

Synthesis and characterisation of high-nuclearity osmium–silver mixed-metal clusters†

Yui-Bing Lee and Wing-Tak Wong*

Received (in Cambridge, UK) 28th June 2007, Accepted 3rd August 2007

First published as an Advance Article on the web 23rd August 2007

DOI: 10.1039/b709860j

The reaction of the triosmium cluster anion, $[\text{Os}_3(\mu\text{-H})(\text{CO})_{11}]^-$ [PPN] (PPN = $[\text{N}(\text{PPh}_3)_2]^+$), with $[\text{AgPF}_6]$ in the presence of $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$ in THF at room temperature affords two new high-nuclearity osmium–silver clusters, $[\text{Os}_{13}\text{Ag}_9(\text{CO})_{48}]^-$ [PPN] (**1**) and $[\text{Os}_9\text{Ag}_9(\mu_3\text{-O})_2(\text{CO})_{30}]$ [PPN] (**2**), and an iridium complex, $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}(\text{O}_2)]$ (**3**).

The chemistry of high-nuclearity metal clusters, in particular heterometallic clusters, has been of increasing interest, as they serve as good catalysts for many economically important industrial reactions, such as the hydrogenation, hydroformylation and carbonylation of olefins.¹ Attention has turned to this class of compounds recently because they serve as good precursors in the synthesis of mixed-metal nanostructures.²

To our knowledge, only a very limited number of osmium–silver clusters have been prepared^{3,4} due to the high oxidizing power of silver salts, which may induce the oxidation of osmium clusters to osmium metal oxides. Lewis⁴ reports the reaction of $[\text{Os}_3(\mu\text{-H})(\text{CO})_{11}]^-$ [PPN] with $[\text{AgPF}_6]$ in refluxing THF, which yielded an osmium–silver cluster, $[\{\text{Os}_3(\mu\text{-H})(\text{CO})_{10}\}_2\text{Ag}]$ [PPN].

In general, silver and its mixed-metal clusters are known to form open-structure metal cores. Only a very few examples have demonstrated a closely packed metal structure, with the central silver metal atoms usually stabilized by closely packed carbonyl ligated transition metal layers.⁵ Silver salts react to form large reactive cationic clusters in the presence of reducing agents that serve as the intermediates in the formation of high-nuclearity mixed-metal clusters.⁶ On the other hand, Vaska's complex, $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$, has been studied for decades and is well-known for its highly reversible oxygenation behaviour.⁷ However, it has not been fully studied as a reducing agent. Herein, we report the synthesis and structural characterization of two high-nuclearity osmium–silver clusters using Vaska's complex as the reducing agent and for its unique irreversible oxygenation.

$[\text{AgPF}_6]$ (35 mg, 0.1384 mmol) was allowed to stir with Vaska's complex, $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$ (30 mg, 0.0384 mmol), in THF (10 mL) at room temperature until white precipitate was observed. Then, the filtrate was transferred to another flask that contained $[\text{Os}_3(\mu\text{-H})(\text{CO})_{11}]^-$ [PPN] (200 mg, 0.1358 mmol) *via* cannula. The mixture was allowed to stir for another 15 min and was then separated by TLC to yield $[\text{Os}_{13}\text{Ag}_9(\text{CO})_{48}]^-$ [PPN] (**1**) (86 mg,

50%), $[\text{Os}_9\text{Ag}_9(\mu_3\text{-O})_2(\text{CO})_{30}]$ [PPN] (**2**) (18.9 mg, 10%) and $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}(\text{O}_2)]$ (**3**) (12.5 mg, 40%). The reaction scheme is shown in Scheme 1.

Red block crystals of **1** that were suitable for single-crystal X-ray analysis were obtained from the saturated solution of dichloromethane–diethyl ether–methanol at $-20\text{ }^\circ\text{C}$ after a week. It was crystallized in its [PPN]⁺ salt with one dichloromethane molecule and two water molecules as the solvents of crystallization inside the crystal lattice.

