(μ-H)$_2$(CO)$_{13}$] in moderate yields. The molecular structure of complex **4** together with the atom labelling scheme is depicted in Fig. 4, while selected bond lengths and angles are in Table 5. The cluster can be viewed as a combination of two {Os$_3$Pd} tetrahedra linked together by two bridging iodide ligands. Clusters with identical metal cages connected by a similar linkage have been obseved in [(HgBr)$_2${Pt$_3$(CO)$_3$[PPh(C$_6$H$_{11}$)$_2$]$_3$}$_2$(μ-HgBr)$_2$][20] and [{Os$_3$Pd-(μ-H)$_2$(CO)$_9$(μ-Cl)}$_2$Cl$_2$].[9] For the latter, the central cluster core consists of a square planar arrangement of {Pd$_2$Cl$_2$}. However, for complex **4**, the central cluster core {Pd$_2$I$_2$} unit deviates from planar geometry and adopts a puckered conformation, which is rarely observed in other known {Pd$_2$X$_2$} (X = Cl, Br or I) cluster cores.[21,22] The dihedral angle between the planes of [Pd(1), I(1), I(2)] and [Pd(2), I(1), I(2)] is 128.4°. A similar dibromo-bridge is also observed in the Ru–Hg complex [{Ru$_3$(CO)$_9$(C$_2$Bu^t)}$_2$(μ-HgBr)$_2$][23] which, while dimeric in the solid state, is monomeric in solution. In contrast, complex **4** is dimeric in both the solid and solution states, as suggested from the fast atom bombardment (FAB) mass spectrum. Each tetrahedral unit possesses 60 cluster valence electrons (CVE) constituting a total of 120 CVE to the entire molecule, and is thus electron precise.

Scheme 1 summarises the products in the reaction. It is interesting that the clusters **1**–**4** all possess a basic tetrahedral unit {Os$_3$Pd(μ-H)$_3$(CO)$_9$}. A similar basic skeleton {Os$_3$M-(μ-H)$_3$(CO)$_9$} (M = Ni or Pt) has been observed in the mixed-metal clusters isolated from reactions of [Os$_3$(μ-H)$_2$(CO)$_{10}$] with complexes of nickel and platinum.[24–29] We believe that systematic cluster build-up using {Os$_3$M(μ-H)$_3$(CO)$_9$} should be possible although we are unable to isolate the simple hydride clusters of {Os$_3$Pd(μ-H)$_4$(CO)$_x$} (x = 10 or 11) from this reaction.

Experimental

Materials

All reactions and manipulations were carried out under an inert atmosphere 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 complex [Os$_3$(μ-H)$_2$(CO)$_{10}$] was prepared by the literature method.[30] Infrared spectra were

Table 6 Crystallographic data and data collection parameters for compounds **1**–**4**

Compound	**1**	**2**	**3**	**4**·CH_2Cl_2
Empirical formula	$C_{18}H_8O_{18}Os_6Pd$	$C_{12}H_4I_2O_{12}Os_4Pd$	$C_{12}H_3I_3O_{12}Os_4Pd$	$C_{18}H_6I_2O_{18}Os_6Pd_2 \cdot CH_2Cl_2$
M	1759.85	1461.17	1587.06	2202.98
Crystal dimensions/mm	0.19 × 0.21 × 0.29	0.14 × 0.23 × 0.27	0.12 × 0.28 × 0.34	0.21 × 0.34 × 0.34
Crystal system	Triclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_12_12_1$ (no. 19)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	10.287(3)	16.257(3)	12.046(1)	13.310(8)
b/Å	16.775(4)	16.607(3)	17.551(1)	16.721(8)
c/Å	10.204(3)	9.181(3)	12.620(1)	9.510(10)
α/°	101.57(3)	—	—	92.14(7)
β/°	113.27(2)	—	94.40(1)	106.15(7)
γ/°	91.43(2)	—	—	103.42(4)
U/Å^3	1574.2(8)	2478.4(8)	2660.2(3)	1965.0(2)
Z	2	4	4	2
D_c/g cm^{-3}	3.713	3.916	3.962	3.722
μ/cm^{-1}	247.30	236.74	232.18	219.62
F(000)	1524	2512	2720	1908
T/K	296	296	293	298
Diffractometer	AFC7R	AFC7R	MAR research	AFC7R
Maximum 2θ/°	48.0	45.0	51.30	45.0
Scan range/ω	0.79 + 0.35 tan θ	0.68 + 0.35 tan θ	—	1.21 + 0.35 tan θ
Reflections collected	5254	1887	21 546	5404
Unique reflections	4940 (R_{int} = 0.03)	1887	4565 (R_{int} = 0.06)	5139 (R_{int} = 0.02)
Observed reflections [$I > 3.00\sigma(I)$]	3280	1501	2605	3674
Transmission factors	0.6097–1.0000	0.3859–1.0000	—	0.2050–1.0000
p in weighting scheme $w = [\sigma_c^2(F_o) + p^2/4(F_o^2)]^{-1}$	0.0100	0.0080	0.0	0.0160
R indices (observed data)	$R = 0.056$, $R' = 0.068$	$R = 0.056$, $R' = 0.057$	$R = 0.047$, $R' = 0.069$	$R = 0.049$, $R' = 0.053$
Goodness of fit	2.72	2.48	3.22	2.22
Largest Δ/σ	0.03	0.02	0.04	0.06
No. parameters	208	160	289	257
Residual extrema in the final difference map (close to Os)/e Å^{-3}	2.22 to −3.15	2.13 to −2.58	1.76 to −2.01	2.17 to −3.56

