DALTON
FULL PAPER

Syntheses and characterization of high-nuclearity osmium–palladium mixed-metal carbonyl clusters; molecular structures of $[Os_4Pd_6(CO)_8(\mu\text{-}CO)_5(\mu_3\text{-}CO)_3(\mu\text{-dppm})_2]\cdot 0.5C_6H_{14}$ and $[Os_5Pd_4(\mu_6\text{-}C)(CO)_{12}(\mu\text{-}CO)_3(\mu\text{-dppm})_2]\cdot CH_2Cl_2$

Janesse Wing-Sze Hui and Wing-Tak Wong *

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China

Treatment of $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ with $[Pd_2(\mu\text{-dppm})_2Cl_2]$ afforded the novel high-nuclearity osmium–palladium mixed-metal carbonyl clusters $[Os_5Pd_6(CO)_{13}(\mu\text{-}CO)_5(\mu\text{-}H)_2(\mu\text{-dppm})_2]$ **1**, $[Os_5Pd_6(CO)_{13}(\mu\text{-}CO)_6(\mu\text{-dppm})_2]$ **2** and $[Os_4Pd_6(CO)_8(\mu\text{-}CO)_8(\mu\text{-dppm})_2]$ **3** in low yield, while the reaction of $[Os_5(\mu_5\text{-}C)(CO)_{15}]$ with $[Pd_2(\mu\text{-dppm})_2Cl_2]$ afforded $[Os_5Pd_4(\mu_6\text{-}C)(CO)_{12}(\mu\text{-}CO)_3(\mu\text{-dppm})_2]$ **4** and $[Os_5(\mu_5\text{-}C)(CO)_{13}(\mu\text{-dppm})]$ **5** in moderate yields. The molecular structures of clusters **3** and **4** have been determined.

The chemistry of heterometallic cluster compounds, especially those containing Group 8 and 10 metals, is progressing rapidly, in part because they represent a synthetic challenge, but more importantly because of their potential in novel catalytic and stoichiometric reactions.[1] The different possible reactivities of the constituent metals and the possible co-operation between the metal centers make multimetallic systems unique.[2,3]

Of particular interest is use of the palladium(I) complex $[Pd_2(\mu\text{-dppm})_2Cl_2]$ to generate mixed-metal systems. However, most investigations have been concerned with the formation of A-frame complexes *via* insertion of small molecules, *e.g.* CO, SO_2 or RCN, into the M–M bond, or their reactivity towards nucleophilic metal reagents, such as carbonylmetalates.[4–8] For example, the reaction of $[Pd_2(\mu\text{-dppm})_2Cl_2]$ with the dianion $[Fe(CO)_4]^{2-}$ yielded the neutral heterotrinuclear complex $[Pd_2Fe(dppm)_2(CO)_4]$ by displacement of the two chloride ligands and the insertion of the iron group into one of the Pd–P bonds. Two Fe–Pd bonds were formed in the process.[8] The reaction with ionic carbonylmetalates $[Mn(CO)_5]^-$ or $[Co(CO)_4]^-$ also led to mixed-metal clusters.[9,10]

Moreover, the rich structural chemistry exhibited by osmium–palladium mixed-metal carbonyl clusters has attracted our attention.[11–18] Our approach to prepare this type of mixed-metal cluster compounds is using the unsaturated cluster $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ and the carbido cluster $[Os_5(\mu_5\text{-}C)(CO)_{15}]$. The use of these two osmium complexes as the building blocks in heterometallic clusters as well as in the synthesis of high-nuclearity clusters is well established.[19–26] We have recently shown that palladium complexes with N-donor ligands are versatile precursors in the synthesis of osmium–palladium carbonyl cluster compounds. However, the reactivity of osmium carbonyl clusters with palladium complexes containing P-donor ligands has not been investigated extensively. This prompted us to present some new results involving the reaction of $[Pd_2(\mu\text{-dppm})_2Cl_2]$ with osmium complexes.

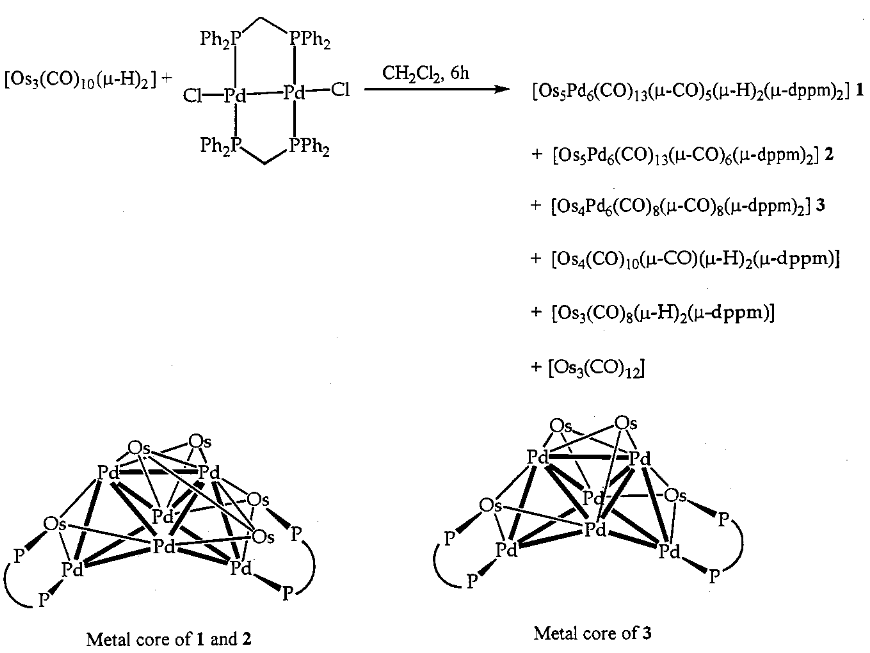
In the course of studying the synthesis and reactivities of osmium–palladium mixed-metal carbonyl clusters, we have recently reported the synthesis and structural characterization of a novel class of mixed-metal carbonyl clusters $[Os_5Pd_6(CO)_{13}(\mu\text{-}CO)_5(\mu\text{-}H)_2(\mu\text{-dppm})_2]$ **1** and $[Os_5Pd_6(CO)_{13}(\mu\text{-}CO)_6(\mu\text{-dppm})_2]$ **2** from the reaction of $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ with a slight excess of $[Pd_2(\mu\text{-dppm})_2Cl_2]$. We report the details of this reaction. In addition, the synthesis of $[Os_5Pd_4(\mu_6\text{-}C)(CO)_{15}(\mu\text{-dppm})_2]$ from $[Os_5(\mu_5\text{-}C)(CO)_{15}]$ and $[Pd_2(\mu\text{-dppm})_2Cl_2]$ is also presented.