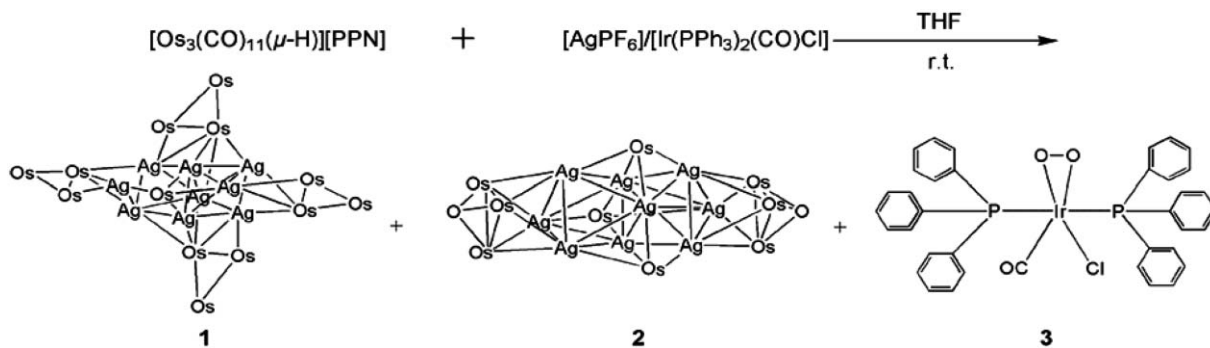
Fig. 1 shows the molecular structure of $[\text{Os}_{13}\text{Ag}_9(\text{CO})_{48}]^-$ (**1**).§§ The metal framework consists of three “Ag₃” units that are arranged in a slightly distorted “ABA” arrangement with a maximum deviation of 8.965° from the average Ag₃ plane. No direct bonding is observed between Ag(2) and Ag(3) [Ag(2)⋯Ag(3), 3.600(3) Å] or between Ag(8) and Ag(9) [Ag(8)⋯Ag(9), 3.595(2) Å]. Four triosmium units are bound at the four sides of the silver core, whereas the middle trisilver unit Ag(4)–Ag(5)–Ag(6) is edge-bridged by another osmium atom (Os(7)) that is lying on the same plane. A similar asymmetric metal core has been observed in another high-nuclearity osmium–rhodium cluster, $[\text{Os}_{12}\text{Rh}_9(\text{CO})_{44}(\mu\text{-Cl})]$.⁸ The average Os–Ag bond length observed is 2.904 Å, which falls into the typical range of Os–Ag bonds (2.85 to 2.95 Å) that have been reported in previous studies.⁴ The mean Ag–Ag bond length observed is 2.856 Å, with two exceptionally longer bonds in Ag(2)–Ag(4) and Ag(5)–Ag(8), of 3.187(3) and 3.149(3) Å, respectively. The average Ag–Ag bond is shorter than that of 2.89 Å in bulk silver metal,⁹ and Dahl suggests that this type of stabilisation in the silver core could be a consequence of the cumulative effects of many weak delocalised Ag–Ag interactions. A similar interaction was also observed in $[\text{Ag}_{16}\text{Ni}_{24}(\text{CO})_{40}]^{4-}$ which has a ccp Ag₁₆ kernel.⁵

The ¹H NMR spectroscopy confirms that there are no associated hydride species, as there is no signal detected between -40 and 0 ppm. Such species are common in high-nuclearity clusters. The metal core of **1** with a length of about 1 nm shows the highest nuclearity of Os–Ag clusters that has ever been reported.

The observation of this type of cluster with a bare metal core that is surrounded by triosmium carbonyl units is rather rare because triosmium clusters usually react with mononuclear complexes in a “3 + 1” manner. The structure of **1** suggests that a cationic “Ag₉” intermediate may be formed prior to its reaction with the triosmium anion to form a large cluster, and the triosmium carbonyl units can therefore stabilize the Ag₉ intermediate. This is a reasonable suggestion, as we have also isolated another osmium–silver mixed-metal cluster, **2**, with a similar Ag₉ skeleton.

