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High-Yield Synthesis of a New Layered High-Nuclearity Carbonyl Osmium-Rhodium Cluster Complex – Synthesis, Structural Characterization, and Electrochemistry of [PPN][$Os_9Rh_3(\mu\text{-}CO)_2(CO)_{26}$]

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A direct and high-yield synthetic route for a novel dodecanuclear osmium-rhodium mixed-metal cluster is presented. The redox properties of the cluster were examined, and it was found that the anion behaves as an "electron reservoir".

Introduction

The synthesis and isolation of the first heteronuclear carbonyl transition-metal complexes in the 1960s[1–3] had a great impact on the field of mixed-metal cluster chemistry. A large number of articles have appeared within the last 20 years that have reported the preparation and characterization of high-nuclearity mixed-metal clusters. The interest in these clusters is due to their fascinating metal core, potential application in catalysis,[4] and ability to act as an electron reservoir, and more recently, as valuable precursors to support nanocatalysts and nanosized metal particles.[5] To date, the majority of high-nuclearity mixed-metal clusters have been achieved by the use of redox coupling reactions between an anionic carbonyl compound and cationic metal electrophiles.[6–8] However, high-nuclearity Os-Rh mixed-metal clusters that have been achieved by a similar approach are rare.[9] We recently established a facile and reliable route for preparing such species in high yield by the simple thermolysis of a neutral Os-Rh cluster, [$Os_3Rh(\mu\text{-}H)_3(CO)_{12}$]. The high yields of the cluster allowed an electrochemical study of the complex and revealed the ability of the cluster to function as an "electron reservoir" that permits the uptake and release of electrons without significant cluster breakdown. We now report the synthesis, structural characterization, and electrochemical study of the novel high-nuclearity osmium-rhodium mixed-metal cluster [PPN][$Os_9Rh_3(\mu\text{-}CO)_2(CO)_{26}$] ([PPN]**1**). The metal framework in **1** is observed for the first time for an M_{12} system.

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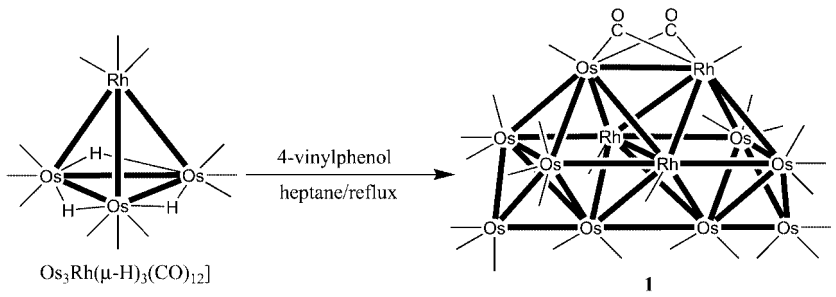
Results and Discussion

The high-nuclearity Os-Rh mixed-metal cluster anion **1** was isolated as a $[PPN]^+$ salt with a 60% yield from the thermolysis of a neutral Os-Rh cluster, [$Os_3Rh(\mu\text{-}H)_3(CO)_{12}$], in *n*-heptane for 2 h (see Scheme 1), together with a number of uncharacterized cluster species in very low quantity. The complex was characterized by spectroscopic methods and by a single-crystal X-ray diffraction study. The arrangement of the metal center of **1** can be described as two fused octahedra that share a common equatorial Rh–Rh edge. Two additional osmium atoms cap the faces of these octahedra in such a way that one adjacent triangular face is capped at the opposite ends of the fused bioctahedral structure (Figure 1). The Rh(1)–Rh(2) bond length [2.781(2) Å] is comparable to other apical-equatorial Rh–Rh distances observed within the compound and those bond lengths that have been observed for other trirhodium faces in osmium-rhodium mixed-metal clusters.[9] The structure of **1** contains 28 carbonyl ligands, and two of them are μ-bridging across the same apical-apical Rh–Os bond (Figure 2). The Rh(3)–Os(9) [2.632(8) Å] distance is slightly shorter than the average apical-equatorial Rh–Os bond [2.672(2) Å] of the cluster but much shorter than all other equatorial-equatorial Rh–Os distances in the molecule. A short Os–Os bond is observed between the apices of the fused octahedra. The Os(2)–Os(3) distance [2.626(1) Å] is shorter than the remaining Os–Os bonds, whose lengths range from 2.721(4) to 2.868(1) Å in the compound and are comparable to the normal average Os–Os distance in other osmium clusters.[10,11] To the best of our knowledge, the metal arrangement in complex **1** has not been observed in an M_{12} system. Essentially, a similar framework structure is adopted by other homo- and heterometallic decanuclear clusters, such as [$Ru_8Pt_2(CO)_{23}(\mu_3\text{-}H)_2$],[12] [$Ru_{10}C_2(CO)_{24}$]$^{2-}$,[13] [$Ru_{10}C_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_3H_4)$]$^{2-}$,[14] [$Ga_{10}${Si-



Scheme 1.

