Syntheses and Structural Characterization of a Series of Hydrido Osmium–Palladium Carbonyl Clusters: $[Os_5Pd(CO)_{16}H_{n+4}(\mu\text{-}Cl)_{2-n}]$ (n = 0–2), $[\{Os_3Pd(CO)_9(\mu\text{-}H)_2(\mu\text{-}Cl)\}_2(\mu\text{-}Cl)_2]\cdot H_2O$ and $[Os_4Pd(CO)_{11}(\mu\text{-}H)_3(\mu\text{-}Cl)_3(C_5H_5N)]\cdot 0.5C_6H_{14}$†

Suzanna Chan and Wing-Tak Wong*
Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

The unsaturated triosmium cluster $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ reacted with the complex *trans*-$[Pd(py)_2Cl_2]$ (py = pyridine) to give a range of complexes including $[Os_5Pd(CO)_{16}(\mu\text{-}H)_6]$ **1**, $[Os_5Pd(CO)_{16}(\mu\text{-}H)_4H(\mu\text{-}Cl)]$ **2**, $[Os_5Pd(CO)_{16}(\mu\text{-}H)_4(\mu\text{-}Cl)_2]$ **3**, $[\{Os_3Pd(CO)_9(\mu\text{-}H)_2(\mu\text{-}Cl)\}_2(\mu\text{-}Cl)_2]$ **4**, $[Os_4Pd(CO)_{11}(\mu\text{-}H)_3(\mu\text{-}Cl)_3(py)]$ **5** and three known osmium clusters, $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$, $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}Cl)]$ and $[Os_4(CO)_{13}(\mu\text{-}H)_2]$. All five mixed-metal clusters were characterized by IR, ^1H NMR and mass spectroscopy and X-ray crystallography. Complexes **1**–**3** have similar metal dispositions but different combinations of bridging hydrides and chlorides. They can be viewed as a diosmium fragment connected to the palladium vertex of the Os_3Pd tetrahedron through a number of bridging ligands. Complex **4** is dimeric with two Os_3Pd tetrahedra tied together by two bridging chlorides in a planar fashion. Complex **5** consists of an Os_3Pd tetrahedron with a fourth osmium atom linked to the palladium vertex by three bridging chlorides. The pyridine ligand is co-ordinated to the singular osmium instead of the palladium atom.

In 1990 Adams *et al.*[1] reported the hydrogenation reaction of $[Os_4Pt_2(CO)_{18}]$ to give a series of hydrido complexes, one of which was $[Os_5Pt(CO)_{16}(\mu\text{-}H)_6]$. The role of these complexes as hydrogen storage materials and the rich reactivities of the large number of osmium–platinum carbonyl clusters synthesized[1–3] has aroused our interest in the synthesis and chemistry of osmium–palladium complexes. We have recently reported the syntheses of two Os–Pd clusters, namely $[Os_6Pd(CO)_{18}(bipy)]$[4] (bipy = 2,2′-bipyridine) and $[Os_3\{Pd(bipy)\}_2(CO)_{12}]$,[5] obtained from the complex $[Pd(bipy)(CO_2Me)_2]$ and activated triosmium clusters. We believe that the presence of a nitrogen-donor ligand stabilizes the mixed-metal clusters, as compared to the intractable intermediates obtained in the coupling reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with palladium(II) salts.[6] Herein, we report the direct synthesis of the palladium analogue of $[Os_5Pt(CO)_{16}(\mu\text{-}H)_6]$ and a number of hydrido mixed-metal complexes by the reaction of $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ and *trans*-$[Pd(py)_2Cl_2]$ (py = pyridine).

Results and Discussion

On treatment of $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ with *trans*-$[Pd(py)_2Cl_2]$ a series of clusters with a common tetrahedral Os_3Pd unit was formed including the new complexes $[Os_5Pd(CO)_{16}(\mu\text{-}H)_6]$ **1**, $[Os_5Pd(CO)_{16}(\mu\text{-}H_4)H(\mu\text{-}Cl)]$ **2**, $[Os_5Pd(CO)_{16}(\mu\text{-}H)_4(\mu\text{-}Cl)_2]$ **3**, $[\{Os_3Pd(CO)_9(\mu\text{-}H)_2(\mu\text{-}Cl)\}_2(\mu\text{-}Cl)_2]$ **4** and $[Os_4Pd(CO)_{11}(\mu\text{-}H)_3(\mu\text{-}Cl)_3(py)]$ **5** and the known clusters $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$, $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}Cl)]$ and $[Os_4(CO)_{13}(\mu\text{-}H)_2]$. Similar basic units had been obtained from reactions of the unsaturated hydridoosmium cluster with complexes of nickel,[7] platinum[8,9] and iridium.[10] A mechanism had been proposed by Stone and co-workers[9] for the formation of $[Os_3Pt(CO)_{10}(\mu\text{-}H)_2\{P(C_6H_{11})_3\}]$. In the *trans*-$[Pd(py)_2Cl_2]$ reaction the formation of the clusters is believed to proceed through chloride-bridged intermediates, as revealed by the presence of chloride groups in four of the five new compounds. The only compound that contains pyridine as ligand is complex **5**, where it is co-ordinated to an osmium atom. This evidences the substitution lability of monodentate pyridine as compared to bidentate bipyridine, the latter being bound to the palladium in both $[Os_6Pd(CO)_{18}(bipy)]$[4] and $[Os_3\{Pd(bipy)\}_2(CO)_{12}]$.[5] Similar ligand transfer has been observed in $[NiOs_3(\mu\text{-}CO)_2(CO)_8(\mu\text{-}H)_2(PPh_3)_2]$[7] and $[Os_3Pt(CO)_{10}(\mu\text{-}H)_2(PPh_3)_2]$.[2] The presence of the Os_2 units in complexes **1**–**3** suggests the detachment of a monoosmium fragment from $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ in the course of reaction, which is trapped in **5** and $[Os_4(CO)_{13}(\mu\text{-}H)_2]$. The formation of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}Cl)]$ is probably the direct outcome of the rearrangement of the intermediate species. The presence of residual moisture from the synthesis of the palladium reactant accounts for the formation of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$. The three known osmium clusters are characterized by IR and ^1H NMR spectroscopy.[11,12]

Spectroscopic Data for Complexes **1**–**5**.—A summary of the spectroscopic data for complexes **1**–**5** is given in Table 1. Only terminal carbonyls were observed in the IR region (ν_{CO} 2200–1600 cm^{-1}) for solutions of the complexes. The presence of hydrides in all the complexes was confirmed by ^1H NMR spectroscopy. For **1** three different metal hydride signals were observed with a total integral of 6. All three signals are singlets due to internal rotation of the metal fragments.[1b] The upfield signal at around δ −16 (which also occurs for the other four complexes) is attributed to the three hydrides bridging the Os–Os bonds of the Os_3Pd unit. The other signals are assigned to hydrides bridging the Os–Pd bonds of the triangular fragment. The more downfield signal is attributed to the double hydride bridge across a single bond which is electron deficient in nature. A similar situation occurs in the platinum analogue $[Os_5Pt(CO)_{16}(\mu\text{-}H)_6]$ which exhibits resonances at δ −7.48, −12.17 and −17.36.[1] Complex **2** also reveals three hydride

