Removing a second mercury atom from [Os$_{18}$Hg$_3$C$_2$(CO)$_{42}$]$^{2-}$: synthesis of [Os$_{18}$HgC$_2$(CO)$_{42}$]$^{4-}$ and crystal structure of [PPh$_3$H]$_3$[Os$_{18}$HgHC$_2$(CO)$_{42}$]

Lutz H. Gade,[a] **Brian F. G. Johnson,**[b] **Jack Lewis,**[a] **Mary McPartlin**[c] **and Ian J. Scowen**[c]

[a] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK*

[b] *Department of Chemistry, University of Edinburgh, Kings Buildings, West Mains Road, Edinburgh EH9 3JJ, UK*

[c] *School of Chemistry, University of North London, Holloway Road, London N7 8DB, UK*

Upon reduction of [N(PPh$_3$)$_2$]$_2$[Os$_{18}$Hg$_x$C$_2$(CO)$_{42}$] (x = 2 or 3) with sodium diphenylketyl in tetrahydrofuran a hexaanionic cluster, [Os$_{18}$Hg$_x$C$_2$(CO)$_{42}$]$^{6-}$, is generated which could only be partially characterised by IR spectroscopy as well as through its chemical reactivity. After chromatographic work-up the tetraanionic cluster [Os$_{18}$HgC$_2$(CO)$_{42}$]$^{4-}$ was isolated as the exclusive reaction product. This was also obtained in low yield (20–30%) by thermolytic degradation of [Os$_{18}$Hg$_2$C$_2$(CO)$_{42}$]$^{2-}$ in CH$_2$Cl$_2$. As a consequence of traces of HCl in the CH$_2$Cl$_2$ as well as degradation of the cation, the salt [PPh$_3$H]$_3$[Os$_{18}$Hg$_2$HC$_2$(CO)$_{42}$] crystallised from the reaction mixture. An X-ray single-crystal analysis of the latter has established its solid-state structure in which two Os$_9$C units are µ$_6$-linked by a central mercury atom. The [Os$_{18}$HgC$_2$(CO)$_{42}$]$^{4-}$ cluster may be converted into the dimercury cluster dianion [Os$_{18}$Hg$_2$C$_2$(CO)$_{42}$]$^{2-}$ by reaction with Hg(O$_3$SCF$_3$)$_2$.

Attempts locally to modify the metal frameworks in high-nuclearity cluster complexes normally lead to more or less complete breakdown of their structures or may initiate reaction cascades of cluster degradation and aggregation generating products which are structurally unrelated to the initial substrate. However, mixed-metal clusters having a domain structure may display metal-core reactivity which is limited to the interfaces between their subunits.[1]

We have recently studied the metal-core reactivity of such a system, the [N(PPh$_3$)$_2$]$^+$ salt of the high-nuclearity osmium–mercury cluster dianion [Os$_{18}$Hg$_3$C$_2$(CO)$_{42}$]$^{2-}$ **1**,[2] from which a single mercury atom could be removed reversibly either by photolysis[3] or reduction of the compound with mild reducing agents.[4] The redox and photochemical reaction products derived from **1** are summarised in Scheme 1. The metal-to-metal charge transfer transition which is believed to be responsible for the photochemically induced mercury extrusion[5] may be viewed as an intramolecular redox reaction in which population of an Os–Hg/Hg–Hg antibonding orbital leads to destabilisation of the central Hg$_3$ unit. It was therefore not surprising that population of the same antibonding orbital from an external electron source, *i.e.* reduction of the cluster, leads to a similar structural transformation. Electrochemical studies of this process by cyclic voltammetry revealed that an irreversible two-electron reduction at *ca.* −0.8 V (*vs.* Ag–AgCl) was associated with this reaction which could therefore be very selectively achieved by chemical reduction with cobaltocene.[4] In view of these results the question arose as to whether it would be possible to remove a second Hg atom from the cluster using a stronger reducing agent than [Co(η-C$_5$H$_5$)$_2$].

In this paper we report the reaction of the previously known Os$_{18}$Hg$_x$ clusters (x = 2 or 3) with sodium diphenylketyl and the isolation and characterisation of clusters which contain only one Hg atom linking the two Os$_9$C units present in all these mixed-metal species.