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, Peoples Republic of China.
E-mail: wt Wong@hkucc.hku.hk; Fax: 852-2547-2933;
Tel: 852-2859-2157

† Electronic supplementary information (ESI) available: detailed synthetic procedures, crystallization experiments and crystallographic data in CIF. See DOI: 10.1039/b709860j



Scheme 1 Reaction pathway (only metal cores are shown for **1** and **2** for clarity).

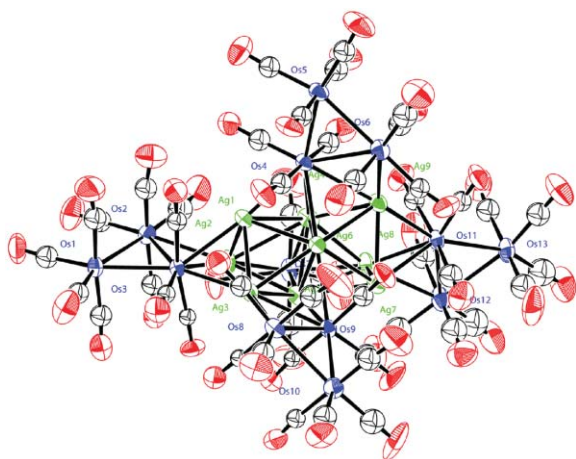


Fig. 1 ORTEP diagram (50% probability thermal ellipsoids) of $[\text{Os}_{13}\text{Ag}_9(\text{CO})_{48}]^-$ of **1** with the atom numbering scheme omitting the labels on the carbonyl ligands for clarity.

Suitable brown block crystals of $[\text{PPN}]^+$ salt of **2** were obtained from the saturated solution of its $[\text{PPN}]^+$ salt in dichloromethane–methanol at $-20\text{ }^\circ\text{C}$ after 10 days. Fig. 2 shows the molecular structure of the metal core of complex **2**. The metal core consists of five layers of the M_3 unit ($\text{M} = \text{Os}$ or Ag) that are arranged in

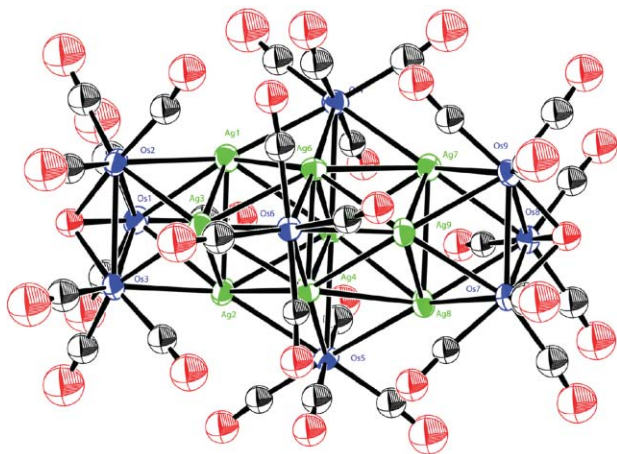


Fig. 2 ORTEP diagram (50% probability thermal ellipsoids) of $[\text{Os}_9\text{Ag}_9(\mu_3\text{-O})_2(\text{CO})_{30}]^-$ of **2** with the atom numbering scheme omitting the labels on the carbonyl ligands for clarity.