Results and Discussion

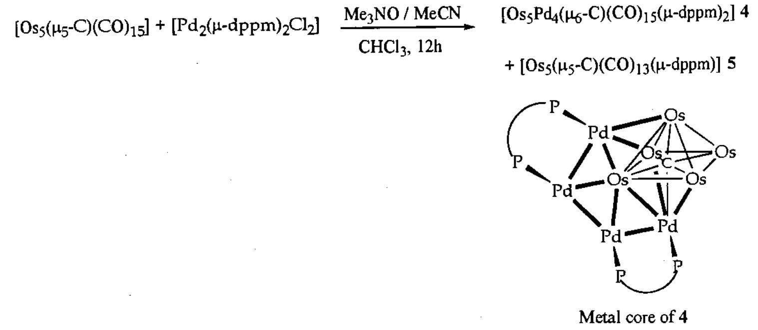
In spite of the previous postulation that the formation of osmium–palladium carbonyl clusters from $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ can only be stabilized by N-donor palladium complexes, such as $[Pd(py)_2Cl_2]$ and $[Pd(bipy)(MeCO_2)_2]$, no such mixed-metal clusters with P-donor ligands are known. We have recently found that treatment of $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ with a slight excess of $[Pd_2(\mu\text{-dppm})_2Cl_2]$ in CH_2Cl_2 at room temperature over a period of 6 h led to formation of a dark brown reaction mixture. Separation of products by TLC on silica afforded three high-nuclearity clusters $[Os_5Pd_6(CO)_{13}(\mu\text{-}CO)_5(\mu\text{-}H)_2(\mu\text{-dppm})_2]$ **1**, $[Os_5Pd_6(CO)_{13}(\mu\text{-}CO)_6(\mu\text{-dppm})_2]$ **2**, $[Os_4Pd_6(CO)_8(\mu\text{-}CO)_8(\mu\text{-dppm})_2]$ **3**, and the phosphine-substituted complexes $[Os_4(CO)_{10}(\mu\text{-}CO)(\mu\text{-}H)_2(\mu\text{-dppm})]$, $[Os_3(CO)_8(\mu\text{-}H)_2(\mu\text{-dppm})]$ and $[Os_3(CO)_{12}]$, see Scheme 1. The clusters **1**–**3** were tentatively characterized in the first instance on the basis of their positive-ion fast atom bombardment mass spectra, which indicate that they are of high nuclearity.

Since the yields of the complexes were quite low, the experimental conditions and stoichiometry of the reactants were screened to improve their yields. Extending the reaction time had little influence on the product ratios, however increased concentrations of $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ decreased the reaction rate and also led to more phosphine-containing clusters in the mixtures. At the same time no new high-nuclearity species were observed. The effects of varying the reaction conditions were also investigated. Increasing the reaction temperature increased the rate, but decreased the yields of the clusters **1**–**3** and also more phosphine-containing clusters (>58%) were observed.

The carbido clusters $[Os_5(\mu_5\text{-}C)(CO)_{15}]$ reacts with 2 equivalents of the oxidative decarbonylation reagent Me_3NO in MeCN afford the unstable complex $[Os_5(\mu_5\text{-}C)(CO)_{13}(MeCN)_2]$. However, upon the addition of a slight excess of $[Pd_2(\mu\text{-dppm})_2Cl_2]$ in $CHCl_3$, and reflux for 12 h, the heterometallic complex $[Os_5Pd_4(\mu_6\text{-}C)(CO)_{12}(\mu\text{-}CO)_3(\mu\text{-dppm})_2]$ **4** and the phosphine-substituted complex $[Os_5(\mu_5\text{-}C)(CO)_{13}(\mu\text{-dppm})]$ **5** are obtained in moderate yields (see Scheme 2). The complex **4** is air stable in the solid state under ambient conditions. It dissolves readily in common polar organic solvents and is highly stable. On reflux in a high boiling point solvent such as xylene, **4** remained unchanged with no observable decomposition. These observations suggested thermodynamic stability for the compound. The presence of the interstitial carbido carbon may confer high stability to the cluster, so that the skeleton can



Scheme 1



Scheme 2

sustain severe reaction conditions. Using an excess of $[Pd_2(\mu\text{-}dppm)_2Cl_2]$ in the reaction led to a higher yield of cluster **4** (46%) at the expense of **5** (22%). However, treatment of cluster **5** with $[Pd_2(\mu\text{-}dppm)_2Cl_2]$ did not lead to the formation of **4**. Therefore **5** is unlikely to be an intermediate for the formation of **4**. Complex **4** was also fully characterized by spectroscopic methods and single-crystal X-ray diffraction studies.

