High-nuclearity mixed-metal carbonyl clusters of osmium and palladium; molecular structures of $[Os_5Pd_6(CO)_{13}(\mu\text{-}CO)_5(\mu\text{-}H)_2(\mu\text{-dppm})_2]\cdot 2CH_2Cl_2\cdot C_6H_{14}$ and $[Os_5Pd_6(CO)_{13}(\mu\text{-}CO)_6(\mu\text{-dppm})_2]$

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The high-nuclearity 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 are synthesized from the reaction of $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ with $[Pd_2(\mu\text{-dppm})_2Cl_2]$; their molecular structures are determined by X-ray analysis.

High-nuclearity mixed-metal clusters have attracted considerable interest due to their novel structural features and interesting chemical and physical properties.[1] Most of these mixed-metal clusters are the combination of late transition metals. For examples, Fe/Pd,[2] Fe/Pt,[3] Fe/Cu,[4] Ru/Pt,[5] Ru/Cu,[6] Os/Pt,[7] Os/Hg,[8] Co/Hg,[9] Rh/Ni,[10] Rh/Pt,[11] Ni/Pt[12] are well established. However, mixed-metal clusters of osmium and palladium are relatively rare.[13] We recently established some reliable synthetic routes to osmium and palladium mixed-metal clusters. These systems are all osmium rich. Herein we report the synthesis and structural characterization of two novel high-nuclearity Os/Pd mixed-metal carbonyl clusters containing an essentially, identical metal core.

The reaction 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 temp for 6 h affords two new osmium–palladium clusters: dark green $[Os_5Pd_6(CO)_{13}(\mu\text{-}CO)_5(\mu\text{-}H)_2(\mu\text{-dppm})_2]$ **1** and brownish–green $[Os_5Pd_6(CO)_{13}(\mu\text{-}CO)_6(\mu\text{-dppm})_2]$ **2** in 5 and 10% yields respectively. The major products isolated from this system are phosphine containing clusters $[Os_3(CO)_8(\mu\text{-dppm})]$ (23%) and $[Os_4(CO)_{10}(\mu\text{-dppm})]$ (18%) (confirmed by IR and ^1H NMR spectroscopy). Both clusters **1** and **2** were isolated as air-stable solids upon thin layer chromatographic separation on silica. Spectroscopic† and analytical data are consistent with their formulations. In order to establish their molecular structures, X-ray analyses have been carried out on single crystals of **1** and **2**.‡ Suitable crystals of **1** and **2** were obtained as dark green prisms **1** and brownish–green blocks **2**, using CH_2Cl_2–*n*-hexane mixture at 0 °C for a period of 2 weeks, respectively. Clusters **1** and **2** were found to have an essentially identical metal core, see Fig. 1. Their full structures are depicted in Fig. 2 and Fig. 3 together with some important bond parameters. The cluster core geometry of **1** and **2** may be viewed as an 'inner' Pd_6 bicapped tetrahedron with several triangular faces asymmetrically capped by Os(1), Os(2), Os(4) and Os(5) on Pd(1)Pd(2)Pd(3), Pd(2)Pd(3)Pd(5), Pd(3)Pd(4)Pd(5) and Pd(4)Pd(5)Pd(6) respectively. In addition, the Os(3) capped onto Os(2)Pd(2)Pd(5) so that the cluster cores become asymmetric or otherwise a twofold axis is possible. The only significant Os–Os interaction is observed between Os(2) and Os(3) [3.0074(7) Å in **1** and 2.8861(9) Å in **2**]. This metal framework can be viewed as a distorted fragment of three close-packed layers of metal atoms and is unprecedented in both homo- and hetero-metallic clusters containing osmium. Of the 18 carbonyl groups in cluster **1**, 13 are terminally bonded and 5 are bridging the Os–Pd bonds. In **2**, the CO distributions are almost identical to that observed in **1**, except for an extra bridging C(10)–O(10) across Os(3)–Pd(5). In **1**, there are two hydride ligands. This was as evident from the ^1H NMR spectroscopy. However, their positions cannot be determined by X-ray analysis directly. Detailed examination of the CO disposition on the ligand envelope and metal–metal bond distances suggested that one may bridge across the Os(2)–Pd(2) edge while the other one may bridge across Os(2)–Os(3). Both of these metal–metal distances are significantly longer than those observed in **2** where no hydride ligands are present.