“ABABA” fashion with a three-fold axis. The middle trisilver unit, $\text{Ag}(4)$, $\text{Ag}(5)$, $\text{Ag}(6)$, was edge-bridged by three osmium atoms, $\text{Os}(4)$, $\text{Os}(5)$, $\text{Os}(6)$, on the same plane. The unique geometry of **2** is that the metal atoms adopt a closed-packing structure, which is rarely observed in mixed-metal clusters.¹⁰ The mean $\text{Os}\text{--}\text{Ag}$ bond observed is 2.857 \AA , which suggests a stronger $\text{Os}\text{--}\text{Ag}$ interaction over **1** and a more favourable and stable geometry of the highly symmetrical triangular column in **2**. However, the mean $\text{Ag}\text{--}\text{Ag}$ bond length observed is 2.959 \AA , which is significantly longer than that of **1**. The two triosmium units at the two ends are capped by an oxygen atom that becomes the centre of the three-fold axis. This type of face-capping oxo ligand is rarely observed in mixed-metal systems. The average $\text{Os}\text{--}\text{O}$ bond length observed is 2.049 \AA , which is similar to the $\text{Os}\text{--}\text{O}$ bond lengths with $\mu_3\text{-O}$ coordination mode that have been reported ($2.02\text{--}2.20\text{ \AA}$).¹¹ The two oxo ligands, $\text{O}(31)$ and $\text{O}(32)$, have out-of-plane distances of 1.220 \AA and 1.217 \AA , respectively.

Air- and photo-stable crystals of **3** were obtained from its saturated solution in dichloromethane–methanol. Fig. 3 shows the molecular structure of **3**, which adopts a trigonal bipyramidal geometry, with the two triphenylphosphine ligands *trans* to each other. Disorder is observed for the carbonyl ligand and the chloride atom. Their occupancy were refined and then fixed for subsequent refinements of the structure. It is highly reminiscent of the structure that was reported by Vaska,⁷ except for the dioxygen molecule. In the reported structure, the dioxygen molecule was added reversibly to the iridium centre, and the adduct is highly

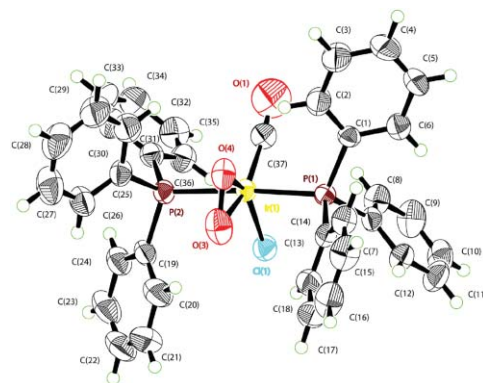


Fig. 3 ORTEP diagram (50% probability thermal ellipsoids) of $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}(\text{O}_2)]$ **3**, showing the disorder carbonyl ligand and chloride at their higher occupancy positions.

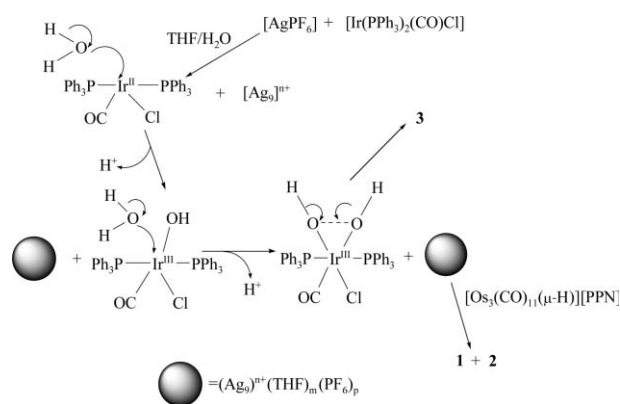


Fig. 4 Schematic diagram showing the proposed mechanism.

photosensitive and will readily release oxygen even in the solid state. The reported bond length is 1.30 Å, which suggests a typical superoxide ion (O_2^-) addition. For complex **3**, however, the bond length observed is 1.475(6) Å, which suggests a peroxide ion (O_2^{2-}), and the addition is totally irreversible. The iodo analog of **3**, $[IrI(CO)(PPh_3)_2(O_2)]$,⁷ which also possesses an irreversible oxygen addition, has been isolated with a bond length of 1.50 Å for the bound O_2 .⁷

