DALTON
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Synthesis, characterisation, molecular and crystal structures of two novel osmium–palladium carbide carbonyl clusters

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The pentaosmium carbide cluster $[Os_5C(CO)_{15}]$ reacted with $[Pd(PPh_3)_4]$ in CH_2Cl_2, giving a new hexanuclear osmium–palladium carbide cluster $[Os_5PdC(CO)_{12}(\mu\text{-}CO)_2(PPh_3)_2]$ in moderate yield; treatment of $[Os_5C(CO)_{15}]$ with $[PdCl_2(PPh_3)_2]$ in refluxing chloroform gave $[Os_5PdC(CO)_{15}(\mu\text{-}Cl)_2(PPh_3)]$ in low yield, which consists of a novel metal core geometry with a Pd–C (carbide) bond.

The chemistry of penta- and hexa-nuclear carbide clusters of ruthenium is well established.[1–4] However, the related osmium systems are not well studied. Some reactivity studies, largely on the nucleophilic substitution reactions and oxidative addition, on the thermodynamically very stable $[Os_5C(CO)_{15}]$ have been reported.[5,6] Isolation of the hexanuclear osmium carbide species has been reported by Hayward and Shapley.[7] However, the prohibitively low yield (< 1%) precludes any investigation of its reactivity. We recently prepared some arene derivatives of hexaosmium carbide clusters,[8] and believe that systematic cluster build up using $[Os_5C(CO)_{15}]$ is possible. As a continuation of our efforts and interest in investigating the chemistry of osmium–palladium mixed-metal clusters,[9–12] we herein report the synthesis and full characterisation of the two novel clusters formed from reaction between $[Os_5C(CO)_{15}]$ and $[Pd(PPh_3)_4]$ or $[PdCl_2(PPh_3)_2]$.

Treatment of $[Os_5C(CO)_{15}]$ with 1 equivalent of $[Pd(PPh_3)_4]$ in dichloromethane at ambient temperature for 6 h gave a deep red mixture. Two red clusters $[Os_5Pd(\mu_5\text{-}C)(CO)_{12}(\mu\text{-}CO)_2(PPh_3)_2]$ **1** and the known species $[Os_5(\mu_5\text{-}C)(CO)_{14}(PPh_3)]$ **2** were isolated in 22 and 18% yield respectively after chromatography on silica. Single crystals of **1** suitable for X-ray analysis were grown by slow evaporation of an *n*-hexane–CH_2Cl_2 solution at −20 °C. This analysis† revealed that compound **1** contains a square-based pyramidal core of five osmium atoms with a $Pd(PPh_3)$ group capping a triangular face of the pyramid, see Fig. 1. The carbide carbon atom occupies the basal plane and deviates from Os(1) by 0.14 Å from the best plane defined by Os(2), Os(3), Os(4) and Os(5). The average Os–Pd distance [2.812(3) Å] is significantly longer than that observed in $[Os_6Pd(CO)_{18}(bipy)]$ (bipy = 2,2′-bipyridine) [average 2.782(3) Å][9] where a μ_4-capped Pd(bipy) moiety is found. There are two CO ligands asymmetrically bridging the Os(2)–Pd(1) and Os(3)–Pd(1) vectors which are most probably due to the electronic balance between the osmium and palladium atoms. However, there is no significant difference in these Os–Pd distances compared to the unbridged Os(1)–Pd(1) bond. The other PPh_3 ligand occupies the axial position of the Os(5) atom presumably due to steric demands. It is believed that steric interactions with adjacent CO ligands will be minimised. The spectroscopic data ‡ of cluster **1** in solution are consistent with the solid-state structure obtained by X-ray analysis.

