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Synthesis and Characterization of a Palladium–Osmium Mixed-metal Cluster; Crystal Structure of $[Os_6Pd(CO)_{18}(bipy)]\cdot CHCl_3$ (bipy = 2,2′-bipyridine)

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The heterometallic cluster $[Os_6Pd(CO)_{18}(bipy)]$ (bipy = 2,2′-bipyridine) has been isolated in moderate yield from the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ and $[Pd(bipy)(CO_2Me)_2]$, and shown by a single-crystal X-ray structure analysis to contain a monocapped octahedral metal core with the palladium occupying one vertex of the octahedron.

Heterometallic clusters containing nickel–osmium or platinum–osmium bonds have been extensively investigated.[1–6] However, mixed-metal clusters of palladium and osmium containing direct osmium–palladium bonds have not been reported. Compounds containing ruthenium–palladium bonds are also rare.[7] It has been reported that $[Os_3(CO)_{10}(MeCN)_2]$ undergoes a coupling reaction to give the 'raft-like' clusters $[Os_6(CO)_{21-n}(MeCN)_n]$ (n = 1 or 2) in the presence of catalytic amounts of $PdCl_2$ or $Pd(O_2CMe)_2$.[8] However, the isolation of osmium–palladium mixed-metal clusters from this system has met with little success.

Herein, we report the synthesis and full characterization of the novel osmium–palladium cluster $[Os_6Pd(CO)_{18}(bipy)]$ **1** (bipy = 2,2′-bipyridine), which contains four unsupported osmium–palladium bonds. A mixture of $[Os_3(CO)_{10}(MeCN)_2]$ and $[Pd(bipy)(CO_2Me)_2]$[9] (1:1) was stirred in CH_2Cl_2 (10 cm^3) under nitrogen at room temperature for 2 h. The solution changed from yellow to dark brown. A dark brown precipitate was formed, which remained uncharacterized due to poor solubility in common organic solvents. Separation of the brown solution by TLC on silica (eluent: *n*-hexane–dichloromethane, 7:3) gave orange $[Os_6Pd(CO)_{18}(bipy)]$ **1** (20%), $[Os_3(CO)_{12}]$ (25%) and a blue product in a trace amount. The ^1H NMR spectrum of **1** reveals the presence of bipy and IR spectroscopy the existence of carbonyl ligands in the terminal co-ordination mode.† Single crystals of **1** suitable for X-ray analysis were obtained by slow evaporation of a $CHCl_3$–cyclohexane (1:1) solution.‡ Its molecular structure, together with some important bond parameters, is shown in Fig. 1. The blue product has not been characterized due to poor yield.