Results and Discussion

Synthesis of [Os$_{18}$HgC$_2$(CO)$_{42}$]$^{4-}$

Titration of a solution of [N(PPh$_3$)$_2$]$_2$[Os$_{18}$Hg$_3$C$_2$(CO)$_{42}$] **1** with a solution of sodium diphenylketyl in tetrahydrofuran (thf) initially leads to the known tetraanionic cluster
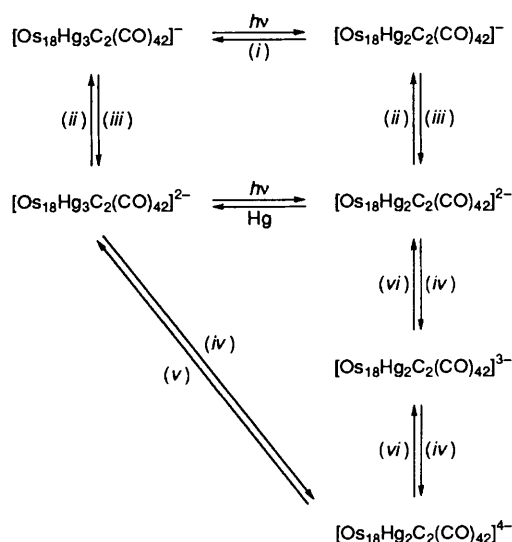
Scheme 1 The previously established redox and photochemical reactions involving Os$_{18}$Hg$_x$ clusters (x = 2 or 3). (*i*) Hg; (*ii*) Ag$^+$; (*iii*) reduction; (*iv*) [Co(η-C$_5$H$_5$)$_2$]; (*v*) Hg^{2+}; (*vi*) [Fe(η-C$_5$H$_5$)$_2$]$^+$

[Os$_{18}$Hg$_2$C$_2$(CO)$_{42}$]$^{4-}$ **2**. Upon further addition of the reducing agent this compound is converted into a cluster with a remarkably simple ν(CO) infrared absorption band pattern: 2030m, 2008vs, 1960s and 1945m (sh) cm^{-1}. The same species is obtained (*via* **2**) in the reduction of [N(PPh$_3$)$_2$]$_2$[Os$_{18}$Hg$_2$C$_2$(CO)$_{42}$] **3** with Na$^+$Ph$_2$CO$^-$, and 4 molar equivalents of the reducing agent are required for the complete conversion in *both* cases. This observed stoichiometry, along with the ν(CO) stretching frequencies in the IR spectrum (Table 1), is consistent with the proposal of a hexaanionic Os$_{18}$Hg$_x$ cluster as the product of the reduction. Addition of an excess of Na$^+$Ph$_2$CO$^-$ does not lead to a further reduction which requires stronger reducing agents such as Na$^+$C$_{10}$H$_8^-$. However, on reaction with the latter only unspecific cluster degradation was observed.

Table 1 The ν(CO) bands in the infrared spectra (recorded in CH$_2$Cl$_2$) of the known Os$_{18}$Hg$_x$ cluster anions

Cluster charge	[Os$_{18}$Hg$_3$C$_2$(CO)$_{42}$][a]	[Os$_{18}$Hg$_2$C$_2$(CO)$_{42}$][a]	[Os$_{18}$HgH$_n$C$_2$(CO)$_{42}$][b]	[Os$_{18}$Hg$_x$C$_2$(CO)$_{42}$][b]
−1	2085m, 2072s, 2022s	2081s, 2073vs, 2022s	—	—
−2	2072m, 2055s, 2005s	2064s, 2057vs, 2007s	—	—
−3	—	2051s, 2044vs, 1994s	2044vs, 2002m, 1991m[c]	—
−4	—	2047m, 2029s, 1980s	2029vs, 1979m, 1973m (sh)[d]	—
−6	—	—	—	2030m, 2008vs, 1960s, 1945m (sh)[e]

[a] Taken from refs. 3 and 4. [b] This work. [c] $n = 1$. [d] $n = 0$. [e] Recorded in thf.

Unfortunately, it proved impossible to isolate the hexaanionic product which did not crystallise as a solid from these reaction mixtures. It was therefore not possible to assess whether the increase in negative charge was accompanied by the ejection of a mercury atom; this species which could only be characterised in solution is therefore tentatively formulated as [Os$_{18}$Hg$_x$C$_2$(CO)$_{42}$]$^{6-}$ **4** ($x = 1$ or 2). The observation that the reaction of **4** with highly dissociated mercury(II) salts such as Hg(O$_3$SCF$_3$)$_2$ leads first to its conversion into the dimercury tetraanion **2** and then to the trimercury dianion **1** may support the formulation of **4** as a monomercury cluster, however, the possibility of a hidden redox reaction involving the mercury salts [mercury(II) salts may simply oxidise high-nuclearity clusters!] is a caveat to this notion.[1]