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Spectroscopic data for compounds **1**–**5**

Compound	IR ($\tilde{\nu}_{CO}$/cm^{-1})[a]	^{1}H NMR (δ)[b]	Mass (*m/z*)[c]
1	2117.1w, 2096.0m, 2085.5s, 2066.7w, 2055.0m, 2037.4m, 2023.3s, 2009.2m, 1989.3w, 1975.2m	−9.45 (s, 2 H) −12.71 (s, 1 H) −15.47 (s, 3 H)	1514 (1512)
2	2103.5w, 2087.5s, 2070.0w, 2045.5w, 2037.2w, 2022.6m, 2015.5m, 2007.5w, 1999.8w, 1982.9w	−10.06 (s, 1 H) −13.34 (s, 1 H) −16.19 (s, 3 H)	1546 (1546)
3	2121.8w, 2103.7w, 2089.0s, 2081.9 (sh), 2043.2m, 2033.9m, 2024.5m, 2017.5s, 2006.9w, 1989.3w	−11.35 (s, 1 H) −16.00 (s, 3 H)	1583 (1582)
4	2090.3s, 2061.4w, 2032.4m, 2020.9s	−16.12 (s, 4 H)	2003 (2005)
5	2088.2s, 2043.0m, 2039.1m, 2019.2s, 2006.8w, 1973.0m	8.94 (d, 2 H) 7.89 (t, 1 H) 7.39 (t, 2 H) −15.96 (s, 3 H)	1362 (1365)

[a] In hexane except for complex **4**, in CH_2Cl_2. [b] In CD_2Cl_2 with $SiMe_4$ as internal reference. [c] Negative FAB except for complex **4**, positive FAB; simulated values in parentheses.

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

Os(1)–Os(2)	2.882(2)	Os(1)–Os(3)	2.873(2)
Os(2)–Os(3)	2.828(2)	Os(4)–Os(5)	2.909(2)
Os(1)–Pd	2.684(3)	Os(2)–Pd	2.682(3)
Os(3)–Pd	2.697(3)	Os(4)–Pd	2.743(3)
Os(5)–Pd	2.997(3)		
Os(1)–Os(2)–Os(3)	60.41(5)	Os(1)–Pd–Os(3)	64.54(7)
Os(2)–Os(3)–Os(1)	60.72(5)	Os(2)–Pd–Os(1)	64.96(7)
Os(3)–Os(1)–Os(2)	58.87(4)	Os(3)–Pd–Os(2)	63.43(7)
Os(4)–Os(5)–Pd	55.33(6)	Os(4)–Pd–Os(5)	60.71(6)

resonances. As for **1**, the upfield singlet originates from the bridging hydrides in the Os_3 triangle. The signal due to the Os–Pd bridging hydride appears slightly downfield while the most downfield signal is ascribed to the terminal hydride on the osmium possessing four carbonyl ligands. A similar terminal hydride has been found in $[Os_4(CO)_{15}H_2]$[13] and $[Os_6(CO)_{19}H_2]$[14] which give comparable signals at δ −9.6 and −9.0 respectively.

Similarly the two signals of complex **3** are assigned to the hydride bridging the osmium and palladium atoms and those bridging the Os–Os bonds. From the electron count, complex **4** is expected to possess two hydrides on each monomer resulting in 60 cluster valence electrons (c.v.e.s) for each tetrahedral unit. These hydrides become chemically equivalent in solution as revealed by the singlet in the ^{1}H NMR spectrum. Thus, unlike $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-Cl})]$,[11] the Os–Os bonds in the Os_3Pd tetrahedra are all singly bridged by either hydride or chloride. Complex **5** is the only one to reveal an *N*-co-ordinated pyridine signal in the NMR spectrum. All the mass spectra reveal molecular-ion peaks conforming to the proposed formulae.

Crystal Structures of Complexes **1**–**5**.—An ORTEP[15] diagram of complex **1** is depicted in Fig. 1, and selected bond lengths and angles are given in Table 2. The metal skeleton of **1** consists of an Os_2Pd triangle fused to an Os_3Pd tetrahedron at the palladium apex. The mixed-metal triangle is almost perpendicular to the Os_3 base of the tetrahedron, with a dihedral angle of 96.10°. Similar metal arrangements have been found in the platinum analogue $[Os_5Pt(CO)_{16}(\mu\text{-H})_6]$[1] and in $[Co_5Ge(CO)_{16}]^-$.[16] The complex $[Os_5Pt(CO)_{16}(\mu\text{-H})_6]$ crystallizes in the centrosymmetric space group $P2_1/n$ while **1** crystallizes in the acentric space group $Pna2_1$. The Os–Os bond lengths range from 2.828(2) to 2.909(2) Å {*cf.* 2.877(3) Å in $[Os_3(CO)_{12}]$[17]}. Each osmium atom has three terminal carbonyl ligands except for Os(5) which has four. The carbonyl ligands of Os(4) and Os(5) are arranged in a staggered manner to release steric constraints. The sides of the basal Os_3 triangle are all bridged by hydrides. Three kinds of Os–Pd bonds are observed in the compound: unsupported [Os(1)–Pd, Os(2)–Pd and Os(3)–Pd], singly hydride-bridged [Os(5)–Pd] and doubly hydride-bridged [Os(4)–Pd]. The unsupported ones comprise the shortest members of the group, which are even shorter than those found in $[Os_6Pd(CO)_{18}(bipy)]$.[4] On the other hand, Os(5)–Pd is the longest and is accounted for by both steric and electronic factors. The cluster has 88 c.v.e.s, which is two short according to electron-counting rules. As mentioned by Adams *et al.*,[1] such electron deficiency accounts for the comparatively short Os(4)–Pd bond despite the existence of the two bridging hydrides.

