Osmium–Palladium Clusters

[{N(PPh₃)₂}₂{Os₁₈Pd₃(μ₆-C)₂(CO)₄₂}]: An Osmium–Palladium Mixed-Metal High-Nuclearity Carbonyl Cluster**

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Dedicated to Professor The Lord Lewis on the occasion of his 75th birthday

High-nuclearity mixed-metal clusters have aroused considerable attention because of their ability to act as an "electron reservoir", the potential to precisely control the ratio and geometry of the two metals involved,[1] and their potential application in catalysis.[2] Reactions of cluster anions with palladium–halide complexes were found to be effective in producing high-nuclearity mixed-metal clusters, for example, $[Fe_6Pd_6(CO)_{24}H]^{3-}$,[3] $[Ru_{10}Pd_8C_2(CO)_{27}(C_3H_5)_4]$,[4] and $[Ni_9Pd_{33}(PPh_3)_6(CO)_{41}]^-$.[5] However, high-nuclearity osmium–palladium mixed-metal clusters prepared by a similar approach are rare.[6] We recently established a reliable route to preparing such species in moderate yield using a deca-osmium cluster anion and a palladium cation as the starting materials. Herein, we report the synthesis and structural characterization of the novel high-nuclearity sandwich osmium–palladium mixed-metal cluster [{N(PPh₃)₂}₂{Os₁₈Pd₃-(μ₆-C)₂(CO)₄₂}] (**1**).

An excess of $[Pd(NCMe)_4](BF_4)_2$[7] was treated with $[\{N(PPh_3)_2\}_2\{Os_{10}(\mu_6\text{-}C)(CO)_{24}\}]$[8] in CH_2Cl_2 at room temperature to yield the novel osmium–palladium cluster anion $[Os_{18}Pd_3(\mu_6\text{-}C)_2(CO)_{42}]^{2-}$, which was isolated as its $[N(PPh_3)_2]^+$ salt (**1**) in 37 % yield. An insoluble black solid was also obtained from the reaction mixture; IR spectroscopy indicated that the solid material may consist of high-nuclearity carbonyl–metal clusters.

Single crystals of **1** suitable for X-ray analysis were obtained as dark-green blocks by slow evaporation of the CH_2Cl_2/MeOH solution mixture at 0°C. The molecular structure, together with some important bond parameters, is depicted in Figure 1. The structure of **1** can be described as a giant dumbbell-shaped bimetallic nanocluster. The cluster core-geometry can be divided into three metallic domains. A triangular Pd_3 metal unit is sandwiched between two tricapped octahedral $\{Os_9(\mu_6\text{-}C)(CO)_{21}\}$ subclusters, which combine to give an overall D_{3h} symmetry. The five ABABA close-packed layers of metal ions (6:3:3:3:6) that are shown in
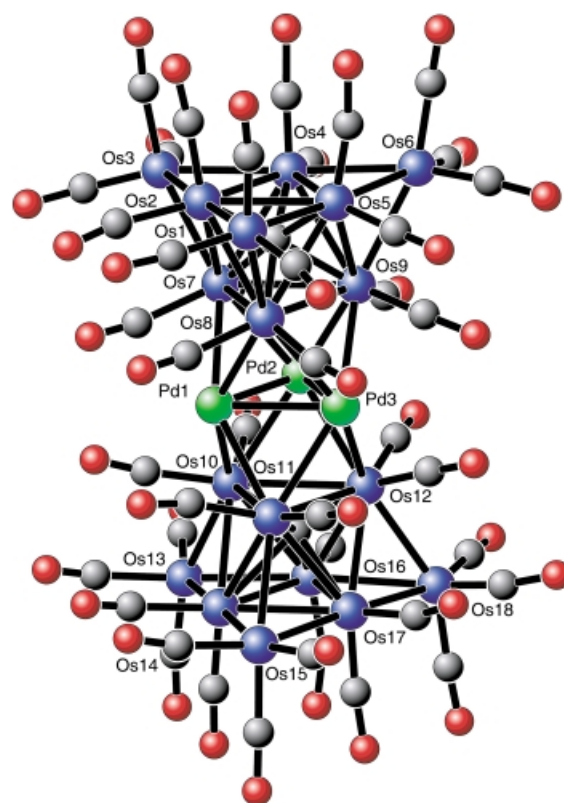
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Figure 1. Molecular structure of cluster anion **1** showing the atomic numbering scheme (with osmium in blue and palladium in green). Selected Os—Os bond lengths (Å): Os1-Os2 2.772(3), Os1-Os4 2.785(3), Os1-Os7 2.778(2), Os2-Os3 2.780(3), Os2-Os4 2.852(3), Os2-Os5 2.840(3), Os2-Os7 2.875(3), Os2-Os8 2.843(3), Os3-Os5 2.772(3), Os3-Os8 2.803(4), Os4-Os5 2.870(3), Os4-Os6 2.774(3), Os4-Os7 2.838(3), Os4-Os9 2.859(3), Os5-Os6 2.772(3), Os5-Os8 2.864(3), Os5-Os9 2.850(3), Os6-Os9 2.814(3), Os7-Os8 2.953(3), Os7-Os9 2.956(3), Os8-Os9 2.951(2), Os10-Os11 2.964(3), Os10-Os12 2.951(3), Os10-Os13 2.811(3), Os10-Os14 2.858(3), Os10-Os16 2.853(3), Os11-Os12 2.969(2), Os11-Os14 2.852(3), Os11-Os15 2.817(3), Os11-Os17 2.831(3), Os12-Os16 2.855(3), Os12-Os17 2.860(3), Os12-Os18 2.822(3), Os13-Os14 2.764(3), Os13-Os16 2.774(3), Os14-Os15 2.773(3), Os14-Os16 2.858(3), Os14-Os17 2.846(3), Os15-Os17 2.785(3), Os16-Os17 2.874(3), Os16-Os18 2.792(3), Os17-Os18 2.779(3); Pd—Pd bonds: Pd1-Pd2 2.733(5), Pd1-Pd3 2.728(5), Pd2-Pd3 2.717(5); Os—Pd bonds: Os7-Pd1 2.751(4), Os7-Pd3 2.770(4), Os8-Pd1 2.773(5), Os8-Pd2 2.744(4), Os9-Pd2 2.774(4), Os9-Pd3 2.764(5), Os10-Pd1 2.777(5), Os10-Pd3 2.766(4), Os11-Pd1 2.732(4), Os11-Pd2 2.766(4), Os12-Pd2 2.768(5), Os12-Pd3 2.777(4).