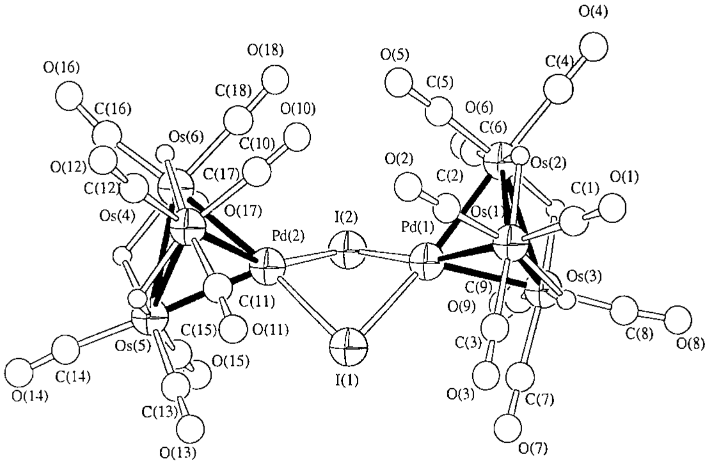


Fig. 4 Molecular structure of complex $[\{Os_3Pd(\mu\text{-}H)_3(CO)_9(\mu\text{-}I)\}_2]$ **4** with the atom numbering scheme

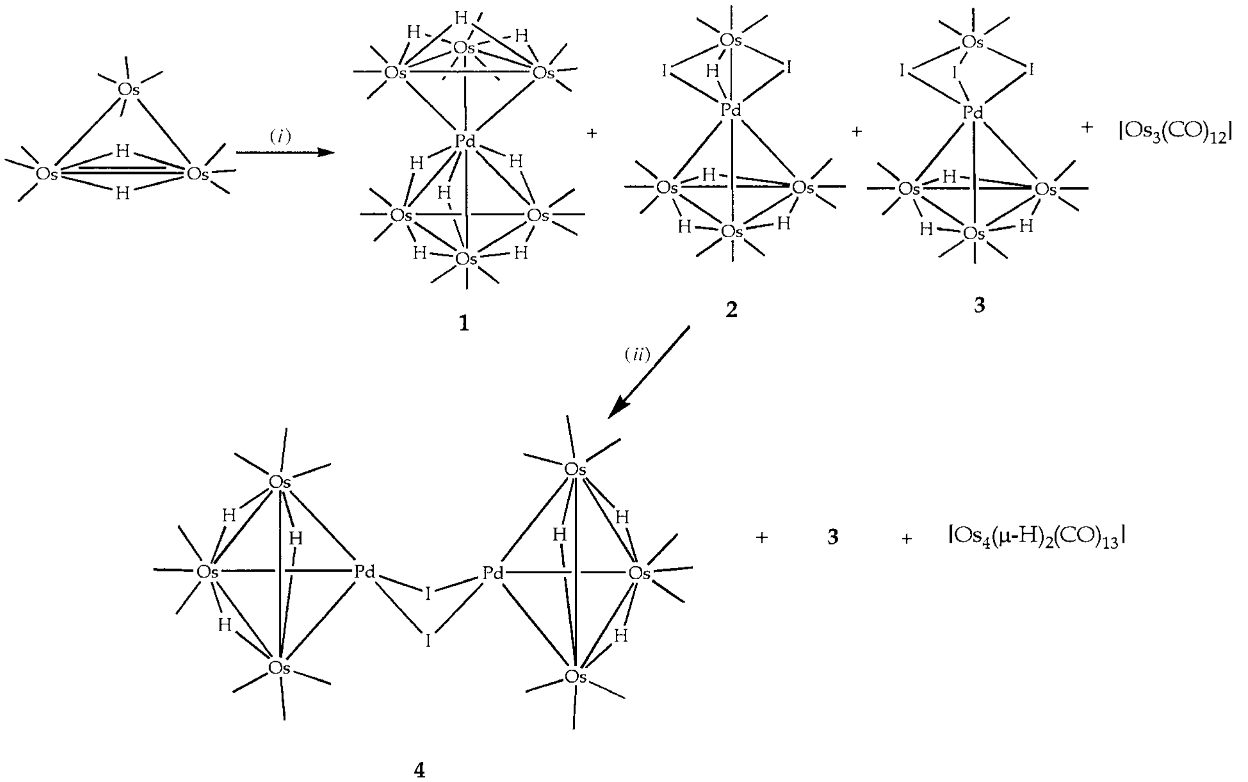
recorded on a Bio-Rad FTS-7 IR spectrometer, using 0.5 mm calcium fluoride solution cells. Proton NMR spectra were recorded on a Bruker DPX 300 NMR spectrometer using CD_2Cl_2 and referenced to $SiMe_4$ (δ 0). Mass spectra were recorded on a Finnigan MAT 95 instrument by the fast atom bombardment technique, using *m*-nitrobenzyl alcohol or α-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 GF_{254}.