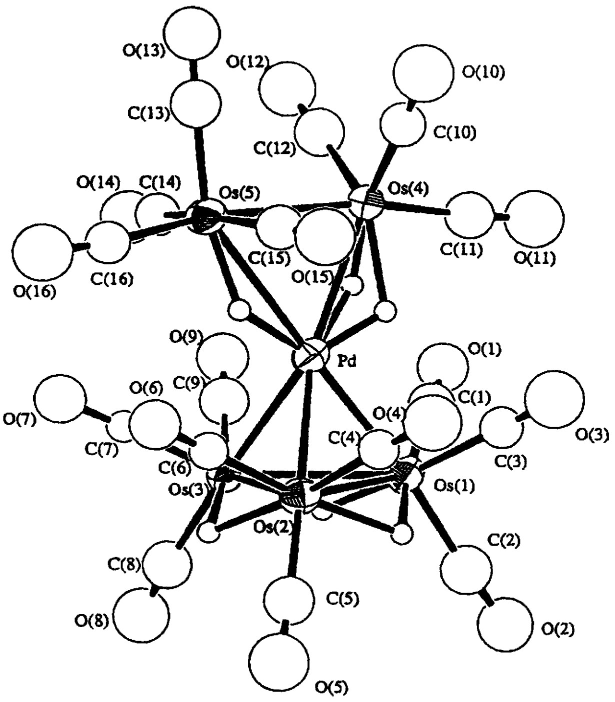


Fig. 1 Molecular structure of $[Os_5Pd(CO)_{16}(\mu\text{-H})_6]$ **1**

The crystal structure of complex **2** is shown in Fig. 2, with a summary of the bond lengths and angles in Table 3. The metal disposition is similar to that of complex **1**, except that no formal Os–Pd bond is expected between Os(5) and the palladium atom [Os(5)···Pd 3.10 Å] from the electron count (see below). A total of four mixed-metal bonds are found, of which three are unsupported. The fourth is doubly bridged by a hydride and a chloride as in $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-Cl})]$,[11] and is slightly longer than the others [2.870(2) Å, *cf.* average 2.677 Å for the unsupported ones]. The four atoms Os(4), Cl, Pd and H(1) lie on a plane, with the ligands bridging on the opposite sides of the Os–Pd bond. Atom Os(5) is the only six-co-ordinated osmium, possessing a terminal hydride and four carbonyl ligands in addition to the Os–Os bonding. Such a terminal hydride is a common feature in the 'spiked' atom configuration as in $[Os_4(CO)_{15}H_2]$[13] and $[Os_6(CO)_{19}H_2]$.[14] The remaining hydrides bridge the Os–Os bonds of the Os_3 face. All the carbonyl ligands are terminal. As in complex **1**, those on Os(4) and Os(5) take up a staggered conformation.

An ORTEP view of complex **3** is depicted in Fig. 3 and selected bonding parameters in Table 4. Unlike **1** and **2**, the Os_2 fragment in complex **3** is connected to the Os_3Pd tetrahedron through the hydride and chloride ligands only. The two chloride ligands bridge Os(4) and Pd with no formal bonding assigned between the metal atoms {*cf.* $[Os_3(CO)_{10}(\mu\text{-Cl})_2]$[18]} while the hydride connects Os(5) to Pd. The seven carbonyl groups are staggered in the Os_2 unit. All the Os–Os bonds are bridged by hydride ligands in the tetrahedron, with three terminal carbonyls on each osmium atom.

The bonding situation of complexes **1**–**3** illustrates the effect of additional electron pairs on a cluster complex as implied by the effective atomic number (e.a.n.) rule or from the classical view of metal–metal bonding (see Scheme 1). The complexes have 88, 90 and 92 c.v.e.s respectively, with the electron pair

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

Os(1)–Os(2)	2.883(1)	Os(1)–Os(3)	2.849(1)
Os(2)–Os(3)	2.864(1)	Os(4)–Os(5)	2.896(1)
Os(1)–Pd	2.678(2)	Os(2)–Pd	2.680(2)
Os(3)–Pd	2.674(2)	Os(4)–Pd	2.870(2)
Os(4)–Cl	2.458(7)	Pd–Cl	2.585(6)
Os(5) • • • Pd(1)	3.10		
Os(1)–Os(2)–Os(3)	59.44(3)	Os(1)–Pd–Os(3)	64.33(5)
Os(2)–Os(3)–Os(1)	60.61(3)	Os(2)–Pd–Os(1)	65.10(5)
Os(3)–Os(1)–Os(2)	59.95(3)	Os(3)–Pd–Os(2)	64.68(5)
Os(5)–Os(4)–Pd	65.14(4)	Os(4)–Cl–Pd	69.3(2)

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

Os(1)–Os(2)	2.9189(8)	Os(1)–Os(3)	2.8488(9)
Os(2)–Os(3)	2.8449(9)	Os(4)–Os(5)	2.921(1)
Os(1)–Pd	2.658(1)	Os(2)–Pd	2.664(1)
Os(3)–Pd	2.682(1)	Os(4)–Cl(1)	2.444(4)
Os(4)–Cl(2)	2.450(5)	Pd–Cl(1)	2.529(4)
Pd–Cl(2)	2.681(5)	Os(4) • • • Pd	3.37
Os(5) • • • Pd	3.23		
Os(1)–Os(2)–Os(3)	59.22(2)	Os(1)–Pd–Os(3)	64.48(4)
Os(2)–Os(3)–Os(1)	61.68(2)	Os(2)–Pd–Os(1)	66.51(4)
Os(3)–Os(1)–Os(2)	59.09(2)	Os(3)–Pd–Os(2)	64.30(4)
Os(4)–Cl(1)–Pd	85.4(1)	Os(4)–Cl(2)–Pd	82.1(1)

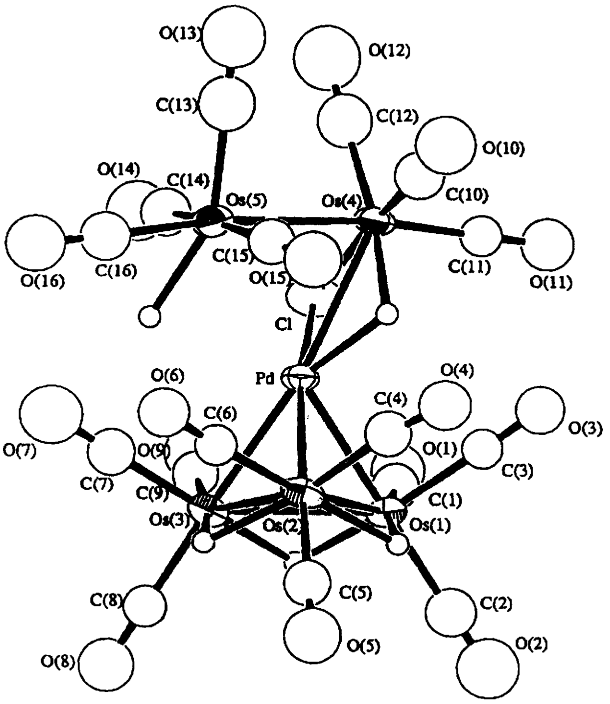


Fig. 2 Molecular structure of $[Os_5Pd(CO)_{16}(\mu\text{-H})_4H(\mu\text{-Cl})]$ **2**