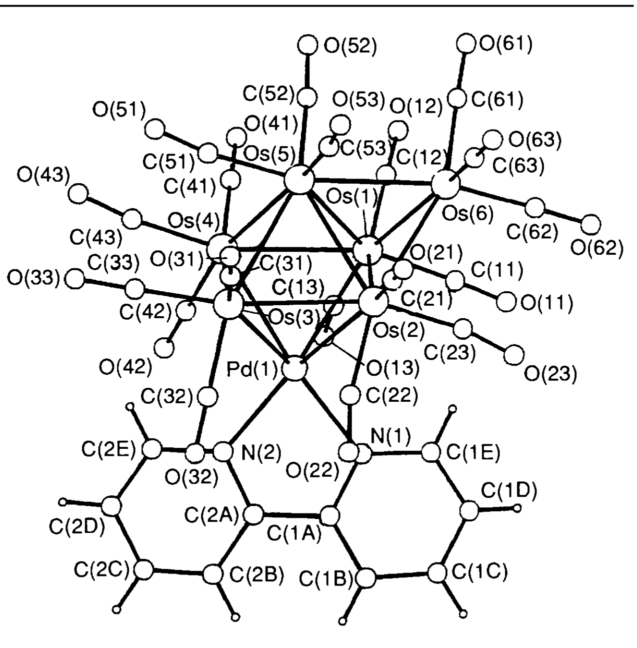

Fig. 1 Molecular structure of $[Os_6Pd(CO)_{18}(bipy)]$ **1** showing the atom numbering scheme. Selected bond distances (Å) and angle (°): Os(1)–Os(2) 2.916(2), Os(1)–Os(4) 2.792(1), Os(1)–Os(5) 2.836(1), Os(1)–Os(6) 2.813(1), Os(1)–Pd(1) 2.791(2), Os(2)–Os(3) 2.780(1), Os(2)–Os(5) 2.827(1), Os(2)–Os(6) 2.803(1), Os(2)–Pd(1) 2.808(2), Os(3)–Os(4) 2.996(1), Os(3)–Os(5) 2.872(1), Os(3)–Pd(1) 2.740(2), Os(4)–Os(5) 2.872(1), Os(4)–Pd(1) 2.790(2), Os(5)–Os(6) 2.855(1), Pd(1)–N(1) 2.17(2), Pd(1)–N(2) 2.15(3), N(1)–C(1A) 1.36(3), N(1)–C(1E) 1.36(3), N(2)–C(2A) 1.37(3), N(2)–C(2E) 1.39(3), C(1A)–C(1B) 1.38(3), C(1A)–C(2A) 1.47(4), C(1B)–C(1C) 1.40(4), C(1C)–C(1D) 1.37(4), C(1D)–C(1E) 1.37(3), C(2A)–C(2B) 1.42(3), C(2B)–C(2C) 1.35(4), C(2C)–C(2D) 1.39(4), C(2D)–C(2E) 1.39(4), N(1)–Pd(1)–N(2) 76.2(7)

The metal core of **1** can be described as a monocapped octahedron with the palladium occupying one vertex of the octahedron. The geometry is similar to that of $[Os_7(CO)_{21}]$,[11] where both compounds have 98 cluster valence electrons. The structure of **1** can be rationalised by polyhedral skeletal electron pair theory[12] and the condensed polyhedral approach.[13] However, this is not entirely expected as there are many mixed-metal clusters of Pt and Os that do not obey simple

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† IR ν(CO)(CH_2Cl_2): 2091w, 2056s, 2047s, 2026m, 2016m, 1984w cm^{-1}. ^1H NMR (CD_2Cl_2): δ 9.33 (dt, 1 H), 8.13 (m, 4 H), 7.99 (td, 1 H), 7.80 (m, 1 H), 7.39 (m, 1 H). FAB mass spectrum: *m/z* 1908 (1908 calc.).

‡ Crystal data: $C_{29}H_9Cl_3N_2O_{18}Os_6Pd$, M = 2027.36 with $CHCl_3$, triclinic, space group $P\bar{1}$ (no. 2), a = 10.041(1), b = 11.409(6), c = 17.076(5) Å, α = 97.89(3), β = 93.49(2), γ = 91.04(2)°, U = 1933.3 $Å^3$, Z = 2, D_c = 3.475 g cm^{-3}, $F(000)$ = 1788, Mo-Kα radiation, λ = 0.710 73 Å, μ(Mo-Kα) = 204.23 cm^{-1}, dark red plate 0.18 × 0.32 × 0.32 mm, 5724 data measured at 293 K on an Enraf–Nonius CAD4 diffractometer ($2.0 < 2\theta < 45.0°$), absorption-corrected, 3678 observed [$F > 3\sigma(F)$]. Structure solved by direct methods (MULTAN)[10a] and Fourier difference techniques, refined by full-matrix least-squares analysis (Os, Pd and Cl anisotropic) to R = 0.041, R' = 0.067, $w = 4F_o^2/[\sigma^2(F_o^2) + 0.04(F_o^2)^2]$; program used SDP.[10b] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

electron-counting rules.[14–16] Unlike those in $[Os_7(CO)_{21}]$, the four equatorial osmium atoms form a rectangle rather than a square, with the bipy group lying along the longer sides. In $[Os_6(CO)_{17}(\mu_4\text{-}S)]$, which has the same geometry as **1** with the palladium atom replaced by sulfur, the four osmium atoms form a trapezium.[17] The lengths of the four Os–Pd bonds range from 2.740(2) to 2.808(2) Å. The best plane for the bipy ligand is almost parallel (3°) to the Os(2)–Os(3) vector and the dihedral angle between the best plane for bipy and the best plane defined by Os(1)–Os(2)–Os(3)–Os(4) is 75.0°, so that **1** possesses approximate mirror symmetry. The observed orientation of bipy is probably due to both steric interaction of the ligands and orbital effects of the bipy ligand itself. However, there are many metallacarboranes containing bipy bonded to a metal in which its orientation is largely determined by the orbital effects.[18,19] The two Pd–N bonds [2.17(2), 2.15(3) Å] in **1** are significantly longer than the Pd–N bonds observed in $[Pd(bipy)_2]^{2+}$ [2.026(1), 2.049(1) Å].[20] The two pyridine rings are slightly twisted with a dihedral angle of 12.7°. Also the deviation from linearity of the carbonyl groups is the greatest for those two pointing towards the pyridine ring [C(13)–O(13) and C(22)–O(22)].

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