Reaction of *trans*-$[Pd(NH_3)_2I_2]$ with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$

A solution of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (30 mg, 0.035 mmol) and *trans*-$[Pd(NH_3)_2I_2]$ (14 mg, 0.035 mmol) in tetrahydrofuran (thf) (15 cm^3) was stirred at room temperature until all starting materials had been consumed (2 h, TLC monitoring). The solvent was removed *in vacuo* and the residue was chromatographed on silica using *n*-hexane–CH_2Cl_2 (4:1) as eluent. The first yellow band was found to be $[Os_3(CO)_{12}]$ (as confirmed by IR spectroscopy). Three consecutive bands were then eluted, namely complex, **1** (R_f 0.52; 11, 0.007, 19), **2** (R_f 0.36, 6, 0.004, 14) and **3** (R_f 0.24, 2 mg, 0.001 mmol, 4%) (Found: C, 12.1; H, 0.4. Calc. for $C_{18}H_8O_{18}Os_6Pd$ **1**: C, 12.25; H, 0.45. Found: C, 10.0; H, 0.3. Calc. for $C_{12}H_4I_2O_{12}Os_4Pd$ **2**: C, 9.9; H, 0.25. Found: C, 9.0; H, 0.15. Calc. for $C_{12}H_3I_3O_{12}Os_4Pd$ **3**: C, 9.05; H, 0.2%).

Thermolysis of 2 in $CHCl_3$

A solution of **2** (20 mg, 0.014 mmol) in $CHCl_3$ (15 cm^3) was refluxed under an argon atmosphere for 20 h. The solution gradually turned from bright red to brown. The reaction mixture was filtered to remove insoluble black material and the



Scheme 1 (*i*) *trans*-[Pd(NH$_3$)$_2$I$_2$], room temperature, 4 h; (*ii*) reflux, CHCl$_3$

filtrate was concentrated *in vacuo*. Chromatography on silica with *n*-hexane–CH$_2$Cl$_2$ (3 : 2, v/v) afforded three bands. The first compound (R_f 0.80) was [Os$_4$(μ-H)$_2$(CO)$_{13}$] (confirmed by IR and ^{1}H NMR spectroscopy). Two consecutive bands were then eluted, namely complex **3** (R_f 0.50, 2 mg, 0.001 mmol, 6%) and **4** (R_f 0.24, 8 mg, 0.003 mmol, 19%) (Found: C, 10.25; H, 0.25. Calc. for $C_{18}H_6I_2O_{18}Os_6Pd_2 \cdot CH_2Cl_2$ **4**·CH$_2$Cl$_2$: C, 10.35; H, 0.25%).

X-Ray data collection and structural determination of complexes 1–4

All pertinent crystallographic data and other experimental details are summarised in Table 6. Data were collected at ambient temperature either on a Rigaku AFC7R diffractometer (complexes **1**, **2** and **4**) or a MAR research image plate scanner (complex **3**), using Mo-Kα radiation ($\lambda = 0.710\ 73$ Å) with a graphite-crystal monochromator in the incident beam. For **1**, **2** and **4**, all the data were collected using the (ω–2θ) scan technique with a scan rate of 16.00 min^{-1} (in ω), for **3**, 65 3° frames with an exposure time of 5 min per frame were used. The diffracted intensities were corrected for Lorentz and polarisation effects. The ψ-scan method was employed for semi-empirical absorption corrections for **1**, **2** and **4**,[31] however, no absorption correction was made for **3**. Scattering factors were taken from ref. 32(*a*) and anomalous dispersion effects[32b] were included in F_c.