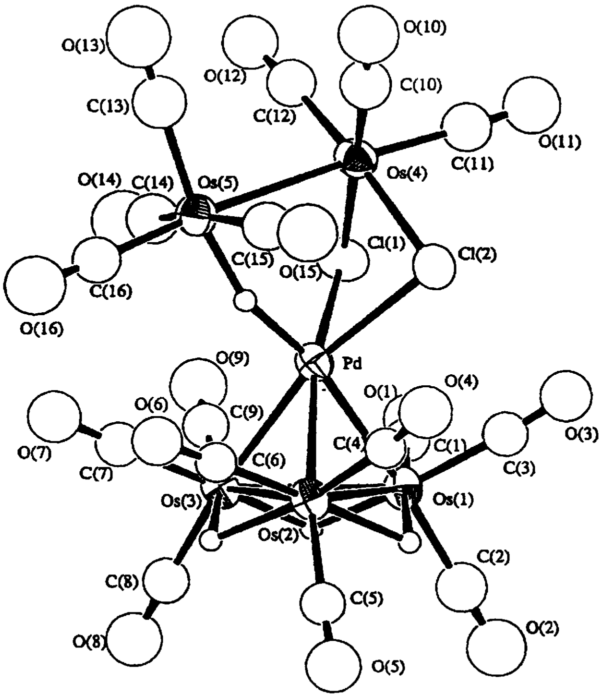
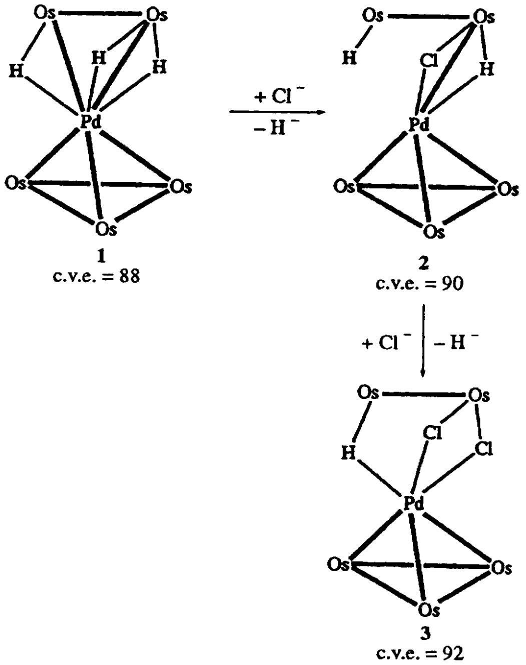


Fig. 3 Molecular structure of $[Os_5Pd(CO)_{16}(\mu\text{-H})_4(\mu\text{-Cl})_2]$ **3**



Scheme 1

added through the substitution of hydride ligands by bridging chlorides. The addition of an extra electron pair results in the rupture of a metal–metal bond, as observed from the subsequent reduction in the number of metal–metal bonds in the complexes. None of the structures is electron precise. They can neither be predicted by the polyhedral skeletal electron-pair theory (PSEPT)[19] nor be rationalized by the condensed polyhedral electron-counting rule.[20]

The bond lengths and angles of complex **4** are summarized in Table 5. Complex **4** is dimeric as shown in the ORTEP plot in Fig. 4. Dimeric clusters are not uncommon and various sorts of linkage of the metal cages have been observed: atomic bridge,[21,22] molecular bridge[23,24] or direct linkage by metal–metal bonding of the apical atoms.[25,26] The asymmetric unit comprises the monomer and a water molecule, with the whole molecule generated by crystallographic inversion symmetry. The two Os_3Pd tetrahedra are connected *via* two chloride bridges [Pd(1)–Cl(1) 2.495(6) and Pd(1)–Cl(1*) 2.432(6) Å]. A central Pd_2Cl_2 unit is a commonly observed structural component in chloroorganopalladium dimeric complexes.[27–29] A similar dibromo-bridge is also observed in $[(HgBr)_2\{Pt_3(\mu\text{-}CO)_3[PPh(C_6H_{11})_2]_3\}_2(\mu\text{-}HgBr)_2]$.[22] A second chloride ligand is found to bridge an Os–Os bond in the asymmetric unit. Two hydride ligands (see above) bridge the remaining Os–Os bonds. An incipient bridging carbonyl ligand occurs, which asymmetrically bridges Os(1)–Pd(1) [Os(1)–C(1)–O(1) 170(2), Pd(1)–C(1)–O(1) 112(1)°]. It is probably imposed by the packing forces in the lattice and may not occur in the solution state. The rest of the carbonyl ligands are all terminal. The fragments Pd(1)–Os(2)–Cl(2)–Os(1) and Cl(1)–Pd(1)–Os(3)–Os(2) are almost planar, with maximum deviations of 0.065 and 0.070 Å respectively. The $OsPdCl_2$ plane is perpendicular to the Os_2PdCl and Os_3 planes. Each tetrahedral unit possesses 60 c.v.e.s, giving a total of 120 to the entire molecule. This is not expected from the PSEPT rule but obeys the e.a.n. rule.

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

Os(1)–Os(2)	3.018(1)	Os(1)–Os(3)	2.928(1)
Os(2)–Os(3)	2.926(1)	Os(1)–Pd(1)	2.706(2)
Os(2)–Pd(1)	2.710(2)	Os(3)–Pd(1)	2.644(2)
Pd(1)–Cl(1)	2.495(6)	Pd(1)–Cl(1*)	2.432(6)
Os(1)–Cl(2)	2.429(5)	Os(2)–Cl(2)	2.440(6)
Os(1)–C(1)	1.89(2)	Pd(1)–C(1)	2.43(2)
Os(1)–Os(2)–Os(3)	59.00(3)	Os(1)–Pd(1)–Os(3)	66.35(4)
Os(2)–Os(3)–Os(1)	62.07(3)	Os(2)–Pd(1)–Os(1)	67.74(4)
Os(3)–Os(1)–Os(2)	58.93(3)	Os(3)–Pd(1)–Os(2)	66.24(4)
Os(1)–C(1)–O(1)	170(2)	Pd(1)–C(1)–O(1)	112(1)
Cl(1)–Pd(1)–Cl(1*)	92.6(2)	Pd(1)–Cl(1)–Pd(1*)	87.4(2)
Os(1)–Cl(2)–Os(2)	76.6(2)		

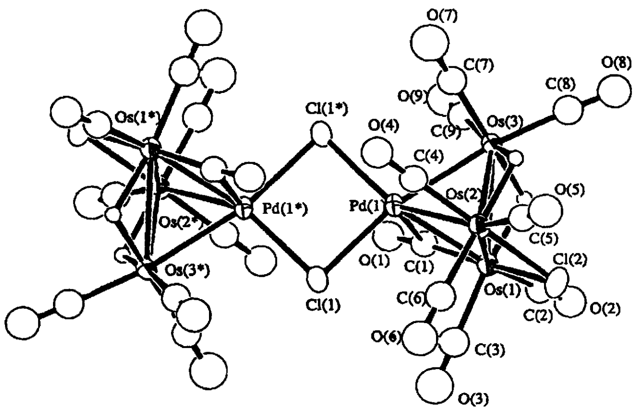


Fig. 4 Molecular structure of $[\{Os_3Pd(CO)_9(\mu\text{-}H)_2(\mu\text{-}Cl)\}_2(\mu\text{-}Cl)_2]\cdot H_2O$ **4**

Complex **5** is the only pyridine-containing product from the reaction, as confirmed by both spectroscopic and structural analyses. An ORTEP plot (Fig. 5) reveals a basic Os_3Pd unit with the fourth osmium 'clamped' to the palladium by three bridging chlorides. Despite the identity of the palladium reagent, the pyridine ligand is co-ordinated to the $Os(CO)_2$ fragment. Each Os–Os bond is bridged by a hydride ligand as in compounds **1**–**3**. All the carbonyl ligands are terminal and the bonding parameters (Table 6) of the pyridine ligand are similar to those observed in other pyridine-containing complexes. In addition to the cluster molecule, the crystal lattice contains a badly disordered hexane solvent molecule. The cluster possesses 78 c.v.e.s consistent with the e.a.n. rule.