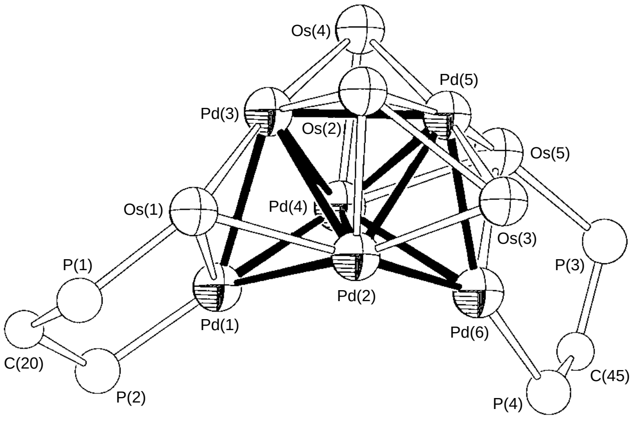

Fig. 1 The metal core geometry of **1** and **2**

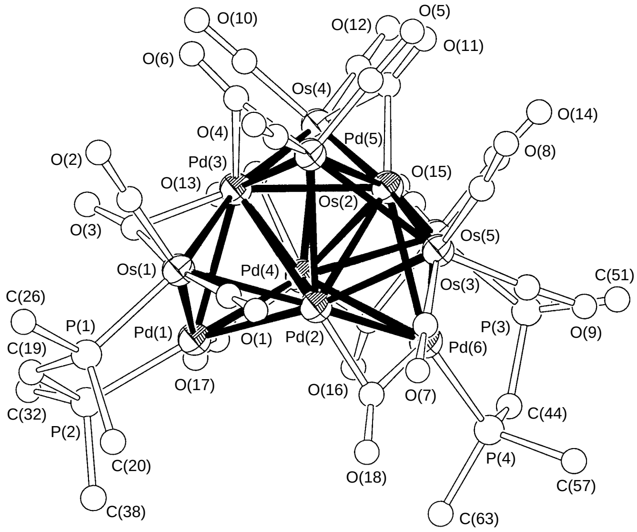

Fig. 2 The molecular structure of **1** showing the atom numbering scheme (phenyl rings are omitted for clarity). Selected bond lengths (Å): Os(1)–Pd(1) 2.935(1), Os(1)–Pd(2) 2.833(1), Os(1)–Pd(3) 2.834(1), Os(2)–Os(3) 3.0074(7), Os(2)–Pd(2) 3.024(1), Os(2)–Pd(3) 2.725(1), Os(2)–Pd(5) 2.779(1), Os(3)–Pd(2) 2.774(1), Os(3)–Pd(5) 2.831(1), Os(4)–Pd(3) 2.890(1), Os(4)–Pd(4) 2.852(1), Os(4)–Pd(5) 2.730(1), Os(5)–Pd(4) 2.791(1), Os(5)–Pd(5) 3.030(1), Os(5)–Pd(6) 3.116(1), Pd(1)–Pd(2) 2.893(2), Pd(1)–Pd(3) 2.943(2), Pd(1)–Pd(4) 2.707(2), Pd(2)–Pd(3) 2.918(1), Pd(2)–Pd(4) 3.097(2), Pd(2)–Pd(5) 2.877(2), Pd(2)–Pd(6) 2.683(1), Pd(3)–Pd(4) 2.759(1), Pd(3)–Pd(5) 2.853(2), Pd(4)–Pd(5) 2.923(2), Pd(4)–Pd(6) 3.013(2), Pd(5)–Pd(6) 2.988(1).