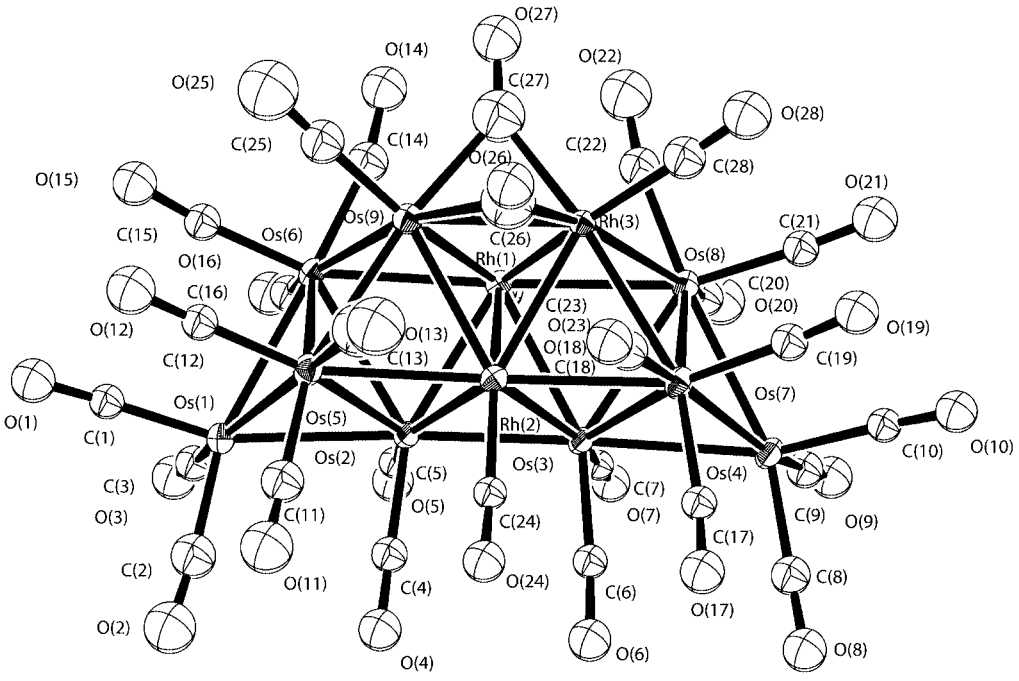


Figure 1. Molecular structure of the anion $[Os_9Rh_3(\mu\text{-}CO)_2(CO)_{26}]^-$ of **1** with the atom numbering scheme; selected bond lengths [Å] and angles [°]: Os(1)–Os(2) 2.793(1), Os(1)–Os(5) 2.815(1), Os(1)–Os(6) 2.847(2), Os(2)–Os(3) 2.626(1), Os(2)–Os(5) 2.833(1), Os(2)–Os(6) 2.825(1), Os(2)–Rh(1) 2.669(2), Os(3)–Os(7) 2.818(1), Os(3)–Os(8) 2.814(1), Os(3)–Rh(1) 2.670(2), Os(3)–Rh(2) 2.682(2), Os(4)–Os(7) 2.799(1), Os(4)–Os(8) 2.826(1), Os(5)–Os(6) 2.868(1), Os(5)–Os(9) 2.721(4), Os(5)–Rh(2) 2.799(2), Os(6)–Os(9) 2.783(3), Os(6)–Rh(1) 2.808(2), Os(7)–Os(8) 2.868(1), Os(7)–Rh(2) 2.783(2), Os(7)–Rh(3) 2.800(8), Os(8)–Rh(1) 2.801(2), Os(8)–Rh(3) 2.950(7), Os(9)–Rh(2) 2.734(4), Os(9)–Rh(3) 2.632(8), Rh(1)–Rh(2) 2.781(2), Rh(1)–Rh(3) 2.806(6), Rh(2)–Rh(3) 2.684; Rh(2)–Rh(1)–Rh(3) 57.4(2), Rh(1)–Rh(2)–Rh(3) 61.8(1), Rh(1)–Rh(3)–Rh(2) 60.8(2).