Experimental

Materials and Methods.—The reaction was performed in an atmosphere of dry dinitrogen. Dichloromethane and aceto-

Table 6 Selected bond lengths (Å) and angles (°) for compound **5**

Os(1)–Os(2)	2.856(1)	Os(1)–Os(3)	2.875(1)
Os(2)–Os(3)	2.894(1)	Os(1)–Pd	2.653(2)
Os(2)–Pd	2.647(2)	Os(3)–Pd	2.650(2)
Os(4)–Cl(1)	2.424(5)	Pd–Cl(1)	2.656(5)
Os(4)–Cl(2)	2.414(6)	Pd–Cl(2)	2.610(5)
Os(4)–Cl(3)	2.429(5)	Pd–Cl(3)	2.577(6)
Os(4)–N	2.10(2)	N–C(12)	1.33(2)
N–C(16)	1.35(2)	C(12)–C(13)	1.39(3)
C(13)–C(14)	1.40(3)	C(14)–C(15)	1.35(3)
C(15)–C(16)	1.36(3)		
Os(1)–Os(2)–Os(3)	60.00(3)	Os(1)–Pd–Os(3)	65.66(4)
Os(2)–Os(3)–Os(1)	59.33(3)	Os(2)–Pd–Os(1)	65.20(4)
Os(3)–Os(1)–Os(2)	60.67(3)	Os(3)–Pd–Os(2)	66.23(4)
Os(4)–Cl(1)–Pd	80.8(2)	Os(4)–Cl(2)–Pd	82.0(2)
Os(4)–Cl(3)–Pd	82.4(2)	C(12)–N–C(16)	117(1)
N–C(12)–C(13)	123(2)	C(12)–C(13)–C(14)	115(2)
C(13)–C(14)–C(15)	120(2)	C(14)–C(15)–C(16)	120(2)
N–C(16)–C(15)	121(2)		

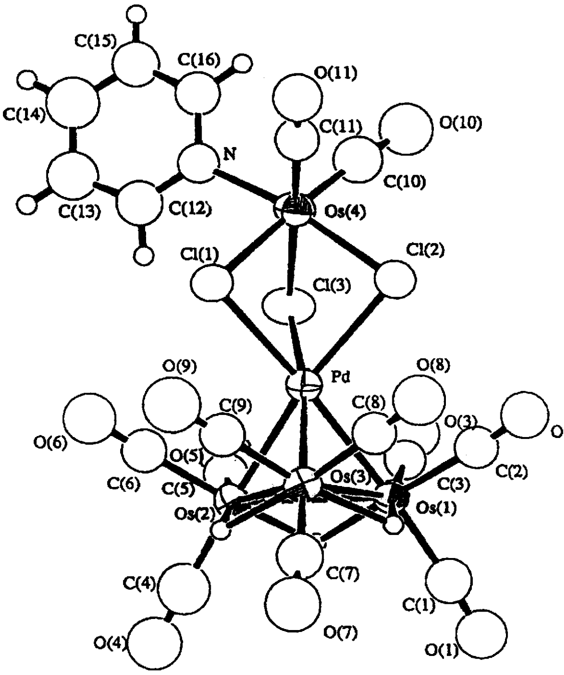


Fig. 5 Molecular structure of $[Os_4Pd(CO)_{11}(\mu\text{-}H)_3(\mu\text{-}Cl)_3(py)]\cdot 0.5C_6H_{14}$ **5**

Table 7 Crystallographic data and data-collection parameters for compounds **1–5**

Compound	$[Os_5Pd(CO)_{16}(\mu\text{-}H)_6]$ **1**	$[Os_5Pd(CO)_{16}(\mu\text{-}H)_4H(\mu\text{-}Cl)]$ **2**	$[Os_5Pd(CO)_{16}(\mu\text{-}H)_4(\mu\text{-}Cl)_2]$ **3**	$[\{Os_3Pd(CO)_9(\mu\text{-}H)_2(\mu\text{-}Cl)\}_2(\mu\text{-}Cl)_2]\cdot H_2O$ **4**	$[Os_4Pd(CO)_{11}(\mu\text{-}H)_3(\mu\text{-}Cl)_3(py)]\cdot 0.5C_6H_{14}$ **5**
Empirical formula	$C_{16}H_6O_{16}Os_5Pd$	$C_{16}H_5ClO_{16}Os_5Pd$	$C_{16}H_4Cl_2O_{16}Os_5Pd$	$C_{18}H_6Cl_4O_{19}Os_6Pd_2$	$C_{19}H_{15}Cl_3NO_{11}Os_4Pd$
M	1511.61	1546.06	1580.50	2022.05	1406.89
Colour, habit	Dark red block	Red diamond	Red leaflet	Red rhombohedral	Red rectangular plate
Crystal size/mm	0.25 × 0.30 × 0.30	0.20 × 0.30 × 0.35	0.10 × 0.20 × 0.30	0.15 × 0.15 × 0.32	0.10 × 0.15 × 0.30
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$Pna2_1$ (no. 33)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)
a/Å	17.597(3)	9.717(2)	10.969(1)	9.236(2)	42.993(8)
b/Å	10.292(2)	15.383(4)	15.350(4)	12.955(6)	9.698(4)
c/Å	15.523(2)	19.305(2)	8.911(2)	9.212(2)	15.194(4)
α/°			91.17(2)	92.42(3)	
β/°		98.16(1)	106.46(1)	110.77(2)	103.02(3)
γ/°			95.73(1)	71.60(2)	
U/Å^3	2811(1)	2856.3(8)	1429.8(5)	974.9(5)	6172(3)
Z	4	4	2	1	8
D_c/g cm^{-3}	3.571	3.595	3.671	3.475	3.023
μ(Mo-Kα)/cm^{-1}	231.88	229.18	229.86	206.98	172.80
F(000)	2624	2688	1376	882	5000
$2\theta_{max}$/°	45.0	45.0	45.0	50.0	50.0
Scan range/°	$1.37 + 0.35\tan\theta$	$1.05 + 0.35\tan\theta$	$1.42 + 0.35\tan\theta$	$1.00 + 0.35\tan\theta$	$0.63 + 0.35\tan\theta$
Transmission factors	0.1655–1.0000	0.4052–1.0000	0.4404–1.0000	0.2697–1.0000	0.4120–1.0000
Reflections collected	4074	4186	3978	3642	5673
Unique reflections	4074	3917	3739	3408	5591
Observed reflections [$I > 3\sigma(I)$]	3253	2853	2844	2705	2983
g in weighting scheme $w = 4F_o^2/[\sigma^2(F_o^2) + g(F_o^2)^2]$	0.008	0.006	0.009	0.004	0.004
R,R'	0.045, 0.054	0.044, 0.047	0.032, 0.036	0.044, 0.058	0.040, 0.040
Goodness of fit	2.43	2.52	1.57	3.08	1.75
Largest Δ/σ	0.01	0.01	0.00	0.00	0.03
No. parameters	182	192	201	127	185
Residual electron density/e Å^{-3}	1.69 to −1.87 close to Os	1.85 to −2.06 close to Os	1.48 to −1.14 close to Os	2.80 to −2.96 close to Os or water	0.85 to −1.09 close to solvent