The corresponding reaction of $[Os_5C(CO)_{15}]$ with $[PdCl_2(PPh_3)_2]$ in refluxing chloroform affords $[Os_5Pd(\mu_5\text{-}C)(CO)_{15}(\mu\text{-}Cl)_2(PPh_3)]$ **3** in 12% yield and **2** in 8% yield after chromatographic separation on silica. However, cluster **2** is found to be the major product (56% yield) if the reaction is carried out at ambient temperature. The identity of **3** cannot be established based solely upon solution spectroscopic data.§ Therefore, X-ray structure analysis¶ was undertaken to

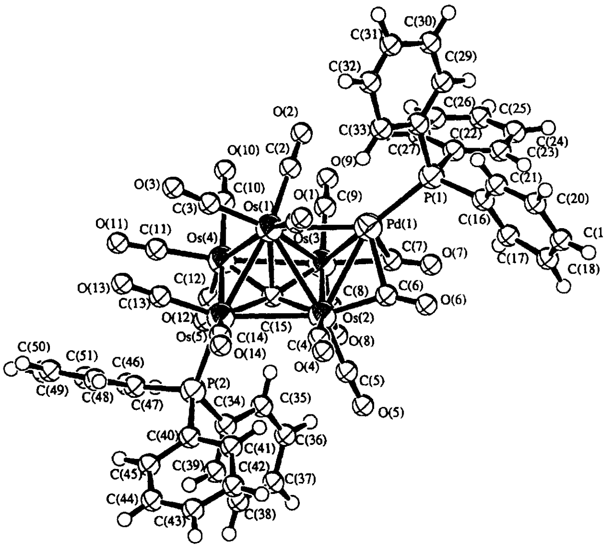

Fig. 1 Molecular structure of the cluster $[Os_5PdC(CO)_{12}(\mu\text{-}CO)_2(PPh_3)_2]$ **1** showing the atom numbering scheme. Some selected bond lengths (Å) and angles (°): Os(1)–Os(2) 2.893(2), Os(1)–Os(3) 2.936(2), Os(1)–Os(4) 2.836(2), Os(1)–Os(5) 2.876(2), Os(1)–Pd(1) 2.809(3), Os(2)–Pd(1) 2.812(3), Os(2)–Os(3) 2.862(2), Os(2)–Os(5) 2.913(2), Os(4)–Os(5) 2.937(2); Os(1)–Pd(1)–P(1) 140.6(3), Os(2)–Pd(1)–P(1) 153.2(3), Os(3)–Pd(1)–P(1) 135.1(3)

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† Crystal data for **1**: $C_{51}H_{30}O_{14}P_2Pd$, M = 1986.14, triclinic, space group $P\bar{1}$, a = 16.260(4), b = 17.221(3), c = 9.954(2) Å, α = 99.19(1), β = 105.13(2), γ = 74.72(2)°, U = 2583.2(9) Å^3, Z = 2, D_c = 2.553 g cm^{-3}, $F(000)$ = 1808.00, Mo-Kα radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 127.09 cm^{-1}, dimensions 0.25 × 0.38 × 0.39 mm. 3463 Observed diffractometer data [$I > 3.00\sigma(I)$], ψ-scan absorption correction, structure solved by direct methods (SIR 88)[13] and Fourier-difference techniques, refined by full-matrix least-squares analysis to R = 0.052, R' = 0.057, $w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o)^2]$.

‡ Spectroscopic data for **1**: IR [ν(CO), hexane] 2076m, 2036s, 2018s, 2007m, 1979w, 1971w cm^{-1}. Negative FAB mass spectrum *m*/*z*: 1986 (1986 calc.). NMR ($CDCl_3$): ^{1}H, δ 7.14–7.40 (m, 30 H, phenyl H); ^{31}P, δ −1.30 and 53.48 (Found: C, 30.65; H, 1.45. Calc. for $C_{51}H_{30}O_{14}Os_5P_2Pd$: C, 30.80; H, 1.50%).

§ Spectroscopic data for **3**: IR [ν(CO), hexane] 2083w, 2074m, 2082s, 2050s, 2027s, 2014m cm^{-1}. Negative FAB mass spectrum: *m*/*z* 1823 (1823 calc.). NMR (CD_2Cl_2): ^{1}H, δ 7.13–7.64 (m, 15 H, phenyl H); ^{31}P, δ 53.49 (Found: C, 22.25; H, 0.75. Calc. for $C_{34}H_{15}Cl_2O_{15}Os_5PPd$: C, 22.30; H, 0.70%).