Figure 2 are unprecedented in existing Os–Pd mixed-metal clusters. The central $\{Os_3Pd_3Os_3\}$ unit, which consists of the Os7, Os8, Os9, Pd1, Pd2, Pd3, Os10, Os11, and Os12 metal ions, forms a face-sharing bioctahedron that is reminiscent of the Rh_9 geometry observed in the $[Rh_9(CO)_{19}]^{3-}$ ion.[9] The palladium ions, which form the edge-sharing face of the bioctahedron only possess metal–metal bonding character; there are no bonds to carbonyl ligands, which is very unusual. This naked metal triangle is relatively exposed, which may facilitate the coordination of nucleophiles. For the two osmium domains, two Os_9 units are in an eclipsed conformation, which is contrary to the closely related osmium–mercury mixed-metal cluster, $[\{N(PPh_3)_2\}_2\{Os_{18}Hg_3(\mu_6\text{-}C)_2(CO)_{42}\}]$.[10]
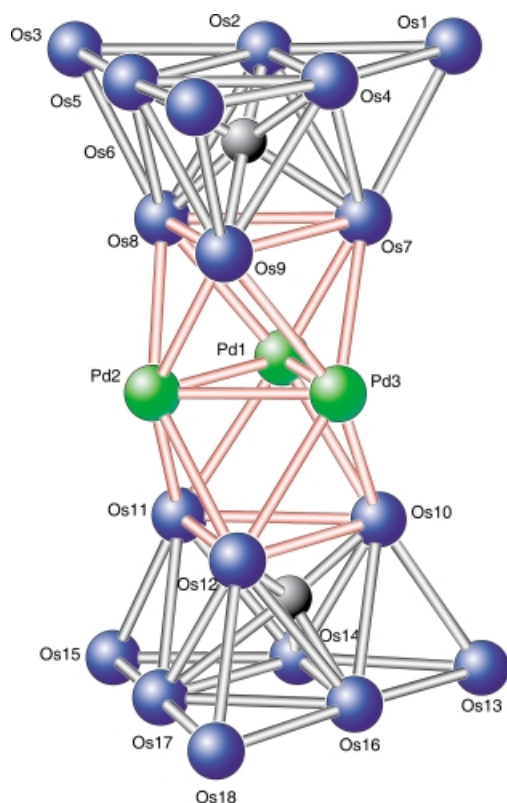
Figure 2. The metal core-geometry of cluster **1** illustrating the position of the carbide ions, which are located above and below the central bimetallic face.