Table 8 Atomic coordinates for compound **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z	Atom	x	y	z
Os(1)	0.790 96(8)	−0.254 8(1)	0.184 4	O(14)	0.879(2)	0.322(3)	0.143(2)
Os(2)	0.719 13(7)	−0.133 1(1)	0.330 4(1)	O(15)	0.937(2)	0.038(3)	0.483(2)
Os(3)	0.710 49(8)	−0.013 4(1)	0.166 7(1)	O(16)	0.801(2)	0.400(3)	0.418(2)
Os(4)	0.994 55(8)	0.017 2(1)	0.232 9(1)	C(1)	0.863(2)	−0.231(3)	0.088(3)
Os(5)	0.907 32(8)	0.215 9(1)	0.322 2(1)	C(2)	0.742(2)	−0.409(4)	0.142(3)
Pd	0.842 6(1)	−0.032 9(2)	0.253 9(2)	C(3)	0.870(2)	−0.345(3)	0.247(2)
O(1)	0.902(2)	−0.214(2)	0.035(2)	C(4)	0.790(2)	−0.203(3)	0.415(2)
O(2)	0.716(2)	−0.504(3)	0.111(2)	C(5)	0.627(2)	−0.203(4)	0.388(3)
O(3)	0.915(2)	−0.394(3)	0.288(2)	C(6)	0.713(2)	0.022(3)	0.399(2)
O(4)	0.834(2)	−0.254(3)	0.462(2)	C(7)	0.702(2)	0.160(3)	0.211(2)
O(5)	0.571(2)	−0.240(3)	0.421(2)	C(8)	0.613(3)	−0.007(3)	0.100(3)
O(6)	0.708(2)	0.114(3)	0.439(2)	C(9)	0.774(2)	0.049(4)	0.074(3)
O(7)	0.696(1)	0.264(2)	0.238(2)	C(10)	1.071(2)	0.028(3)	0.316(2)
O(8)	0.562(2)	−0.011(3)	0.060(2)	C(11)	1.033(2)	−0.129(3)	0.176(3)
O(9)	0.811(2)	0.087(2)	0.023(2)	C(12)	1.034(2)	0.137(4)	0.150(3)
O(10)	1.120(2)	0.040(3)	0.370(2)	C(13)	0.994(2)	0.319(3)	0.344(3)
O(11)	1.061(2)	−0.218(3)	0.145(2)	C(14)	0.892(2)	0.284(3)	0.209(2)
O(12)	1.057(2)	0.215(3)	0.105(2)	C(15)	0.927(2)	0.108(3)	0.429(3)
O(13)	1.049(2)	0.380(3)	0.351(2)	C(16)	0.839(2)	0.324(3)	0.383(2)

nitrile were distilled over calcium hydride. Diethyl ether was dried over sodium wire. Acetone (GR) was stored over 4 Å molecular sieves prior to use. All chemicals were obtained from commercial sources. The complex $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ was prepared by the literature method.[30] Infrared spectra were recorded on a Bio-Rad FTS-7 IR spectrometer, using 0.5 mm calcium fluoride solution cells, NMR spectra on a JEOL GSX 270FT-NMR spectrometer with $SiMe_4$ as internal reference and mass spectra on a Finnigan MAT 95 instrument by the fast atom bombardment technique. Products were separated by thin-layer chromatography on plates coated with Merck Kieselgel 60 GF_{254}.

Synthesis of trans-$[Pd(py)_2Cl_2]$.—The complex was prepared by an improved synthesis of the analogous compound $[Pd(bipy)Cl_2]$.[31] Palladium(II) chloride (0.1 g, 0.56 mmol) was dissolved in boiling acetonitrile (30 cm^3). After filtration a five-fold excess of pyridine (0.25 cm^3, 3.09 mmol) was added to the boiling solution. Bright yellow needles gradually formed on stirring. The volume of the solution was reduced to 20 cm^3, and then digested for 4 h. The precipitate was filtered off and washed with acetonitrile (2 × 3 cm^3), acetone (2 × 3 cm^3) and diethyl ether (3 cm^3). The product was dried *in vacuo* and its geometry confirmed by IR spectroscopy.[32] Yield: 0.16 g (87%).

Table 9 Atomic coordinates for compound **2** with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Os(1)	−0.210 53(9)	0.341 35(6)	0.896 49(5)	O(14)	0.404(2)	0.283(2)	0.814(1)
Os(2)	−0.179 03(10)	0.155 43(6)	0.908 79(5)	O(15)	−0.073(2)	0.029(1)	0.731(1)
Os(3)	0.026 25(10)	0.269 33(6)	0.980 99(5)	O(16)	0.362(2)	0.009(1)	0.861(1)
Os(4)	0.021 6(1)	0.280 23(6)	0.697 89(5)	C(1)	−0.134(3)	0.450(2)	0.885(1)
Os(5)	0.188 83(10)	0.141 94(7)	0.768 25(5)	C(2)	−0.361(3)	0.399(2)	0.938(2)
Pd	−0.013 2(2)	0.254 2(1)	0.841 60(9)	C(3)	−0.306(2)	0.342(1)	0.804(1)
Cl	0.115 0(7)	0.381 7(4)	0.791 3(4)	C(4)	−0.282(3)	0.126(2)	0.821(1)
O(1)	−0.082(2)	0.518(1)	0.880(1)	C(5)	−0.304(3)	0.092(2)	0.961(1)
O(2)	−0.453(2)	0.423(2)	0.959(1)	C(6)	−0.065(2)	0.056(2)	0.912(1)
O(3)	−0.361(2)	0.347(1)	0.748(1)	C(7)	0.179(3)	0.193(2)	0.984(1)
O(4)	−0.355(2)	0.111(1)	0.771(1)	C(8)	0.046(2)	0.276(2)	1.080(1)
O(5)	−0.379(2)	0.058(1)	0.991(1)	C(9)	0.140(3)	0.371(2)	0.973(1)
O(6)	0.008(2)	−0.001(1)	0.910 5(10)	C(10)	−0.059(3)	0.200(2)	0.635(1)
O(7)	0.275(2)	0.145(1)	0.985(1)	C(11)	−0.102(2)	0.369(2)	0.662(1)
O(8)	0.059(2)	0.281(1)	1.141(1)	C(12)	0.173(3)	0.308(2)	0.648(2)
O(9)	0.203(2)	0.432(1)	0.967(1)	C(13)	0.251(3)	0.114(2)	0.678(2)
O(10)	−0.106(2)	0.148(1)	0.596(1)	C(14)	0.324(3)	0.229(2)	0.795(2)
O(11)	−0.182(2)	0.421(1)	0.638(1)	C(15)	0.032(3)	0.067(2)	0.744(1)
O(12)	0.265(3)	0.325(2)	0.615(1)	C(16)	0.290(3)	0.057(2)	0.826(2)
O(13)	0.286(2)	0.095(2)	0.627(1)				