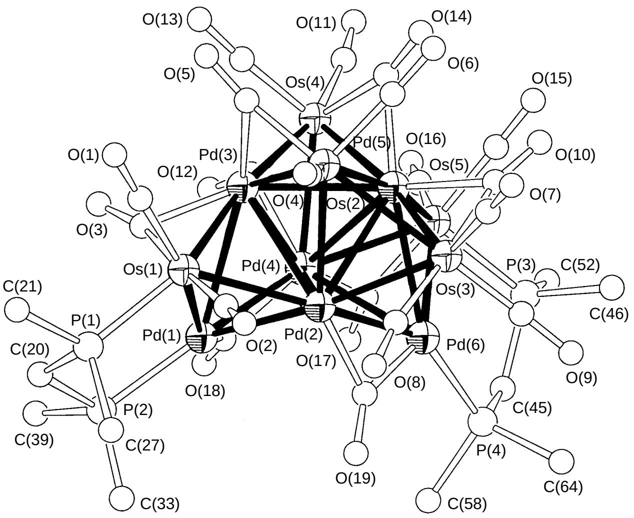

Fig. 3 The molecular structure of **2** showing the atom numbering scheme (phenyl rings are omitted for clarity). Selected bond lengths (Å): Os(1)–Pd(1) 2.963(2), Os(1)–Pd(2) 2.868(1), Os(1)–Pd(3) 2.819(1), Os(2)–Os(3) 2.8861(9), Os(2)–Pd(2) 2.913(1), Os(2)–Pd(3) 2.716(1), Os(2)–Pd(5) 2.768(1), Os(3)–Pd(2) 2.756(1), Os(3)–Pd(5) 2.787(1), Os(4)–Pd(3) 2.841(1), Os(4)–Pd(4) 2.839(2), Os(4)–Pd(5) 2.747(1), Os(5)–Pd(4) 2.837(1), Os(5)–Pd(5) 3.016(1), Os(5)–Pd(6) 3.180(2), Pd(1)–Pd(2) 2.828(2), Pd(1)–Pd(3) 3.004(2), Pd(1)–Pd(4) 2.722(2), Pd(2)–Pd(3) 2.881(2), Pd(2)–Pd(4) 3.162(2), Pd(2)–Pd(5) 2.914(2), Pd(2)–Pd(6) 2.706(2), Pd(3)–Pd(4) 2.786(1), Pd(3)–Pd(5) 2.867(2), Pd(4)–Pd(5) 2.939(2), Pd(4)–Pd(6) 2.935(2), Pd(5)–Pd(6) 2.948(2).

It is a common observation that the metal–metal bond elongates as it is bridged by hydride.[14] Although the solid-state structure of **1** revealed two hydride environment, in solution some dynamic processes may be possible and a broad ^{1}H NMR singlet is observed. Both **1** and **2** possess 146 CVE. However, their structures can not be rationalized by common electron counting rules.[15] This is not entirely unexpected as many Os/Pd or Os/Pt mixed–metal clusters do not obey simple electron counting rules owing to an alternative stable 16-electron configuration of Pd and Pt.

Our present results establish new examples of the high-nuclearity Os/Pd clusters. Although the yields are quite low, the syntheses under these experimental conditions are reproducible. At this stage, we do not detect any interconversion between **1** and **2** even though their molecular structures are very similar. Further studies would screen the experimental conditions and stoichiometry of the reactants to improve the yield of these novel species so that their chemical reactivities can be investigated.

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Footnotes and References

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† *Spectroscopic data*: **1**: IR [ν(CO), CH_2Cl_2] 2076w, 2046s, 2034vs, 2019m, 1992m, 1968w cm^{-1}; Negative FAB mass spectrum: m/z = 2861 (2863 calc.); ^{1}H NMR(CD_2Cl_2) δ −14.93 (s, br, 2 H), 5.35 [t, J(HP) 1.04 Hz, 4 H], 7.45–7.59 (m, 40 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 24.5 [d, ^2J(PP) 88.7 Hz], 11.0 [d, ^2J(PP) 88.7 Hz], −1.9 [d, ^2J(PP) 84.4 Hz], −5.3 [d, ^2J(PP) 84.4 Hz].

2: IR [ν(CO), CH_2Cl_2] 2074w, 2053s, 2034vs, 2015m, 1992m, 1968w cm^{-1}; Negative FAB mass spectrum: m/z = 2886 (2890 calc.); ^{1}H NMR (CD_2Cl_2) δ 5.22 [t, J(HP) 1.04 Hz, 4 H], 7.48–7.62 (m, 40 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 30.4 [d, ^2J(PP) 88.6 Hz], 9.2 [d, ^2J(PP) 88.6 Hz], 1.3 [d, ^2J(PP) 83.2 Hz], −3.5 [d, ^2J(PP) 83.6 Hz].

‡ *Crystal data*: **1**: $C_{76}H_{64}Cl_4O_{18}Os_5P_4Pd_6$, M = 3118.42, primitive monoclinic, space group $P2_1/c$ (no. 14), a = 14.348(1), b = 21.721(2), c = 28.797(2) Å, β = 97.48(2)°, U = 8898(1) Å^3, Z = 4, D_c = 2.328 g cm^{-3}, F(000) = 5784, Mo-Kα radiation (λ = 0.71073 Å), μ(Mo-Kα) = 85.38 cm^{-1}, dimensions 0.19 × 0.21 × 0.25 mm. MAR research image plate scanner. 69022 reflections were collected and merged to give 9312 (R_{int} = 0.04) observed data [$I > 3.00\sigma(I)$]. Structure solved by direct methods (SIR88)[17] and Fourier-difference techniques, refined by full-matrix least-squares analysis to R = 0.040, R' = 0.037.

2: $C_{69}H_{44}O_{19}Os_5P_4Pd_6$, M = 2890.39, trigonal R-centered, space group $R\bar{3}$ (no. 148), a = 47.060(2), c = 20.568(1) Å, U = 39448(2) Å^3, Z = 18, D_c = 2.190 g cm^{-3}, F(000) = 23868, Mo-Kα radiation (λ = 0.71073 Å), μ(Mo-Kα) = 85.40 cm^{-1}, dimensions 0.18 × 0.19 × 0.23 mm. MAR research image plate scanner. 102482 reflections were collected and merged to give 9044 (R_{int} = 0.04) observed data [$I > 3.00\sigma(I)$]. Structure solved and refined as for **1** to R = 0.049, R' = 0.057. CCDC 182/604.

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