Crystallography

Fig. 1 illustrates the molecular structure of complex **3** and the intramolecular distances are listed in Table 1. Cluster **3** crystallizes with 0.5 C_6H_{14} the disorder of which could not be resolved. The molecule possesses C_2 symmetry with a non-crystallographically imposed two-fold axis passing through the midpoints of the Os(2)–Os(3) and Pd(3)–Pd(4) edges. The metal framework (Fig. 2) can be regarded as a central bicapped tetrahedron of six Pd atoms having four faces symmetrically capped by Os(1), Os(2), Os(3) and Os(4) on Pd(1)Pd(2)Pd(3), Pd(2)Pd(3)Pd(5), Pd(2)Pd(4)Pd(5) and Pd(4)Pd(5)Pd(6) respectively. The inner Pd_6 metal core is not observed in other hexanuclear palladium clusters $[Pd_6(CO)_4(PMe_3)_7]$[27] or $[Pd_6Cl_2(CO)_4(PPh_3)_4]$,[28] which adopt a slightly distorted octahedron and two triangular fragments joined by bridging chlorine atoms, respectively. A relatively large range of Pd–Pd distances is observed in cluster **3**, ranging from 2.679(2) to 3.136(2) Å. This imposes difficulty in the electron counting of these clusters. A similar observation has also been made for the complex $[Pd_6Ru_6(CO)_{24}]^{2-}$ which has a trigonally elongated octahedron of Pd atoms with the six faces capped by six Ru atoms.[29] In the structure the interlayer Pd · · · Pd distances also span a wide range of 3.068(1)–3.274(2) Å. No Os–Os interaction is observed in the cluster **3**. The Os–Pd bond distances in **3**, 2.645(1)–3.001(1) Å, are similar to those in **1** and **2**. Two dppm ligands bridge across Os(1)–Pd(1) and Os(4)–Pd(6) edges and are directed away from the metal core of the cluster. The bond parameters within the two dppm ligands do not deviate significantly from the expected values.

Table 1 Selected bond lengths (Å) of complex **3**

Os(1)–Pd(2)	2.839(1)	Os(1)–Pd(1)	3.001(1)
Os(2)–Pd(2)	2.663(2)	Os(1)–Pd(3)	2.833(1)
Os(2)–Pd(5)	2.822(1)	Os(2)–Pd(3)	2.832(2)
Os(3)–Pd(4)	2.836(2)	Os(3)–Pd(2)	2.854(1)
Os(4)–Pd(4)	2.860(1)	Os(3)–Pd(5)	2.645(1)
Os(4)–Pd(6)	2.975(1)	Os(4)–Pd(5)	2.843(1)
Pd(1)–Pd(3)	2.905(2)	Pd(1)–Pd(2)	3.029(2)
Pd(2)–Pd(3)	2.916(2)	Pd(1)–Pd(4)	2.679(2)
Pd(2)–Pd(5)	3.136(2)	Pd(2)–Pd(4)	2.760(2)
Pd(3)–Pd(5)	2.783(2)	Pd(3)–Pd(4)	3.020(2)
Pd(4)–Pd(5)	2.887(2)	Pd(3)–Pd(6)	2.684(2)
Pd(5)–Pd(6)	3.001(2)	Pd(4)–Pd(6)	2.924(2)
Os(4)–P(4)	2.336(4)	Os(1)–P(2)	2.332(5)
Pd(6)–P(3)	2.311(4)	Pd(1)–P(1)	2.296(5)

