Synthesis and characterization of high-nuclearity osmium–rhodium mixed-metal carbonyl clusters; molecular and crystal structures of $[Os_{12}Rh_9(CO)_{44}(\mu_3\text{-}Cl)]\cdot 2CH_2Cl_2$ and $[Os_4Rh_3(\mu_3\text{-}H)(CO)_{14}(\mu_3\text{-}CO)(\eta^4\text{-}C_7H_8)_2]$

Sarah Yeuk-Wah Hung and Wing-Tak Wong*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, PR China

The anionic triosmium cluster $[N(PPh_3)_2][Os_3(\mu\text{-}H)(CO)_{11}]$ reacts with $[Rh(nbd)Cl]_2$ (nbd = norbornadiene) in the presence of $AgPF_6$ to give two new high-nuclearity osmium–rhodium clusters $[Os_{12}Rh_9(CO)_{44}(\mu_3\text{-}Cl)]$ 1 and $[Os_4Rh_3(\mu_3\text{-}H)(CO)_{14}(\mu_3\text{-}CO)(\eta^4\text{-}C_7H_8)_2]$ 2 in moderate yields.

Mixed-metal clusters of osmium and rhodium are of interest as the rhodium tends to have a stable, coordinatively unsaturated 16 electron configuration,[1] while the osmium clusters display very rich chemistry and are kinetically stable. In addition, both osmium and rhodium metals have a well established background of catalytic applications.[2–6] One route to synthesize the mixed-metal osmium clusters is *via* nucleophilic addition of rhodium reagents to the coordinatively unsaturated cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ which has been extensively applied for the development of Os–Rh clusters.[7] An obvious alternative route into these systems is the interaction of the anion $[Os_3(\mu\text{-}H)(CO)_{11}]^-$ and cationic rhodium fragment but this has previously met limited success. However, this kind of ionic coupling strategy works well in many other mixed-metal systems.

Herein we report the reaction of a cationic mononuclear rhodium complex, $[Rh(nbd)]^+$,[8] (nbd = norbornadiene) with the anionic carbonyl cluster, $[Os_3(\mu\text{-}H)(CO)_{11}]^-$, which results in a novel class of high-nuclearity mixed-metal osmium–rhodium clusters. A mixture of $[Rh(nbd)Cl]_2$ and $AgPF_6$ (1 : 1) in thf was filtered and then treated with $[N(PPh_3)_2][Os_3(\mu\text{-}H)(CO)_{11}]$ under nitrogen at room temp.[9] An immediate change from red to brown was observed. Separation of the brown solution by TLC on silica [eluent: *n*-hexane–dichloromethane (1 : 4)] gave red $[Os_{12}Rh_9(CO)_{44}(\mu\text{-}Cl)]$ **1** (20%) and brown $[Os_4Rh_3(\mu_3\text{-}H)(CO)_{14}(\mu_3\text{-}CO)(\eta^4\text{-}C_7H_8)_2]$ **2** (10%) together with two uncharacterized products in low yield. Complexes **1** and **2** were fully characterized by spectroscopic techniques† and X-ray crystallography.‡

Single crystals of $\mathbf{1}\cdot 2CH_2Cl_2$ suitable for X-ray analysis were obtained by slow evaporation of a CH_2Cl_2–*n*-hexane solution. Its molecular structure, together with some important bond parameters, is depicted in Fig. 1. The structure of **1** [Fig. 1(*a*)] can be viewed as four '$Os_3(CO)_{11}$' units clipping onto the nanorhodium cluster metal core so that an asymmetric metal core results as illustrated in Fig. 1(*b*). The Rh_9 core geometry may be described as the fusion of an octahedron, Rh(1)Rh(2)Rh(3)Rh(4)Rh(5)Rh(6), with another virtual octahedron, Rh(4)Rh(5)Rh(6)Rh(7)Rh(8)Rh(9), in which there is no direct bonding between Rh(7) and Rh(9) or Rh(8) and Rh(9).