Figure 3. Cyclic voltammogram of $[\{N(PPh_3)_2\}_2\{Os_{18}Pd_3(\mu_6\text{-}C)_2(CO)_{42}\}]$ in acetone containing 0.1 M tBu$_4$NPF$_6$; glassy carbon working electrode, platinum auxiliary electrode, and Ag/AgNO$_3$ reference electrode; the scan rate was varied from 50 to 1000 mVs^{-1}.

The average Os–Pd bond length is 2.764(5) Å, which falls well within the normal range for Os–Pd bonds (2.6–2.9 Å).[6] The Os–Os bonds in the two layers either side of Pd$_3$ subcluster are elongated (2.958(3) Å) when compared to the remaining Os–Os bonds (av. 2.806(5) Å). This phenomenon is also observed in the $[Os_{18}Hg_3(\mu_6\text{-}C)_2(CO)_{42}]^{2-}$ [11] and $[Ru_{18}Hg_3(\mu_6\text{-}C)_2(CO)_{42}]^{2-}$ ions.[12] All carbonyl groups are terminally bound to the cluster, as suggested by solution IR spectroscopy. In addition, ^{1}H NMR spectroscopy confirms that there are no associated hydride species, since there are no signals detected between −40 and 10 ppm; such species are common in high-nuclearity clusters. The UV/Vis spectrum of **1** shows an absorption peak at 664 nm, which is believed to be a charge-transfer band, and is commensurate with its dark-green color. The negative FAB mass spectrum of **1** shows a signal for the parent monoanion centered at m/z 4944 (calcd 4944) and another at m/z 2472 (calcd 2472) for the dianionic species. Cluster **1** contains 57 metal–metal bonds and 268 cluster valence electrons (CVE). However, this structure cannot be rationalized by common electron-counting rules.[13] This is not entirely unexpected, as many Os–Pd or Os–Pt mixed-metal clusters do not obey such as alternative stable 16-electron configurations of Pd and Pt can exist. Nevertheless, this bimetallic system can be viewed as having two $[Os_9(\mu_6\text{-}C)(CO)_{21}]^{2-}$ ions sandwiching the central {Pd$_3$$^{2+}$} unit.

To investigate the redox properties of this new mixed-metal cluster anion, the electrochemistry of **1** at room temperature was examined (Figure 3); the electrochemical
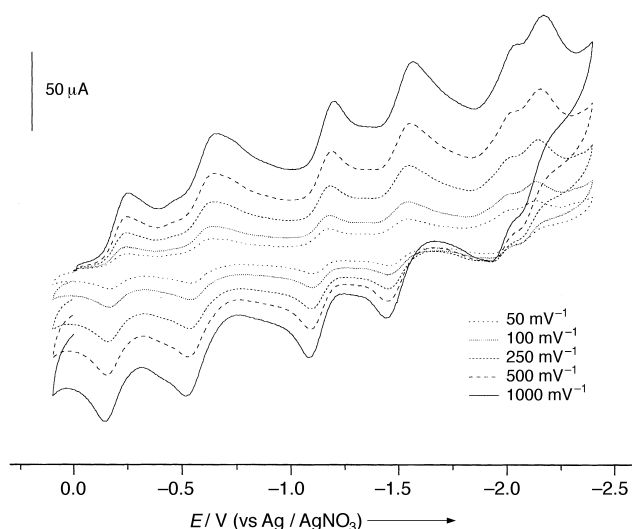
data are summarized in Table 1. Cluster **1** exhibits five reversible cathodic waves at $E_{pc} = -0.14$, -0.52, -1.08, -1.51, and -2.02 V versus a Ag/AgNO$_3$ electrode in acetone. The cathodic wave at $E_{pc} = -1.94$ V results from the presence of the $[N(PPh_3)_2]^+$ ion, which is the counterion of the cluster, and cannot be removed. Analysis of the cyclic voltammetric responses relating to these five peaks, with the scan rate varying from 50 to 1000 mVs^{-1}, indicates that the peak current ratio i_{pa}/i_{pc} remains close to unity. The current function is essentially constant and the peak-to-peak separation lies between 50–80 mV, which is comparable with that of ferrocene under the same experimental conditions. The increase in anionic charge on the cluster does not prevent the cluster from accepting electrons, as the gaps between the cathodic waves do not increase significantly. The trend of these reversible cathodic waves shows that this mixed-metal nanocluster can act as an electron reservoir, with the ability to gain or lose electrons without significant decomposition. The observed electrochemical behavior is significantly different to that of the analogous mercury cluster. Upon receiving electrons, a Hg ion is eliminated to form a more stable

Table 1: Electrochemical data[a] for cluster **1**.