Of the sixteen carbonyl groups in cluster **3**, eight are termin-

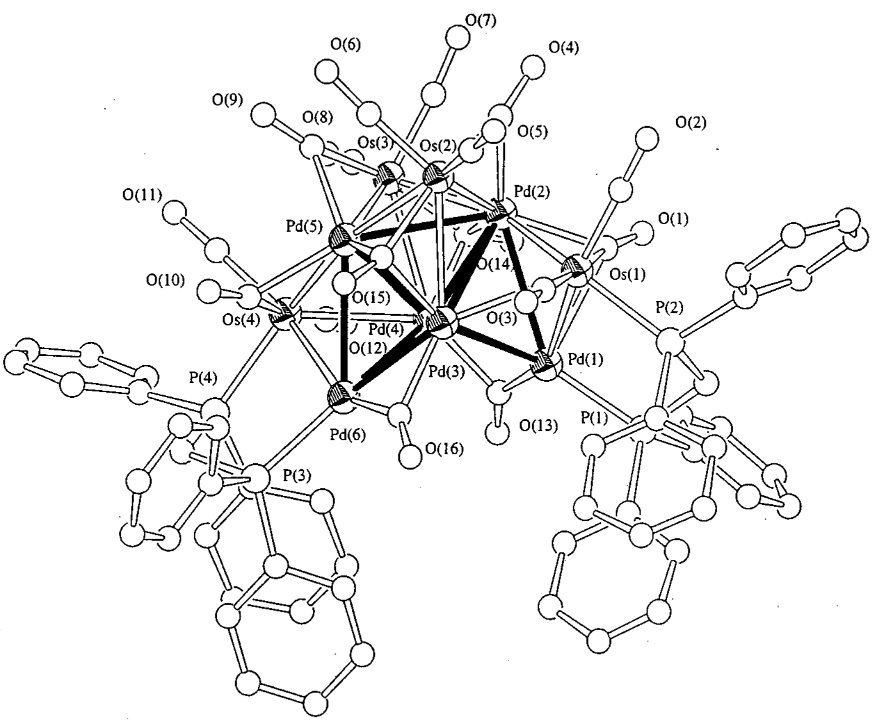


Fig. 1 Molecular structure of the complex [$Os_4Pd_6(CO)_8(\mu\text{-}CO)_5(\mu_3\text{-}CO)_3(\mu\text{-dppm})_2$] **3** with the atomic numbering scheme

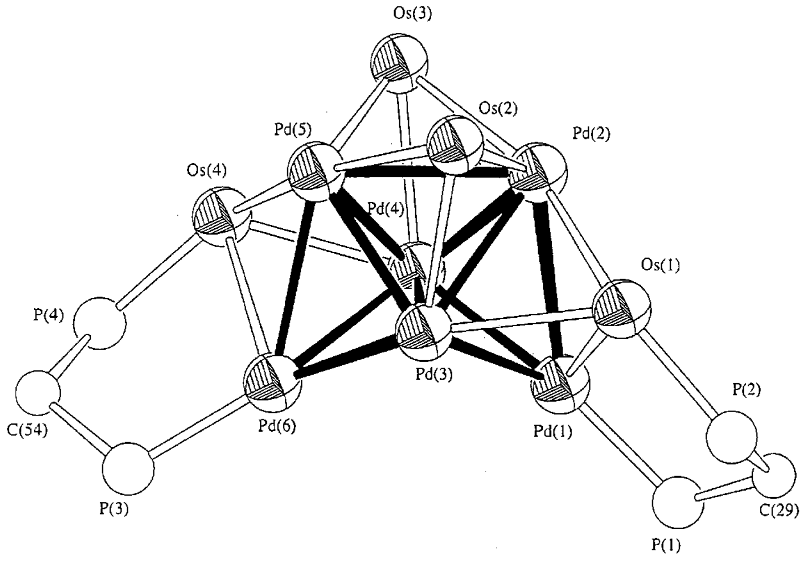


Fig. 2 The metal core geometry of complex **3**

ally bonded, five are edge-bridging and three are face bridging on the metal framework, with CO(1), CO(14) and CO(15) spanning faces Os(1)Pd(1)Pd(2), Os(3)Pd(2)Pd(4) and Os(2)-Pd(3)Pd(5) respectively. As we observed, the metal–metal bonds associated with the bridging or face bridging CO are longer than the others. Also, it is noteworthy that bridging and capping CO ligands are common in high-nuclearity palladium clusters, and Pd-containing mixed-metal clusters, as the electron excess in the clusters can be relieved by formation of the CO caps.[30,31]

The molecular structure of cluster **4** is depicted in Fig. 3 and some important bond parameters are given in Table 2. The molecule consists of an octahedral Os_5Pd cluster with an interstitial carbido ligand, ligated by three Pd atoms on the Os(1)–Os(4) and Os(4)–Pd(1) edges. The carbide carbon atom is displaced from the centroid of the four metals constituting the square-based pyramid by 0.231(1) Å and toward Pd(1). The average Os (basal)–Os (basal) [2.928(4) Å] and Os (apical)–Os (basal) (2.918 Å) bond distances in **4** are slightly longer than the corresponding parameters in the precursor [$Os_5(\mu_5\text{-}C)(CO)_{15}$],[32] 2.88(2) and 2.85(3) Å, respectively. The Os–Os bonds associated with the capping Pd(4) are significantly longer [average 2.98(3) Å] than the unsupported one [2.888(3) Å].

Two kinds of Pd–Pd bonds are observed in the compound: CO supported [Pd(2)–Pd(3) 2.732(5) Å] and dppm bridged [Pd(1)–Pd(2) 2.711(6) Å, Pd(3)–Pd(4) 2.702(7) Å]. The lengthening of Pd(2)–Pd(3) is possibly due to the steric bulk of the phenyl substituents. Another interesting feature of cluster **4** is the formation of an almost planar six-membered ring by the atoms Os(1), Os(3), Pd(1), Pd(2), Pd(3) and Pd(4) with maximum deviation of 0.01 Å. The metal connectivity of Os(4) is eight and is one of the highest that has been observed in metal clusters of this size. It is also attached to the carbido atoms and to two carbonyl ligands, giving it a co-ordination number of 11. The cluster core of **4** (Fig. 4) is also surrounded by two dppm ligands, twelve terminal CO and three CO ligands bridging the