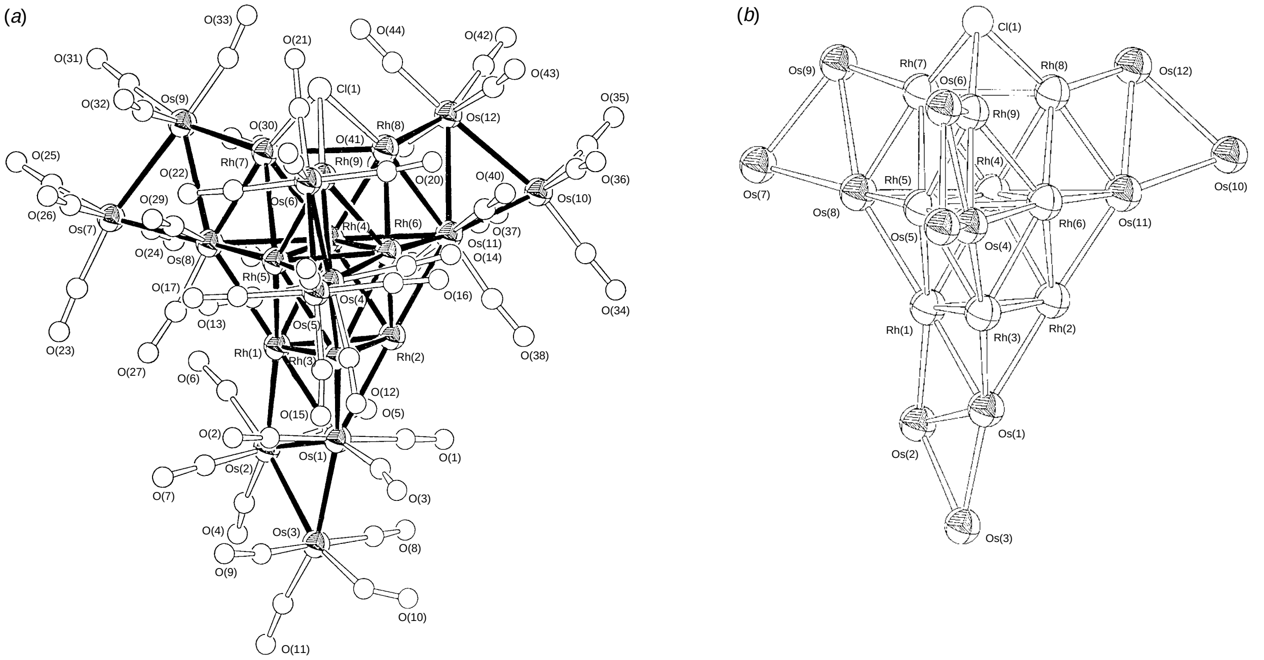

Fig. 1 (*a*) Molecular structure of the cluster $[Os_{12}Rh_9(CO)_{44}(\mu_3\text{-}Cl)]$ **1** showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): Os(1)–Os(2) 2.983(2), Os(1)–Os(3) 2.842(2), Os(2)–Os(3) 2.903(2), Os(4)–Os(5), 2.882(2) Os(4)–Os(6) 3.063(2), Os(5)–Os(6), 2.906(2) Os(7)–Os(8) 2.874(4), Os(7)–Os(9), 2.898(2) Os(8)–Os(9) 3.094(2), Os(10)–Os(11), 2.890(2) Os(10)–Os(12) 2.897(2), Os(11)–Os(12), 3.078(2) Os(1)–Rh(1) 2.806(3), Os(1)–Rh(2), 2.867(3) Os(1)–Rh(3) 2.766(3), Os(2)–Rh(1), 2.996(3) Rh(1)–Rh(2) 2.868(6), Rh(1)–Rh(3), 3.051(3) Rh(1)–Rh(5) 2.991(4), Rh(2)–Rh(3), 2.716(3) Rh(5)–Rh(7) 2.981(3), Rh(7)–Rh(8), 2.976(4) Rh(7)–Rh(9) 3.372(2), Rh(8)–Rh(9), 3.361(2) Os(1)–C(2) 2.867(3), Rh(7)–Cl(1), 2.533(7) Rh(8)–Cl(1) 2.586(7), Rh(9)–Cl(1), 2.558(6); Os(11)–Rh(4)–Rh(2) 59.65(7), Rh(7)–Cl(1)–Rh(8), 71.1(2) Rh(7)–Cl(1)–Rh(9) 83.0(2), Rh(8)–Cl(1)–Rh(9), 81.5(2). (*b*) The metal core geometry of **1**.