¶ Crystal data for **3**: $C_{34}H_{15}Cl_2O_{15}Os_5PPd$, M = 1822.76, monoclinic, space group $P2_1/c$ (no. 14), a = 9.604(2), b = 15.118(3), c = 28.993(3) Å, β = 94.79(2)°, U = 4186(1) Å^3, Z = 4, D_c = 2.892 g cm^{-3}, $F(000)$ = 3256.00, Mo-Kα radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 157.59 cm^{-1}, dimensions 0.26 × 0.28 × 0.44 mm. 3166 Observed diffractometer data [$I > 3.00\sigma(I)$]; ψ-scan absorption correction, structure solved and refined as for **1** to R = 0.040, R' = 0.041. 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.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/134.

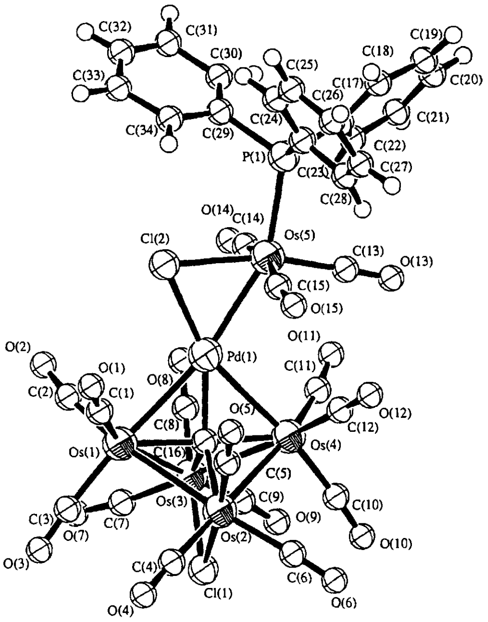

Fig. 2 Molecular structure of the cluster $[Os_5PdC(CO)_{15}(\mu\text{-}Cl)_2(PPh_3)]$ **3** showing the atom numbering scheme. Some selected bond lengths (Å) and angles (°): Os(1)–Os(2) 2.909(1), Os(1)–Os(3) 2.910(2), Os(1)–Pd(1) 2.820(2), Os(2)–Os(4) 2.908(1), Os(3)–Os(4) 2.896(1), Os(4)–Pd(1) 2.787(2), Os(5)–Pd(1) 2.674(2), Os(1)–C(16) 1.98(2), Os(2)–C(16) 2.14(2), Os(3)–C(16) 2.07(2), Os(4)–C(16) 1.96(2), Pd(1)–C(16) 2.04(2); Os(1)–Pd(1)–Os(4) 89.24(6), Os(1)–Pd(1)–Os(5) 168.70(8), Os(4)–Pd(1)–Os(5) 102.04(7), Os(5)–Cl(2)–Pd(1) 67.7(2)

characterise the compound. Its molecular structure, together with some important bond parameters, is shown in Fig. 2. The metal core of **3** consists of a butterfly of four osmium atoms with the two 'wing-tip' atoms, Os(1) and Os(4), bridged by the Pd atoms and an additional $Os(PPh_3)(CO)_3$ moiety is connected to the Pd apex. A chloride ligand is found to bridge the Os(5)–Pd(1) vector while another chloride ligand is found to bridge the hinge of the butterfly [*i.e.* Os(2)–Os(3)]. There are significant differences between the three Os–Pd bonds in **3** [Os(1)–Pd(1) 2.820(2), Os(4)–Pd(1) 2.787(2), Os(5)–Pd(1) 2.674(2) Å]. The carbide carbon atom resides within the centre of the bridged butterfly core which has a distorted trigonal-bipyramidal environment. The molecule exhibits an approximate C_s symmetry with the mirror plane containing P(1), Os(5), Cl(2), Pd(1), Os(1), Os(4), C(16) and Cl(1). Cluster **3** gives a valence electron count of 92 for which eight metal–metal bonds would be expected. However, only seven metal–metal bonds are found. It is interesting that one osmium atom is detached from the Os_5C metal core in **3** as we previously believed that such a metal core is extremely stable.[14]

Acknowledgements

W.-T. W. acknowledges financial support from the Groucher 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.

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Received 19*th April* 1996; *Communication* 6/02742C