However, reactions between Vaska's complex and other silver salts such as $[AgBF_4]$, $[AgNO_3]$ and $[Ag_2O]$ have ended up with halide-replaced cationic iridium species,¹² and no silver clusters or mixed-metal clusters of osmium–silver can be isolated. Replacing the reaction medium with chlorinated solvents such as CH_2Cl_2 , $CHCl_3$ or methanol also leads to some triosmium clusters instead of the formation of high-nuclearity osmium–silver mixed-metal clusters. Although the mechanistic detail of these cluster buildup reactions is usually difficult to delineate, a few key steps that are involved can be put forward. It is likely that $[AgPF_6]$ oxidized Vaska's complex to give a Ir^{II} species in THF. The successive hydrolysis of this Ir^{II} intermediate through the trace amount of water that was present led to the iridium dioxygen species **3**. A schematic drawing of this suggested mechanism is shown in Fig. 4. An increase in C–O stretching frequency in the IR spectrum was observed when $[AgPF_6]$ was mixed with Vaska's complex (from 1967 cm^{-1} to 2052 cm^{-1}). In contrast, the halide abstraction reaction with other silver salts ($AgBF_4$, $AgNO_3$) on Vaska's complex gave only a slight increase in the C–O stretching frequencies (from 1967 cm^{-1} to 1989 cm^{-1}). The role of Vaska's complex– H_2O as a reducing agent is crucial for the formation of the $[Ag_9]^{n+}$ core. Replacing Vaska's complex with its reversible oxygen adduct, $[Ir(PPH_3)_2(CO)Cl(O_2)]$, or the irreversible iodo oxygen adduct, $[Ir(PPH_3)_2(CO)I(O_2)]$, did not lead to any osmium–silver mixed-metal clusters. The formation of **3** from hydrolysis is evident in ^{18}O -labelling studies. A 250 μL sample of ^{18}O -enriched water was introduced in a pre-dried THF solvent for the preparation. Infrared spectroscopic study shows that **3** displayed three absorption bands at 856, 833 and 808 cm^{-1} that correspond to the ^{16}O – ^{16}O , ^{16}O – ^{18}O and ^{18}O – ^{18}O stretching vibrations, respectively. The results are in good agreement with reports and calculations¹³ in the literature and, therefore, confirm that the oxygen atom in water was oxidized and bound to the iridium centre to give complex **3**.

We have successfully demonstrated the introduction of Vaska's complex as a reducing agent for silver salts to yield two new high-nuclearity osmium–silver clusters and suggested the probable mechanism that was involved in the reaction.

We gratefully acknowledge the financial support of the Hong Kong Research Grants Council and The University of Hong Kong. Y.-B. Lee acknowledges the receipt of a Postgraduate Studentship from The University of Hong Kong.

Notes and references

† Spectroscopic data: **1**: IR [$\nu(CO)$, CH_2Cl_2] 2112 m, 2072 m, 2036 s, 2000 m. m/z : 4790 (calc. 4790, M^+). 1H NMR (CD_2Cl_2): δ 7.4–7.8 (m, 30H, PPN).

2: IR [$\nu(CO)$, CH_2Cl_2] 2070 m, 2038 s, 2019 m, 1985 m. m/z : 3558 (calc. 3557, M^+). 1H NMR (CD_2Cl_2): δ 7.4–7.8 (m, 30H, PPN).

3: IR [$\nu(CO)$, CH_2Cl_2] 2052 m [$\nu(O-O)$, CH_2Cl_2] 860 s. m/z : 812 (calc. 812, M^+). 1H NMR (CD_2Cl_2): δ 7.2–7.4 (m, 30H, PPh₃).

§ Crystallographic data: Refinements of all structures were based on full-matrix least refinement on F . Detailed experimental procedures can be found in the supporting information†.