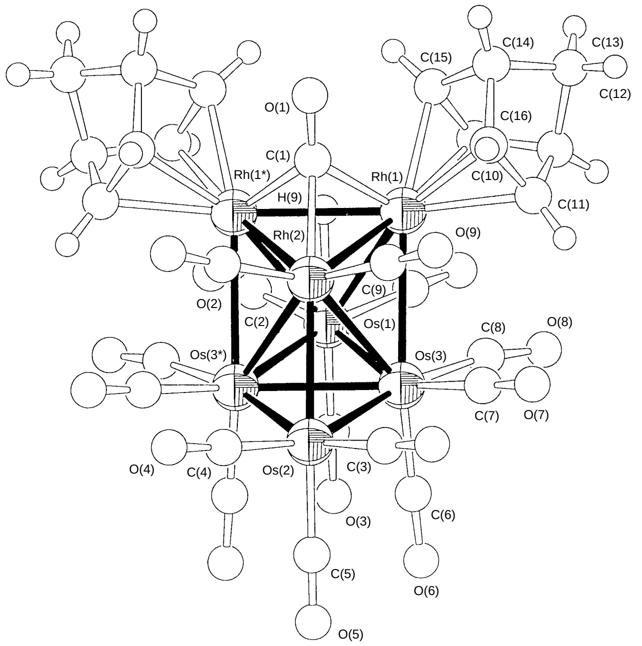

Fig. 2 Molecular structure of the cluster $[Os_4Rh_3(\mu_3\text{-}H)(CO)_{14}(\mu_3\text{-}CO)(\eta^4\text{-}C_7H_8)_2]$ **2** showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): Os(1)–Os(3) 2.839(1), Os(2)–Os(3) 2.800(1), Os(3)–Os(3*) 2.795(2), Os(1)–Rh(1) 3.003(2), Os(2)–Rh(2) 2.741(3), Os(3)–Rh(1) 2.915(2), Rh(1)–Rh(1*) 2.847(4), Rh(1)–Rh(2) 2.761(3), Rh(1)–C(1) 2.15(2), Rh(2)–C(1) 2.11(3), Rh(1)–C(10) 2.22(2), Rh(1)–C(11) 2.24(3), Rh(1)–C(15) 2.19(2), Rh(1)–C(16) 2.21(2), Os(1)–H(9) 2.03, Rh(1)–H(9) 1.85, O(1)–C(1) 1.19(3); Rh(1)–C(1)–Rh(1*) 83.1(9), Rh(1)–C(1)–Rh(1*) 83.0(9), Rh(1)–C(1)–Rh(2) 80.9(8), Os(1)–H(9)–Rh(1) 101.5, Rh(1)–H(9)–Rh(1*) 100.8.

In the Rh_9 core, one chloro-ligand caps onto three rhodium atoms, Rh(7), Rh(8) and Rh(9), and the rest of rhodium atoms, Rh(1), Rh(2), Rh(3), Rh(4), Rh(5) and Rh(6), have no ligand groups attached to them but are coordinated to metal atoms only. A salient structural feature of **1** is these relatively exposed Rh atoms which may facilitate the coordination of nucleophiles. All the carbonyl ligands are essentially terminally bonded to the osmium atoms except an incipient bridging CO interaction which is found between Os(4) and Rh(3), [Rh(3)···C(12) 2.44(3) Å]. However, in solution all carbonyls are terminally bonding as suggested by IR spectroscopic data. We do not detect any hydride in the variable-temperature ^1H NMR studies [−50 to 25 °C]. Although satisfactorily elemental analysis was obtained, a satisfactory mass spectrum of **1** cannot be obtained by either EI, FAB or ESI techniques. If the triosmium units are each considered to have a formal 2− charge, $[Os_3(CO)_{11}]^{2-}$, each rhodium atom should be in an oxidation state of +1. Cluster **1** contains 50 metal–metal bonds and 268 cluster valence electrons (CVE) and hence does not obey the simple electron counting rules.[10–12] This is not entirely unexpected as it is common for rhodium to have a stable 16 electron configuration.