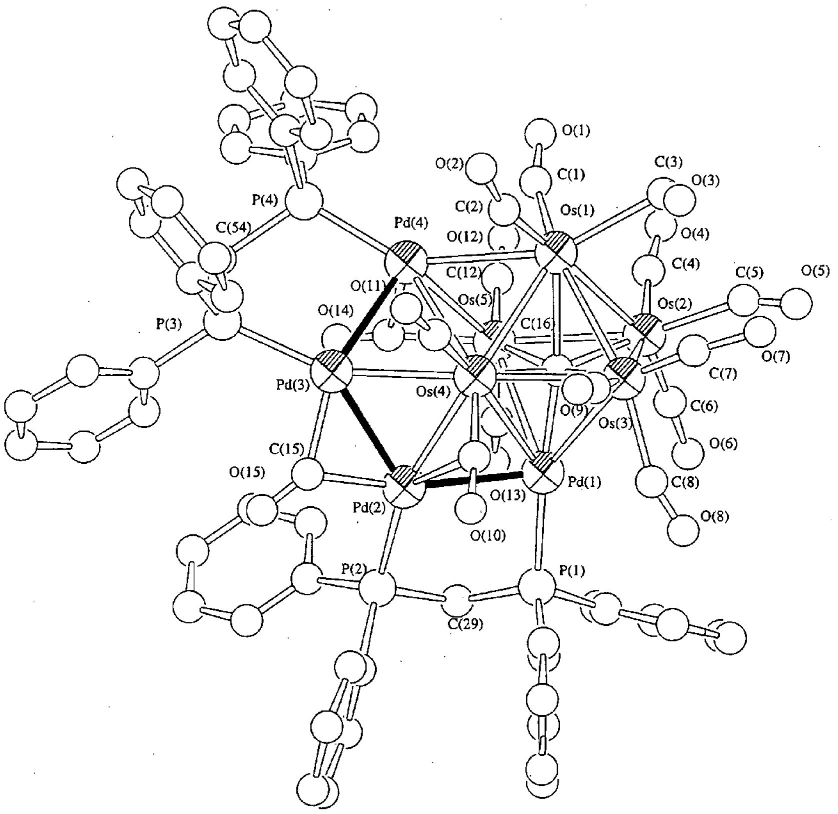


Fig. 3 Molecular structure of the complex $[Os_5Pd_4(\mu_6\text{-}C)(CO)_{12}(\mu\text{-}CO)_3(\mu\text{-}dppm)_2]$ **4** with the atomic numbering scheme

Table 2 Selected bond lengths (Å) of complex **4**

Os(1)–Os(2)	2.841(3)	Os(1)–Os(3)	2.931(3)
Os(1)–Os(4)	2.914(4)	Os(1)–Os(5)	2.986(3)
Os(2)–Os(3)	2.912(3)	Os(2)–Os(5)	2.906(3)
Os(3)–Os(4)	2.851(4)	Os(4)–Os(5)	3.044(3)
Os(1)–Pd(4)	2.896(5)	Os(3)–Pd(1)	3.100(5)
Os(4)–Pd(1)	2.829(4)	Os(4)–Pd(2)	2.727(5)
Os(4)–Pd(3)	2.742(5)	Os(4)–Pd(4)	2.854(4)
Os(5)–Pd(1)	2.925(4)	Os(5)–Pd(4)	2.782(4)
Pd(1)–Pd(2)	2.711(6)	Pd(2)–Pd(3)	2.732(5)
Pd(3)–Pd(4)	2.702(7)	Pd(1)–P(1)	2.29(1)
Pd(2)–P(2)	2.30(2)	Pd(3)–P(3)	2.29(1)
Pd(4)–P(4)	2.30(1)		

Os(4)–Pd(2), Os(5)–Pd(4) and Pd(2)–Pd(3) vectors. The presence of the bridging CO ligands has no significant lengthening effect on the corresponding bonds.

Conclusion

We have observed previously that the reaction of $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ with a N-donor palladium complex yields a series of osmium–palladium cluster complexes having structures based on vertex-shared triangles or tetrahedra which are osmium rich. However, in this case, reaction of $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ with $[Pd_2(\mu\text{-}dppm)_2Cl_2]$ resulted in no analogous complexes being formed. Instead, high-nuclearity undeca- and deca-nuclear mixed-metal clusters possessing segregated stacks of palladium core and osmium caps were obtained. This type of irregular fused-polyhedral cluster skeletons found in **1**–**3** is somewhat unusual, and may be compared with a series of high-nuclearity osmium–platinum clusters, *e.g.* $[Os_6Pt_4(CO)_{21}(\mu\text{-}H)_2(cod)]$,[33] $[Os_6Pt_5(CO)_{21}(cod)_2]$, $[Os_6Pt_4(CO)_{22}(cod)_2]$,[34] $[Os_4Pt_3(CO)_{11}(cod)_3]$[35] and $[Os_6Pt_7(CO)_{21}(cod)_2]$.[34] The metal skeleton of these species have layering of staggered triangles. The same segregation effect is also observed in rhodium–[36,37] and nickel–platinum[38,39] species. These examples show the tendency for the platinum atoms to segregate in homo- or hetero-platinum species. Here we show the first examples of aggregation phenomenon in the osmium–palladium system. However, this aggregation process leading to these clusters is not simple and a mixture of products is formed. The stoichiometry of the reactants therefore seems to be a determining factor for the products obtained.

Finally, it is worth pointing out that the electron counts found in these osmium–palladium clusters do not always agree with those predicted by skeletal electron counting rules. This may simply be ascribed to the ability of Pd to be satisfied with both 16- and 18-electron counts.