$(SiMe_3)_3\}_6]$,[15] and $Os_{10}(CO)_{24}\{Au(PPh_2R)\}_4]$[10] (R = Ph or Me). Cluster **1** contains 31 short contacts, and has an overall electron count of 156. This electron count cannot be obtained by the application of any of the usual electron counting schemes.[16,17] This is not entirely unexpected, as it is common for rhodium to have a stable 16-electron configuration.

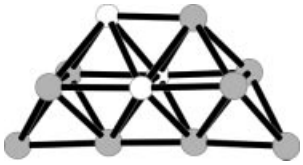


Figure 2. Metal core geometry of $[PPN][Os_9Rh_3(\mu\text{-}CO)_2(CO)_{26}]$ (**1**) (Os in grey and Rh in white).

To investigate the redox properties of this new mixed-metal cluster anion, a cyclic voltammetry of **1** in CH_2Cl_2 with *n*-tetrabutylammonium hexafluorophosphate (TBAHFP) as the supporting electrolyte at room temperature was carried out, the result of which is depicted in Figure 3. The electrochemical data are summarized in Table 1. Cluster **1** exhibits four successive reversible cathodic waves at E_{pc} = –0.34, –0.72, –1.12, and –1.42 V, and two irreversible anodic waves at 0.71 and 0.80 V vs. $Ag/AgNO_3$, which is similar to that observed in the high-nuclearity osmium-palladium mixed-metal cluster $[PPN]_2[Os_{18}Pd_3(\mu\text{-}C)_2(CO)_{42}]$.[8] The four successive reversible cathodic waves reveal that the anionic charge of the cluster itself does not prevent it from accepting more electrons and releasing them reversibly. This suggests that cluster **1** can act as an electron reservoir, and has the ability to gain or lose electrons with-

out significant decomposition. Controlled potential coulometry was performed at –0.53 V for **1**, indicating that each redox process consumes one electron per molecule. With regard to oxidation, two irreversible anodic waves were also observed, and this oxidation process is believed to lead to the breakdown of the cluster.

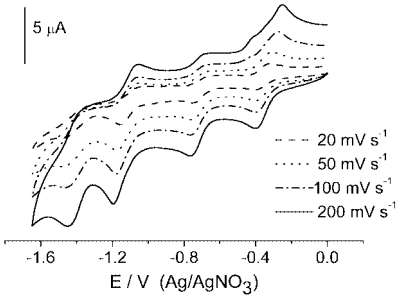


Figure 3. Cyclic voltammogram of [PPN][$Os_9Rh_3(\mu\text{-}CO)_2(CO)_{26}$] in CH_2Cl_2 containing 0.1 M tBu$_4$NPF$_6$ in CH_2Cl_2; glass carbon electrode, platinum auxiliary electrode and Ag/$AgNO_3$ reference electrode; scan rate that varied from 20 to 200 mV s^{-1}.

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

Reduction [V][b,c]		Oxidation [V][b]	
E_{pc1}	(–0.34)	E_{pa1}	0.71
E_{pc2}	(–0.72)	E_{pa2}	0.80
E_{pc3}	(–1.12)		
E_{pc4}	(–1.42)		

[a] Ca. 10^{-3} M cluster in 0.1 M tBu$_4$NPF$_6$ in CH_2Cl_2 at 298 K, the working electrode was a glassy carbon electrode, the auxiliary electrode was a platinum electrode, and the reference electrode was Ag/$AgNO_3$ (0 V) under the same conditions, calibrated with ferroence. The scan rate was 100 mV s^{-1}. [b] E_{pa} and E_{pc} are the anodic and cathodic potential, respectively. [c] The values in parentheses are the $E_{1/2}$, half-wave potential values.

It is noteworthy that the average separation (ΔE_{av}) between the formal electrode potentials of the consecutive redox couples observed in **1** is significantly smaller than those found in the dodecanuclear metal clusters that have been reported (see Table 2). An estimated value of ΔE_{av} for an M_{12} cluster that is based on the nuclearity should be around 0.6 V.[24] The number of cluster valence electrons (CVE) found in **1** is 156 and is fewer than 158, as predicted by the Condensed Polyhedron Electrons (CPE) theory.[17] However, the observed CVE for other M_{12} clusters that have been reported are all higher than the expected electron count using the CPE approach. The intrinsic electron deficiency of **1** may allow for the uptake of more electrons and a smaller ΔE_{av}.