Table 10 Atomic coordinates for compound **3** with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Os(1)	1.019 01(7)	0.148 48(4)	0.252 76(8)	O(13)	0.290(2)	0.383(1)	−0.038(2)
Os(2)	1.033 41(7)	0.339 47(4)	0.258 09(8)	O(14)	0.504(2)	0.218(1)	0.355(2)
Os(3)	0.945 36(7)	0.243 90(4)	0.484 39(8)	O(15)	0.673(2)	0.428 9(10)	−0.135(2)
Os(4)	0.529 08(7)	0.184 38(4)	−0.092 09(8)	O(16)	0.624(2)	0.507(1)	0.328(2)
Os(5)	0.566 01(7)	0.341 74(5)	0.112 72(9)	C(1)	0.924(2)	0.040(1)	0.284(2)
Pd	0.813 6(1)	0.235 03(7)	0.179 9(1)	C(2)	1.180(2)	0.103(1)	0.310(2)
Cl(1)	0.647 0(5)	0.103 0(3)	0.124 9(6)	C(3)	0.988(2)	0.118(1)	0.038(2)
Cl(2)	0.737 8(5)	0.226 6(3)	−0.134 2(5)	C(4)	1.006(2)	0.363(1)	0.046(2)
O(1)	0.879(1)	−0.022 3(8)	0.311(1)	C(5)	1.203(2)	0.395(1)	0.312(2)
O(2)	1.279(2)	0.079 0(10)	0.344(2)	C(6)	0.956(2)	0.440(1)	0.288(2)
O(3)	0.960(1)	0.093 9(8)	−0.092(2)	C(7)	0.850(2)	0.328(1)	0.534(2)
O(4)	0.981(1)	0.382 8(8)	−0.084(2)	C(8)	1.049(2)	0.243(1)	0.690(2)
O(5)	1.307(1)	0.425 2(9)	0.342(2)	C(9)	0.826(2)	0.154(1)	0.515(2)
O(6)	0.910(1)	0.500 5(8)	0.310(1)	C(10)	0.445(2)	0.247(1)	−0.252(2)
O(7)	0.791(1)	0.381 8(8)	0.563(2)	C(11)	0.518(2)	0.083(1)	−0.231(2)
O(8)	1.116(1)	0.240 3(9)	0.817(2)	C(12)	0.379(2)	0.149(1)	−0.039(2)
O(9)	0.752(1)	0.098 3(9)	0.530(2)	C(13)	0.391(2)	0.365(1)	0.020(3)
O(10)	0.385(2)	0.287 1(10)	−0.353(2)	C(14)	0.529(2)	0.265(1)	0.261(2)
O(11)	0.507(2)	0.028 2(10)	−0.322(2)	C(15)	0.634(2)	0.397(1)	−0.045(2)
O(12)	0.292(1)	0.124 4(9)	0.005(2)	C(16)	0.603(2)	0.443(1)	0.249(2)

Reaction of trans-[Pd(py)$_2$Cl$_2$] *with* [Os$_3$(CO)$_{10}$(μ-H)$_2$].—The complex [Os$_3$(CO)$_{10}$(μ-H)$_2$] (34 mg, 0.040 mmol) was treated with *trans*-[Pd(py)$_2$Cl$_2$] (20 mg, 0.060 mmol) in CH$_2$Cl$_2$ (20 cm^3) at room temperature. The mixture was stirred for 2 h prior to reduction in volume. The products were separated by TLC on silica, with CH$_2$Cl$_2$–hexane (1 : 7, v/v) as eluent, as six bands. The first yellow band was a mixture, which was subjected to TLC again using pure hexane as eluent to afford [Os$_3$(CO)$_{10}$(μ-H)(μ-OH)] (4 mg, 0.0046 mmol, 11%) and [Os$_3$(CO)$_{10}$(μ-H)(μ-Cl)] (7 mg, 0.0079 mmol, 20%). An orange compound (R_f 0.50) was then eluted and confirmed by IR and NMR spectroscopy to be [Os$_4$(CO)$_{13}$(μ-H)$_2$] (4 mg, 0.0035 mmol, 9%). Three consecutive bands were then eluted, namely complex **1** (R_f 0.36; 8 mg, 0.0053 mmol, 13%), **2** (R_f 0.31; 7 mg, 0.0045 mmol, 11%) and **3** (R_f 0.25; 4 mg, 0.0025 mmol, 6%). The red baseline portion was extracted with CH$_2$Cl$_2$ and subjected to fractional crystallization to give pure **4** (10 mg, 0.0050 mmol, 12.5%) and then **5** (4 mg, 0.0029 mmol, 7%).

X-Ray Data Collection and Structural Determination of Complexes **1**–**5**.—All pertinent crystallographic data and other experimental details are summarized in Table 7. Data were collected at ambient temperature on a Rigaku AFC7R diffractometer, using Mo-Kα radiation (λ = 0.710 73 Å) with a graphite-crystal monochromator in the incident beam. The unit-cell parameters were determined from 25 accurately centred reflections. All the data were collected at room temperature (298 K) using the ω–2θ scan technique with a scan rate of 16.0° min^{-1} (in ω). The weak reflections were rescanned (up to four scans) and the counts were accumulated. The stability of the crystals was monitored at regular intervals using three standard reflections and no significant decay was observed. The diffracted intensities were corrected for Lorentz and polarization effects. The ψ-scan method was employed for semiempirical absorption corrections.[33] Scattering factors were taken from ref. 34(*a*) and anomalous dispersion effects [34b] were included in F_c.