Experimental

Materials and methods

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 obtained commercially and used as received. The complexes $[Os_3(CO)_{10}(\mu\text{-}H)_2]$,[40] $[Os_5C(CO)_{15}]$[41,42] and $[Pd_2(\mu\text{-}dppm)_2Cl_2]$[43] were prepared by the literature method. Trimethylamine *N*-oxide dihydrate ($Me_3NO\cdot 2H_2O$), Aldrich, was sublimed [90 °C, 0.1 Torr (*ca.* 133 Pa)] before use. Infrared spectra were recorded on a Bio-Rad FTS-7 spectrometer, using 0.5 mm calcium fluoride solution cells, proton NMR spectra on a Bruker DPX 300 spectrometer using CD_2Cl_2 and referenced to $SiMe_4$ (δ 0), ^{31}P NMR spectra on a Bruker DPX 500 spectrometer using $CDCl_3$ as solvent with 85% H_3PO_4 as reference and mass spectra 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 on plates coated with Merck Kieselgel 60 GF_{254}.

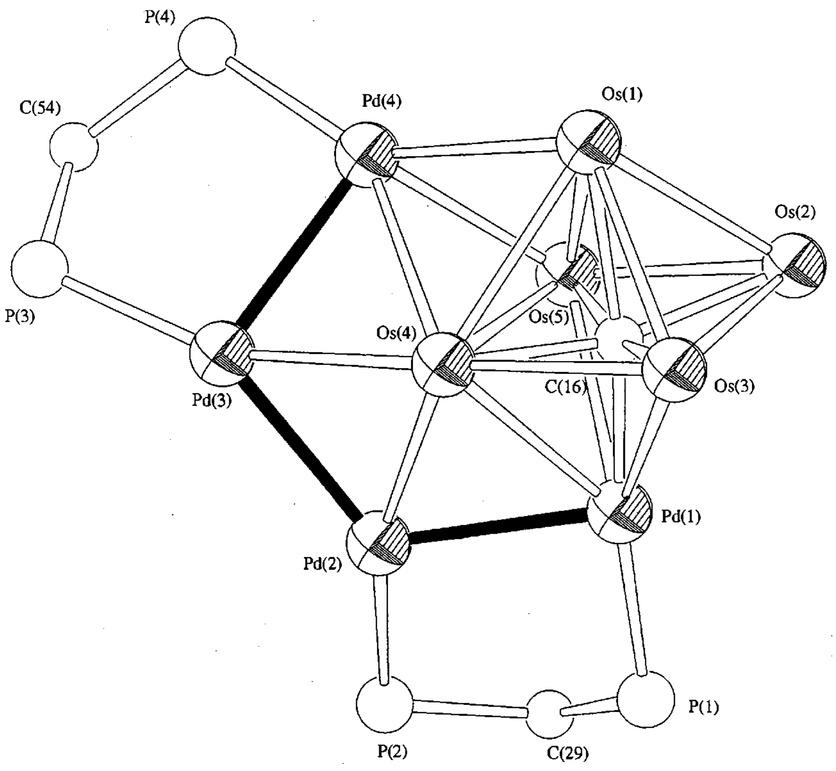


Fig. 4 The metal core geometry of complex **4**

Reaction of $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ with $[Pd_2(\mu\text{-dppm})_2Cl_2]$

A solution of $[Pd_2(\mu\text{-dppm})_2Cl_2]$ (130 mg, 0.6 mmol) in CH_2Cl_2 (20 cm^3) was added dropwise to $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ (500 mg, 0.586 mmol) in CH_2Cl_2 (50 cm^3) at room temperature under a nitrogen atmosphere. The initial deep red solution changed to dark brown upon stirring. Stirring was continued for 6 h and the solvent then removed under reduced pressure. The residue was redissolved in CH_2Cl_2 (5 cm^3) and separated by preparative TLC using the eluent *n*-hexane–CH_2Cl_2 (60:40, v/v) to afford six bands, which were extracted from silica to yield dark green complex **1** (50 mg, 0.018 mmol, 5%), brownish green **2** (52 mg, 0.037 mmol, 10%), dark green **3** (102 mg, 0.038 mmol, 9%), $[Os_4(CO)_{11}H_2(dppm)]$ (204 mg, 0.115 mmol, 26%), $[Os_3(CO)_8H_2(dppm)]$ (98 mg, 0.12 mmol, 20%) and $[Os_3(CO)_{12}]$ (53 mg, 0.0375 mmol, 6%) in the order of elution. For compound **3**. IR (CH_2Cl_2): ν(CO) 2127w, 2092w, 2061s, 2038vs, 2011m and 1992w cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.54–6.85 (40 H, m, C_6H_5) and 4.51 [4 H, t, $^2J(PH) = 9.3$ Hz, CH_2]. $^{31}P\text{-}\{^1H\}$ NMR (CD_2Cl_2): δ 8.9 [d, $^2J(PP)$ 86.4] and −0.51 [d, $^2J(PP)$ 86.4 Hz] (Found: C, 30.09; H, 1.69. Calc. for $C_{66}H_{44}O_{15}Os_5P_4Pd_4$: C, 29.80; H, 1.65%).