Brown crystals of **2** were grown from a CH_2Cl_2–*n*-hexane solution of the complex. A perspective drawing of cluster **2** with atomic numbering scheme is shown in Fig. 2 together with some selected bond parameters. Cluster **2** is much more symmetrical and consists of a crystallographic mirror plane that relates the two halves of the molecules. The metal framework contains a mixed-metal monocapped octahedron with four osmium atoms and three rhodium atoms. A μ_3-bridging hydride capping the Os(1)–Rh(1)–Rh(1*) face is suggested by potential-energy calculations[13] and supported by ^1H NMR spectroscopic measurements and difference Fourier synthesis based on log-angle data in the X-ray analysis. The metal core geometry of cluster **2** is similar to that of $[Os_7(CO)_{21}]$,[14] where both compounds have 98 CVE. This can be rationalised by the polyhedral skeletal electron pair theory[15] and the condensed polyhedral approach.[16] The mechanisms of formation of **1** and **2** have not been established. However, it seems reasonable to suggest that $[Rh(nbd)Cl]_2$ undergoes chloride dissociation upon reaction with silver(I) salts to give the active rhodium reagent, $[Rh(nbd)]^+$,[8] which reacts with the osmium cluster anion, $[Os_3(\mu\text{-}H)(CO)_{11}]^-$ *via* a complicated redox condensation, instead of a simple ionic coupling reaction. Cyclic voltammetric studies of $[N(PPh_3)_2][Os_3(\mu\text{-}H)(CO)_{11}]$ in thf at 25 °C showed an irreversible oxidation at +0.66 V *vs.* Ag/AgNO$_3$ while the preformed $[Rh(nbd)]^+$ cation showed an irreversible reduction at −0.02 V in thf *vs.* Ag/AgNO$_3$.[17] Further work on the mechanistic details and the chemical reactivities of these new high-nuclearity clusters is in progress.

We gratefully acknowledge financial support from the Hong Kong Research Grants Council and the University of Hong Kong. S. Y.-W. H. acknowledges the receipt of a postgraduate studentship, administrated by the University of Hong Kong.

Footnotes and References

* E-mail: chemmail@hkucc.hku.hk

† *Spectroscopic data*: **1**: IR [ν(CO), CH_2Cl_2] 2109m, 2099m, 2068vs, 2035vs, 2016m(sh), 2001m(sh). Elemental analysis: Anal. Calc. for $C_{44}ClO_{44}Os_{12}Rh_9$: C, 11.80. Found: 12.02%.

2: IR[ν(CO), CH_2Cl_2] 2082m, 2068s, 2055vs, 2032m(sh), 2016vs, 1607m. Positive FAB mass spectrum: *m/z* 1674 (calc. 1674). ^1H NMR (CD_2Cl_2): δ −19.47 (m, 1 H, metal hydride), 1.62 (m, 2 H, methylene), 4.33 (m, 2 H, methine), 4.96 (m, 4 H, alkene). Elemental analysis: Anal. Calc. for $C_{29}H_{17}O_{15}Os_4Rh_3$: C, 20.78, H, 1.01. Found: 20.99, 0.98%.

‡ *Crystal data*: $Os_{12}Rh_9C_{44}O_{44}Cl\cdot 2CH_2Cl_2$ **1**, M = 4474.5 (4646.33 with solvents), triclinic, space group $P\bar{1}$ (no. 2), a = 14.853(4), b = 22.012(5), c = 14.259(4) Å, α = 95.429(2)°, β = 113.50(2)°, γ = 71.06(2)°, U = 4040(2) Å^3, Z = 2, D_c = 3.819 g cm^{-3}, $F(000)$ = 4068.00, Mo-Kα radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 207.96 cm^{-1}, dimensions 0.12 × 0.14 × 0.16 mm. 11 035 observed diffractometer data [$I > 3.00\sigma(I)$]; ψ-scan absorption correction, structure solved by direct methods (SIR92) and Fourier techniques, refined by full-matrix least-squares analysis to R = 0.047, R' = 0.049, $w = 1/\sigma(F_o)$.

2: $C_{29}H_{17}O_{15}Os_4Rh_3$, M = 1674.96, orthorhombic, space group *Pnma* (no. 62), a = 17.425(3), b = 17.828(4), c = 10.963(3) Å, U = 3405(1) Å^3, Z = 4, D_c = 3.266 g cm^{-3}, $F(000)$ = 3000, Mo-Kα radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 163.37 cm^{-1}, dimensions 0.12 × 0.18 × 0.23 mm 4804 observed diffractometer data [$I > 3.00\sigma(I)$]; ψ-scan absorption correction, structure solved and refined as for **1** to R = 0.038, R' = 0.041. CCDC 182/607.

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Received in Cambridge, UK, 19th August 1997; 7/06080G