CCDC 644530–644532. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709860j

- B. C. Gates, *Chem. Rev.*, 1995, **95**, 511; N. Toshima and T. Yonezawa, *New J. Chem.*, 1998, **22**, 1179; A. K. Smith and J. M. Basset, *J. Mol. Catal.*, 1977, **2**, 229; G. L. Geoffroy and W. L. Gladfelter, *J. Am. Chem. Soc.*, 1977, **99**, 6775; P. J. Dyson, *Coord. Chem. Rev.*, 2004, **248**, 2458.
- A. Siani, B. Captain, O. S. Alexeev, E. Stafyla, A. B. Hungria, P. A. Midgley, J. M. Thomas, R. D. Adams and M. D. Amiridis, *Langmuir*, 2006, **22**, 5160; M. W. DeGroot, H. Rosner and J. F. Corrigan, *Chem.–Eur. J.*, 2006, **12**, 1547; P. Jena, S. N. Khanna and B. K. Pao, *Clusters and Nano-assemblies, Physical and Biological systems*, Richmond, Virginia, USA, 2003.
- B. F. G. Johnson, J. Lewis and M. Monari, *J. Chem. Soc., Dalton Trans.*, 1990, 3525; B. F. G. Johnson, R. Khattar, J. Lewis and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1989, 1421; S. R. Drake, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1989, 505; S. R. Drake, B. F. G. Johnson and J. Lewis, *J. Organomet. Chem.*, 1988, **340**, C31; S. B. Colbran, C. M. Hay, B. F. G. Johnson, F. J. Lahoz, J. Lewis and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1986, 1766; M. I. Bruce, E. Horn, J. G. Matison and M. R. Snow, *J. Organomet. Chem.*, 1985, **286**, 271; J. A. Ladd, H. Hope and A. L. Balch, *Organometallics*, 1984, **3**, 1838.
- M. Fajardo, M. P. Gomez-Sal, H. D. Holden, B. F. G. Johnson, J. Lewis, R. C. S. McQueen and P. R. Raithby, *J. Organomet. Chem.*, 1984, **267**, C25.
- J. Zhang and L. F. Dahl, *J. Chem. Soc., Dalton Trans.*, 2002, 1269; V. G. Albano, L. Grossi, G. Longoni, M. Monari, S. Mulley and A. Sironi, *J. Am. Chem. Soc.*, 1992, **114**, 5708; B. K. Teo, H. Zhang and X. Shi, *Inorg. Chem.*, 1994, **33**, 4086; B. K. Teo and H. Zhang, *J. Cluster Sci.*, 2001, **12**, 349; B. K. Teo, H. Dang, C. F. Campana and H. Zhang, *Polyhedron*, 1998, **17**, 617.
- J. Sinzig, L. L. de Jongh, A. Ceriotti, R. della Pergola, G. Longoni, M. Stener, K. Albert and N. Rosch, *Phys. Rev. Lett.*, 1998, **81**, 3211.
- J. A. McGinney, R. J. Doedens and J. A. Ibers, *Science*, 1967, **155**, 709; L. Vaska, L. S. Chen and C. V. Senoff, *Science*, 1971, **174**, 587; L. Vaska, *Science*, 1963, **140**, 809; S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, 1965, **87**, 2581; J. A. McGinney, R. J. Doedeats and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 2243.
- S. Y. W. Wong and W. T. Wong, *Chem. Commun.*, 1997, 2099.
- J. Donohue, *The Structure of Elements*, J. Wiley & Sons, NY, 1974, 209.
- K. F. Yung and W. T. Wong, *Angew. Chem., Int. Ed.*, 2003, **42**, 553; O. A. Belyakova and Yu. L. Slovokhotov, *Russ. Chem. Bull.*, 2003, **52**, 2299.
- J. S. Y. Wong and W. T. Wong, *Organometallics*, 2003, **22**, 4798; K. S. Y. Leung and W. T. Wong, *J. Chem. Soc., Dalton Trans.*, 1997, 4357.
- D. J. Liston, C. A. Reed, C. W. Eigenbrot and W. R. Scheidt, *Inorg. Chem.*, 1987, **26**, 2739; J. Peone, Jr. and L. Vaska, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 511.
- K. Takao, Y. Fujiwara, T. Imanaka, M. Yamamoto, K. Hirota and S. Teranishi, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 2249.