The structures were solved by direct methods (SIR 88)[33] and expanded by Fourier-difference techniques. The solutions were refined on *F* by full-matrix least-squares analysis with Os, Pd and I atoms refined anisotropically. The hydrogen atoms of the CH$_2$Cl$_2$ molecule in **4** and the Os–Pd bridging hydrides (**1**–**4**) were located on the Fourier-difference map using low-angle data, whilst the Os–Os bridging hydrides for all the complexes were estimated by potential energy calculations.[34] 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.[35]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/449.

Acknowledgements

W.-T. W. gratefully acknowledges financial support from the Croucher Foundation and the University of Hong Kong. J. W.-S. H. acknowledges the receipt of a postgraduate studentship administered by the University of Hong Kong.

References

1 L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 155.
2 L. J. Farrugia, J. A. K. Howard, O. Mitrprachachon, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 162.
3 R. D. Adams, G. Chen, D. A. Katahira, J. T. Tanner and W. Wu, *Inorg. Chem.*, 1990, **29**, 3269.
4 R. D. Adams, M. P. Pompeo and W. Wu, *Inorg. Chem.*, 1991, **30**, 2899.
5 B. F. G. Johnson, J. Lewis and P. A. Kilty, *J. Chem. Soc. A*, 1968, 2589.
6 S. Chan and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1994, 1605.
7 S. Chan and W.-T. Wong, *J. Organomet. Chem.*, 1995, **489**, C78.
8 S. Chan, S.-M. Lee, Z. Lin and W.-T. Wong, *J. Organomet. Chem.*, 1996, **510**, 219.
9 S. Chan and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1995, 3987.
10 K.-H. Dahmen, Ph.D. Thesis, ETH Zurich N, 1986.
11 R. D. Adams, M. P. Pompeo and W. Wu, *Inorg. Chem.*, 1991, **30**, 2425.
12 Y. Yamamoto, H. Yamazaki and T. Sakurai, *J. Am. Chem. Soc.*, 1982, **104**, 2329.
13 A. Albinati, K.-H. Dahmen, A. Togni and L. M. Venanzi, *Angew. Chem.*, 1985, **97**, 760.
14 M. F. Hallam, D. M. P. Mingos, T. Adatia and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1987, 335.
15 D. G. DeBoer and M. R. Churchill, *Inorg. Chem.*, 1977, **16**, 878.
16 R. G. Teller and R. Bau, *Struct. Bonding (Berlin)*, 1981, **44**, 1.

17 M. R. Churchill, *ACS Symp. Ser.*, 1978, 167.
18 D. M. P. Mingos and A. S. May, *The Chemistry of Metal Cluster Complexes*, eds. D. F. Shriver, H. D. Kaesz and R. D. Adams, VCH Publishers, New York, 1990, ch. 2.
19 D. M. P. Mingos and D. G. Evans, *J. Organomet. Chem.*, 1983, **251**, C13.
20 A. Albinati, K.-H. Dahmen, F. Demartin, J. M. Forward, C. J. Longley, D. M. P. Mingos and L. M. Venanzi, *Inorg. Chem.*, 1992, **31**, 2223.
21 R. Uson, J. Fornies, F. Martinez and M. Tomas, *J. Chem. Soc., Dalton Trans.*, 1980, 888.
22 B. Bandoli and D. A. Clemente, *Acta Crystallogr., Sect. B*, 1981, **37**, 490.
23 R. Fahmy, K. King, E. Rosenberg, A. Tiripicchio and M. T. Camellini, *J. Am. Chem. Soc.*, 1980, **102**, 3626.
24 E. Sappa, M. Lanfranchi, A. Tiripicchio and M. T. Camellini, *J. Chem. Soc., Chem. Commun.*, 1981, 995.
25 S. G. Shore, W. K. Hsu, C. R. Weisenberger, M. L. Caste, M. R. Churchill and C. Bueno, *Organometallics*, 1982, **1**, 1405.
26 G. B. Karet, R. L. Espe, C. L. Stern and D. E. Shriver, *Inorg. Chem.*, 1992, **31**, 2658.
27 C. Couture, D. H. Farrar and R. J. Goudsmit, *Inorg. Chim. Acta*, 1984, **89**, 229.
28 C. Couture and D. H. Farrar, *J. Chem. Soc., Dalton Trans.*, 1987, 2245.
29 R. D. Adams, J.-C. Lii and W. Wu, *Inorg. Chem.*, 1992, **31**, 2556.
30 E. Sappa and M. Ville, *Inorg. Synth.*, 1989, **26**, 367.
31 A. C. T. North, D. C. Philips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
32 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, (*a*) Table 2.2B; (*b*) Table 2.3.1.
33 M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidor, R. Spagna and D. Viterbo, SIR 88, *J. Appl. Crystallogr.*, 1989, **22**, 389.
34 A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2509.
35 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.

Received 23*rd December* 1996; *Paper* 6/08596B