Reaction of $[Os_5(\mu\text{-}C)(CO)_{15}]$ with $[Pd_2(\mu\text{-dppm})_2Cl_2]$

An acetonitrile solution (50 cm^3) of freshly sublimed Me_3NO (10 mg, 0.008 mmol) was added dropwise to a $CHCl_3$ solution (150 cm^3) of $[Os_5(\mu_5\text{-}C)(CO)_{15}]$ (50 mg, 0.035 mmol) over a period of 30 min. After the addition of Me_3NO was complete, the solution faded from bright orange to light yellow. Then, a $CHCl_3$ solution (50 cm^3) of $[Pd_2(\mu\text{-dppm})_2Cl_2]$ (35 mg, 0.035 mmol) was added. The reaction was then stirred at reflux for 12 h after all the starting materials had been consumed. The color gradually turned from bright red to deep brown. After reduction in volume, the filtrate was separated by preparative TLC on silica with an eluent of *n*-hexane–CH_2Cl_2 (60:40, v/v) to give two bands, which were extracted from silica to yield dark green complexes **4** (42 mg, 0.016 mmol, 47%) and **5** (17 mg, 0.008 mmol, 24%). When the complex $[Os_5C(CO)_{15}]$ was treated with dppm in refluxing $CHCl_3$ for 24 h, **5** was also obtained in 83% yield. For compound **4**. IR (CH_2Cl_2): ν(CO) 2115w, 2099m, 2088s, 2037w, 2026s and 2007m cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.43–6.96 (40 H, m, C_6H_5), 4.36 [2 H, t, $^2J(PH) = 9.3$, CH_2] and 3.97 [2 H, t, $^2J(PH) = 9.6$ Hz, CH_2]. $^{31}P\text{-}\{^1H\}$ NMR (CD_2Cl_2): δ 10.7 [d, $^2J(PP)$ 61.2], 7.5 [d, $^2J(PP)$ 64.4], 2.7 [d, $^2J(PP)$ 61.2] and 0.4 [d, $^2J(PP)$ 64.5 Hz] (Found: C, 29.92; H, 1.72. Calc. for $C_{66}H_{44}O_{16}Os_5P_4Pd_6$: C, 29.75; H, 1.65%).

Crystallography

Pertinent crystallographic data and other experimental details are summarized in Table 3. Data were collected at ambient temperature on a MAR research image-plate scanner, using Mo-Kα radiation (λ = 0.710 73 Å) with a graphite-crystal monochromator in the incident beam. For both complexes **3** and **4**, sixty-five 3° frames with an exposure time of 5 min per frame were used. Intensity data were corrected for Lorentz-polarization effects. An approximate absorption correction by interimage scaling was also applied. Scattering factors were taken from ref. 44(*a*) and anomalous dispersion effects[44b] were included in F_c.

The structures were solved by direct methods (SIR 88)[45] and expanded by Fourier-difference techniques. The solutions were refined on *F* by full-matrix least-squares analysis with Os, Pd and P atoms treated anisotropically, the carbon atoms isotropically. Hydrogen atoms of organic moieties were placed in ideal positions. All the hydrogen atoms were included in the structure factors but the parameters were fixed without further refinement. Calculations were performed on a Silicon-Graphics computer, using the program package TEXSAN.[46]

CCDC reference number 187/977.

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, a Hung Hing Ying Scholarship and a Li Po Chun Scholarship, all administered by the University of Hong Kong, and the Sir Edward Youde Memorial Fellowship 1996–1998 administered by the Sir Edward Youde Memorial Fund Council.

Table 3 Crystallographic data and data collection parameters for compounds **3** and **4**

	$\mathbf{3}\cdot0.5C_6H_{14}$	$\mathbf{4}\cdot CH_2Cl_2$
Empirical formula	$C_{66}H_{44}O_{16}Os_4P_4Pd_6$	$C_{66}H_{44}O_{15}Os_5P_4Pd_4$
M	2615.20 (2659.25 with solvent)	2576.60 (2662.49 with solvent)
Crystal dimensions/mm	0.22 × 0.32 × 0.33	0.07 × 0.23 × 0.24
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	13.082(1)	16.188(1)
b/Å	24.615(1)	17.412(1)
c/Å	23.524(1)	29.388(1)
β/°	103.03(1)	105.16(1)
U/Å^3	7380.0(7)	7995.2(8)
Z	4	4
D_c/g cm^{-3}	2.400	2.212
μ/cm^{-1}	84.28	89.87
F(000)	4960	4904
Maximum 2θ/°	51.2	50.9
Reflections collected	54 752	51 524
Unique reflections	12 032	6329
Observed reflections [$I > 3.00\sigma(I)$]	6010	2805
Weighting scheme p in $w = \{\sigma_c^2(F_o) + [p^2/4(F_o^2)]\}^{-1}$	0.024	0.016
R, R' (observed data)	0.045, 0.046	0.069, 0.077
Goodness-of-fit indicator	1.29	2.04
Largest Δ/σ	0.01	0.05
Number of parameters	455	242
Residual extrema in the final difference map (close to Os)/e Å^{-3}	1.18 to −1.19	1.34 to −1.36

References

1 J. Xiao and R. J. Puddephatt, *Coord. Chem. Rev.*, 1995, **143**, 457.

2 D. F. Shriver, H. D. Kaesz and R. D. Adams (Editors), *The Chemistry of Metal Cluster Complexes*, VCH, New York, 1990.

3 M. C. Comstock and J. R. Sharpley, *Coord. Chem. Rev.*, 1995, **143**, 501.

4 P. Braunstein, J.-M. Jud, Y. Dusausoy and J. Fischer, *Organometallics*, 1983, **2**, 180.

5 P. Braunstein, J.-M. Jud and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1983, 5.

6 M. C. Grossel, R. P. Moulding and K. R. Seddon, *J. Organomet. Chem.*, 1983, **253**, C50.

7 P. Braunstein, C. de Meric de Bellefon and M. Ries, *J. Organomet. Chem.*, 1984, **262**, C14.

8 P. Braunstein, J. Kervennal and J.-L. Richert, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 768.

9 P. Braunstein, C. de Meric de Bellefon, M. Ries, J. Fischer, S.-E. Bouaoud and D. Grandjean, *Inorg. Chem.*, 1988, **27**, 1327.