The structures were solved by direct methods[35] and expanded by Fourier techniques. The solutions were refined on F by full-matrix least-squares analysis with Os, Pd and Cl atoms refined anisotropically. The hydrogen atoms of the pyridine ligand in complex **5** were generated in their ideal positions (C–H 0.95 Å). The hydrogen atoms of the water molecule in **4**, the terminal (**2**) and the Os–Pd bridging hydrides (**1**–**3**) were located on the Fourier-difference map of the low-angle data, whilst the Os–Os bridging hydrides for all the complexes were

Table 11 Atomic coordinates for compound **4** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.528 90(6)	0.210 61(4)	0.870 74(6)	Cl(1*)	1.054 1(4)	−0.034 4(3)	1.201 7(4)
Os(2)	0.770 93(6)	0.334 68(4)	0.960 68(6)	Pd(1*)	1.144 7(1)	−0.115 82(7)	0.985 5(1)
Os(3)	0.709 79(6)	0.229 76(4)	1.198 09(6)	Os(1*)	1.471 10(6)	−0.210 61(4)	1.129 26(6)
Pd(1)	0.855 3(1)	0.115 82(7)	1.014 5(1)	Os(2*)	1.229 07(6)	−0.334 68(4)	1.039 32(6)
Cl(1)	0.945 9(4)	0.034 4(3)	0.798 3(4)	Os(3*)	1.290 21(6)	−0.229 76(4)	0.801 91(6)
Cl(2)	0.475 5(4)	0.404 6(2)	0.824 1(4)	C(1*)	1.386(1)	−0.059(1)	1.077(2)
O(1)	0.646(1)	−0.035 6(8)	0.943(1)	Cl(2*)	1.524 5(4)	−0.4046(2)	1.175 9(4)
O(2)	0.175(1)	0.226 5(8)	0.795(1)	C(2*)	1.695(2)	−0.221(1)	1.180(2)
O(3)	0.512(1)	0.170 1(10)	0.536(2)	C(3*)	1.484(2)	−0.184(1)	1.343(2)
O(4)	1.139(1)	0.229 3(8)	1.143(1)	C(4*)	0.998(2)	−0.262(1)	0.922(2)
O(5)	0.815(1)	0.559 7(9)	1.000(1)	C(5*)	1.205(2)	−0.478(1)	1.018(2)
O(6)	0.816(1)	0.315 2(9)	0.644(1)	C(6*)	1.198(2)	−0.320(1)	1.238(2)
O(7)	1.049(1)	0.194 2(10)	1.455(2)	C(7*)	1.078(2)	−0.203(1)	0.640(2)
O(8)	0.501(1)	0.383 0(9)	1.363(1)	C(8*)	1.418(2)	−0.325(1)	0.696(2)
O(9)	0.696(1)	0.019 9(9)	1.327(1)	C(9*)	1.300(2)	−0.098(1)	0.721(2)
O(10)	0.097 0	0.450 7	0.425 7	O(1*)	1.354(1)	0.035 6(8)	1.057(1)
C(1)	0.614(1)	0.059(1)	0.923(2)	O(2*)	1.825(1)	−0.226 5(8)	1.205(1)
C(2)	0.305(2)	0.221(1)	0.820(2)	O(3*)	1.488(1)	−0.170 1(10)	1.464(2)
C(3)	0.516(2)	0.184(1)	0.657(2)	O(4*)	0.861(1)	−0.229 3(8)	0.857(1)
C(4)	1.002(2)	0.262(1)	1.078(2)	O(5*)	1.185(1)	−0.559 7(9)	1.000(1)
C(5)	0.795(2)	0.478(1)	0.982(2)	O(6*)	1.184(1)	−0.315 2(9)	1.356(1)
C(6)	0.802(2)	0.320(1)	0.762(2)	O(7*)	0.951(1)	−0.194 2(10)	0.545(2)
C(7)	0.922(2)	0.203(1)	1.360(2)	O(8*)	1.499(1)	−0.383 0(9)	0.637(1)
C(8)	0.582(2)	0.325(1)	1.304(2)	O(9*)	1.304(1)	−0.019 9(9)	0.673(1)
C(9)	0.700(2)	0.098(1)	1.279(2)				

Table 12 Atomic coordinates for compound **5** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.887 07(2)	0.010 05(8)	0.220 59(5)	C(1)	0.900 3(6)	0.155(2)	0.154(2)
Os(2)	0.896 95(2)	−0.269 94(9)	0.175 51(6)	C(2)	0.878 5(5)	0.135(2)	0.308(1)
Os(3)	0.934 56(2)	−0.151 69(9)	0.340 34(6)	C(3)	0.844 1(5)	0.015(2)	0.159(1)
Os(4)	0.817 19(2)	−0.308 23(9)	0.417 85(6)	C(4)	0.918 0(7)	−0.311(3)	0.083(2)
Pd	0.872 54(4)	−0.201 4(2)	0.314 6(1)	C(5)	0.857 0(6)	−0.296(2)	0.101(1)
Cl(1)	0.868 0(1)	−0.417 1(5)	0.418 6(4)	C(6)	0.896 6(6)	−0.452(2)	0.217(2)
Cl(2)	0.846 8(1)	−0.094 7(5)	0.439 0(3)	C(7)	0.976 9(6)	−0.119(2)	0.351(2)
Cl(3)	0.813 5(1)	−0.270 2(6)	0.257 8(3)	C(8)	0.932 3(5)	−0.051(2)	0.443(1)
O(1)	0.908 9(4)	0.240(2)	0.111(1)	C(9)	0.941 1(6)	−0.321(2)	0.403(1)
O(2)	0.874 6(4)	0.205(2)	0.366(1)	C(10)	0.780 8(6)	−0.223(3)	0.415(2)
O(3)	0.816 8(4)	0.019(2)	0.125(1)	C(11)	0.822 8(6)	−0.339(2)	0.542(2)
O(4)	0.931 4(4)	−0.335(2)	0.027(1)	C(12)	0.805 7(6)	−0.587(2)	0.330(2)
O(5)	0.830 4(4)	−0.304(2)	0.051(1)	C(13)	0.794 0(7)	−0.719(3)	0.310(2)
O(6)	0.897 4(4)	−0.565(2)	0.246(1)	C(14)	0.768 1(7)	−0.756(3)	0.347(2)
O(7)	1.005 4(5)	−0.107(2)	0.358(1)	C(15)	0.755 6(6)	−0.665(2)	0.396(2)
O(8)	0.930 9(4)	0.011(2)	0.508(1)	C(16)	0.770 0(6)	−0.540(2)	0.418(1)
O(9)	0.946 2(5)	−0.425(2)	0.442(1)	C(17)	0.505 4	0.232 6	0.590 4
O(10)	0.756 9(4)	−0.154(2)	0.413(1)	C(18)	0.520 6	0.222 7	0.709 7
O(11)	0.827 1(4)	−0.359(2)	0.618(1)	C(19)	0.500 0	0.260 7	0.750 0
N	0.795 9(4)	−0.503(2)	0.387(1)	C(20)	0.500 0	0.124 9	0.750 0

located by potential-energy calculations.[36] All the hydrogen atoms were included in the structure factors but the parameters were fixed without further refinement. Owing to the disorder of the hexane molecule in complex **5**, no hydrogen atoms were introduced. The carbon atoms were fixed as obtained but included in the structure factor for subsequent refinement of the structure. Calculations were performed on a Silicon-Graphics computer, using the program package TEXSAN.[37] Positional parameters for the non-hydrogen atoms of the complexes are given in Tables 8–12.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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