Conclusions

The formation of a high-yield synthesis of high-nuclearity osmium-rhodium mixed-metal cluster by thermolysis of the neutral cluster [$Os_3Rh(\mu\text{-}H)_3(CO)_{12}$] has been developed. An unprecedented metal skeleton of this M_{12} system is observed. The electrochemical studies revealed four reversible redox couples with unusually smaller separations for this cluster anion.

Experimental Section

Synthesis: All manipulations were carried out under nitrogen with dry deoxygenated solvents. Thermolysis of [$Os_3Rh(\mu\text{-}H)_3(CO)_{12}$] (200 mg, 0.2 mmol) in n-heptane (50 mL) for 2 h led to a dark brown suspension upon stirring. The solution was then filtered to remove the black residue, and the filtrate was reduced under reduced pressure to 3 mL. An excess amount of [$N(PPh_3)_2Cl$] (110 mg, 0.5 mmol) in MeOH (3 mL) was added to the solution. TLC separation using n-hexane/CH_2Cl_2 (2:1, v/v) as an eluent afforded the [$Os_9Rh_3(\mu\text{-}CO)_2(CO)_{26}]^-$ salt (337 mg, 0.12 mmol, 60%) with an uncharacterized red brown complex in very small quantities. Black crystals of compound [PPN]**1** were obtained by slow concentration of an octane/CH_2Cl_2 solution mixture at –20 °C for 5–7 d in the presence of excess [PPN]$^+$ salts. $C_{64}H_{30}NO_{28}Os_9Rh_3$ (3281.45): calcd. C 22.99, H 0.90, N 0.42, P 1.85; found C 22.90, H 0.88, N 0.45, P 1.90. IR [CH_2Cl_2, ν(CO)]: $\tilde{\nu}$ = 2068 (vs), 2035 (vs), 2026 (m), 1610 (w) cm^{-1}. MS (FAB, +ve): 2804 (calcd. 2804). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.50 (m, 24 H, Ph), 7.52 (m, 6 H, Ph) ppm.

Crystallographic Data for 1: [$C_{28}O_{28}Os_9Rh_3{\cdot}C_{36}H_{30}NP_2$]·0.5($CH_2Cl_2$), M = 3385.86, triclinic, space group $P\bar{1}$ (#2), a = 17.115(5), b = 16.146(6), c = 19.686(7) Å, α = 104.32(4), β = 102.55(1), γ = 99.07(1)°, V = 3843(3) Å, Z = 2, $D_{calcd.}$ = 2.926 g/cm^3, T = 298 K, $F(000)$ = 3030.00, Mo-K_α radiation (λ = 0.7107 Å), μ(Mo-K_α) = 155.8 cm^{-1}, crystal dimensions 0.25 × 0.30 × 0.35 mm. 9566 observed diffraction data [$I > 1.50\sigma(I)$] and R_{int} = 0.055. The structure was solved by Patterson methods and expanded by using Fourier difference techniques,[18] and refined by full-matrix least-squares analysis on F to R = 0.056, Rw = 0.058, and $\omega = 1/\sigma^2(F_o)$. All metal atoms were refined anisotropically and the other non-hydrogen atoms were refined isotropically. The hydrogen atoms were generated in their ideal positions and were included in the structure factor calculations using the riding mode. The osmium atoms Os(9) and Os(10) were found to be disordered in a 50:50 amount with the Rh(4) and Rh(3) atoms at the apices of the fused bioctahedra, respectively. Refinement converged with 50% occupancy of each atom type at each of the two sites. A highly disordered dichloromethane molecule was also present with 50% occupancy. All calculations were performed with a computer using the program package Crystal Structure.[19] CCDC-297120 contains the

Table 2. Summary of the relationship between the number of valence electrons and the average separation between the formal electrode potentials of consecutive redox couples.

Structure	CVE[a]	CPE[b]	ΔE_{av} [V]	No. of redox couple peaks	Ref.
1	156	158	0.37	4	this work
[$Co_{10}Rh_2(N)_2(CO)_{24}]^{2-}$	168	162	0.53	3	[20]
[$Fe_6Ni_6(N)_2(CO)_{24}]^{2-}$	168	160	0.53	3	[21]
[$Fe_6Pd_6H(CO)_{24}]^{3-}$	160	158	0.75	3	[22]
[$Ir_{12}(\mu\text{-}CO)_5(CO)_{19}]^{2-}$	158	154	0.58	3	[23]

[a] Cluster Valence Electrons. [b] Expected valence electron count based on the Condensed Polyhedral Electron Count.

supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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