10 P. Braunstein, C. de Meric de Bellefon and M. Ries, *Organometallics*, 1988, **7**, 332.

11 S. Chan and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1994, 1605.

12 S. Chan and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1995, 3987.

13 S. Chan and W.-T. Wong, *J. Organomet. Chem.*, 1995, **489**, C78.

14 S. Chan, S.-M. Lee, Z. Lin and W.-T. Wong, *J. Organomet. Chem.*, 1996, **510**, 219.

15 J. W.-S. Hui and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1996, 2887.

16 J. W.-S. Hui and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1997, 1515.

17 J. W.-S. Hui and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1997, 2445.

18 J. W.-S. Hui and W.-T. Wong, *Chem. Commun.*, 1997, 2009.

19 A. B. Antonova, S. V. Kovalenko, E. D. Korniets, A. A. Johansson, Yu. T. Struchkov and A. I. Yanovsky, *J. Organomet. Chem.*, 1984, **267**, 299.

20 L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 171.

21 L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, J. L. Spencer, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1978, 260.

22 L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 155.

23 B. F. G. Johnson, J. Lewis, P. R. Raithby, S. N. Azman, B. Syed Mustaffa, M. J. Taylor, K. H. Whitmire and W. Clett, *J. Chem. Soc., Dalton Trans.*, 1984, 2111.

24 R. Khattar, B. F. G. Johnson, J. Lewis, P. R. Raithby and M. J. Rosales, *J. Chem. Soc., Dalton Trans.*, 1990, 2167.

25 B. F. G. Johnson, J. Lewis, P. R. Raithby, M. J. Rosales and D. A. Welch, *J. Chem. Soc., Dalton Trans.*, 1986, 453.

26 D. H. Farrar, B. F. G. Johnson, J. Lewis, P. R. Raithby and M. J. Rosales, *J. Chem. Soc., Dalton Trans.*, 1982, 2051.

27 H.-F. Klein, M. Mager, W. Florke and H.-J. Haupt, *Organometallics*, 1992, **11**, 3915.

28 E. G. Mednikov, N. K. Eremenko, Yu. L. Slovokhotov and Yu. T. Struchkov, *Metallorg. Khim.*, 1989, **2**, 1289.

29 E. Brivio, A. Ceriotti, R. D. Pergola, L. Garlaschelli, F. Demartin, M. Manassero, M. Sansoni, P. Zanello, F. Laschi and B. T. Heaton, *J. Chem. Soc., Dalton Trans.*, 1994, 3237.

30 R. Jund, P. Lemoine, M. Gross, R. Bender and P. Braunstein, *J. Chem. Soc., Dalton Trans.*, 1985, 711.

31 R. Jund, P. Lemoine, M. Gross, R. Bender and P. Braunstein, *J. Chem. Soc., Chem. Commun.*, 1983, 86.

32 P. F. Jackson, B. F. G. Johnson, J. Lewis and J. N. Nicholls, *J. Chem. Soc., Chem. Commun.*, 1980, 564.

33 R. D. Adams, J.-C. Lii and W. Wu, *Inorg. Chem.*, 1991, **30**, 3613.

34 R. D. Adams, J.-C. Lii and W. Wu, *Inorg. Chem.*, 1992, **31**, 2556.

35 R. D. Adams and W. Wu, *Inorg. Chem.*, 1991, **30**, 3605.

36 A. Fumagalli, S. Martinengo and G. Ciani, *J. Organomet. Chem.*, 1984, **273**, C46.

37 A. Fumagalli, S. Martinengo, G. Ciani, N. Masciocchi and A. Sironi, *Inorg. Chem.*, 1992, **31**, 336.

38 A. Ceriotti, F. Demartin, B. T. Heaton, G. Longoni, M. Manassero, G. Piro, G. Piva and M. Sansoni, *J. Organomet. Chem.*, 1986, **301**, C5.

39 A. Ceriotti, F. Demartin, G. Longoni, M. Manassero, M. Marchionna, G. Piva and M. Sansoni, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 697.

40 E. Sappa and M. Ville, *Inorg. Synth.*, 1989, **26**, 367.

41 B. F. G. Johnson, J. Lewis, W. J. H. Nelson, J. N. Nicholls, J. Puga, P. R. Raithby, M. J. Rosales, M. Schroder and M. D. Vargas, *J. Chem. Soc., Dalton Trans.*, 1983, 2447.

42 C. R. Eady, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1975, 2606.

43 L. S. Benner and A. L. Balch, *J. Am. Chem. Soc.*, 1978, **100**, 6099.

44 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.

45 M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidor, R. Spagna and D. Viterbo, SIR 88, *J. Appl. Crystallogr.*, 1989, **22**, 389.

46 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.

Received 30*th January* 1998; *Paper* 8/00817E