Reduction potential [V][b]		Oxidation potential [V][b]	
E_{pa1}	(−0.14)[c]	E_{pc2}	0.48
E_{pa2}	(−0.52)	E_{pc1}	0.29
E_{pa3}	(−1.08)		
E_{pa4}	(−1.51)		
E_{pa5}	(−2.02)		

[a] Approximately 10^{-3} M of **1** in acetone containing 0.1 M tBu$_4$NPF$_6$ at 298 K; the working electrode was a glassy carbon electrode, the auxiliary electrode was platinum, and the reference electrode was Ag/AgNO$_3$ (0 V, calibrated with ferrocene); the scan rate was 100 mVs^{-1}. [b] E_{pa} and E_{pc} are the anodic and cathodic potentials, respectively. [c] The values in parentheses are half-wave potential ($E_{1/2}$) values.

cluster, $[\{N(PPh_3)_2\}_2\{Os_{18}Hg_2(\mu_6\text{-}C)_2(CO)_{42}\}]$.[14] The average separation between the cathodic waves is 0.47 V, which is consistent with the trend observed for the average separation of the electrode potentials of consecutive redox couples, with respect to cluster nuclearity.[15] With regard to oxidation, cluster **1** exhibits two irreversible anodic waves at $E_{pa} = +0.29$ and $+0.48$ V versus the Ag/AgNO$_3$ electrode in acetone. Thus, the oxidation process leads to a breakdown of the cluster.

The coordination of further ligands to cluster **1** is possible as a result of its ability to exhibit various reversible electronic states, in addition to possessing an exposed naked palladium site for the coordination of targeted substrate molecules. Further study on the reactivity of this cluster is in progress.

Experimental Section

All experiments were carried out under a nitrogen atmosphere with dry deoxygenated solvents. $[\{N(PPh_3)_2\}_2\{Os_{10}(\mu_6\text{-}C)(CO)_{24}\}]$ was stirred with an excess of $[Pd(NCMe)_4](BF_4)_2$ in CH_2Cl_2 at room temperature for one hour. The $[Os_{18}Pd_3(\mu_6\text{-}C)_2(CO)_{42}]^{2-}$ ion, which was isolated as the $[\{N(PPh_3)_2\}]^+$ salt, is obtained in 37% yield. Cluster **1** was fully characterized by spectroscopic techniques (IR, FAB MS, ^{1}H NMR) and X-ray crystallography.

1: IR (CH_2Cl_2): $\tilde{\nu} = \nu(CO) = 2060$ (s), 2008 cm^{-1} (s); ^{1}H NMR (300 MHz, CD_2Cl_2): no hydride signal detected; negative FAB mass spectrum: $m/z = 4944$ (monoanion; calcd 4944), 2472 (dianion; calcd 2472); UV/Vis (CH_2Cl_2): $\lambda_{max} = 664$ nm $\varepsilon = 40\,100$ mol dm^{-3} cm^{-1}; elemental analysis (%) calcd for $C_{116}H_{60}N_2O_{42}P_4Pd_3Os_{18}$: C 23.139, H 1.004, N 0.465, P 2.057; found: C 23.151, H 1.023, N 0.472, P 2.086.

Crystal data of **1**: $C_{116}H_{60}N_2O_{42}P_4Os_{18}Pd_3$, $M_W = 6020.43$, triclinic, space group $P\bar{1}$ (no. 2), $a = 15.607(1)$, $b = 18.357(1)$, $c = 25.350(2)$ Å, $\alpha = 85.14(1)$, $\beta = 83.08(1)$, $\gamma = 76.95(1)°$, $V = 7011.2(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.852$ g cm^{-3}, $F_{(000)} = 5344$, $\mu(Mo_{K\alpha}) = 167.15$ cm^{-1}, dimensions $0.12 \times 0.13 \times 0.15$ mm. 40 769 reflections were collected with 29 169 unique reflections and merged to give 13 454 ($R_{int} = 0.119$) observed data $[I > 1.50\sigma(I)]$. The data were collected on a Bruker SMART 1K CCD diffractometer. Structures were solved by direct methods (SHELXS 86) and Fourier-difference techniques, refined by full-matrix least-squares analysis to give $R = 0.098$ and $R_w = 0.094$. CCDC-194450 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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