On chromatographic work-up (silica column) of the brown-red reaction product {in the presence of added [N(PPh$_3$)$_2$]Cl} the colour changed to brown-green. The only product which was isolated (yield 48%) was the salt of a cluster tetraanion which on the basis of its infrared spectrum (assignment of the charge), negative-ion FAB mass spectrum (formulation of the cluster) as well as the ^{13}C NMR spectrum of the 50% ^{13}C-enriched species (molecular symmetry of the cluster, see Fig. 1) was formulated as [Os$_{18}$HgC$_2$(CO)$_{42}$]$^{4-}$ **5**. The proposed structure of this cluster therefore contains a central Hg atom linking two Os$_9$C(CO)$_{21}$ units. The Hg atom most probably caps the 'open' Os$_3$ triangle in both tricapped octahedral osmium subclusters in a geometrical arrangement related to that first reported by Yamamoto et al.[6] in the Pt–Hg cluster [Hg{Pt$_3$(2,6-Me$_2$C$_6$-H$_3$NC)$_6$}$_2$] and Braunstein et al.[7] in [{RuCo$_3$(CO)$_{12}$}$_2$Hg].

Thermal degradation of [N(PPh$_3$)$_2$]$_2$[Os$_{18}$Hg$_2$C$_2$(CO)$_{42}$] 3 and structure of [PPh$_3$H]$_2$[Os$_{18}$HgHC$_2$(CO)$_{42}$]

In our previous studies of the properties of the dianionic dimercury cluster **3** which is photochemically generated from **1** we noted the significantly lower thermal stability of this particular species in comparison to most other high-nuclearity Os–Hg clusters. Whereas thermolysis in high-boiling solvents leads to unspecific decomposition of all these compounds, they are, with the exception of **3**, stable upon refluxing in solvents such as dichloromethane, acetone or tetrahydrofuran.

However, on refluxing cluster **3** in CH$_2$Cl$_2$ slow degradation sets in which may be monitored by infrared spectroscopy. After 20 h no starting material is detected in solution. Work-up of the reaction mixture by thin-layer chromatography (TLC) (CH$_2$Cl$_2$, silica) yielded, apart from a substantial amount of material remaining at the baseline (accounting for ca. 50% of the overall mass balance), two major fractions which were isolated. A violet cluster fraction (ca. 10%) was identified as containing the tetraanionic cluster **2** (IR and negative-ion FAB mass spectrometry) while the second burgundy-red fraction was a hitherto unknown cluster species from which black crystals were obtained with yields (obtained in several preparations) ranging from 20 to 30%. The negative-ion FAB mass spectrum of the compound displayed peaks centred around m/z 4827 (most abundant isotopomer) attributable to the molecular
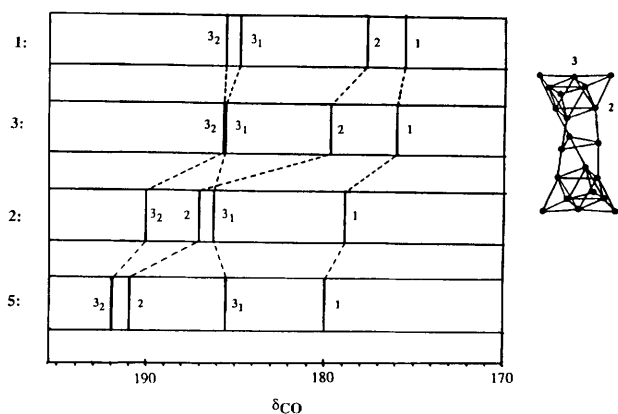

Fig. 1 Comparison of the ^{13}C NMR chemical shifts of the carbonyl resonances of the known Os$_{18}$Hg$_x$ clusters ($x = 1$–3). Note that the resonances due to the carbonyls co-ordinated to the Os(2)–Os(3)–Os(6) triangle (position 2) adjacent to the mercury units are most strongly affected by the changes within the mercury domain

cluster ion which is consistent with a cluster of the same composition as that of **5**. Associated with this peak were two less-intense mass peak distributions shifted by 263 and 526 units to higher m/z. As with all previously studied cluster salts, these are due to complexes of the cluster anion and its cations. The pattern observed here is typical for the salt of a trianionic cluster and the mass difference between the peaks suggested the presence of [PPh$_3$H]$^+$ probably generated from the [N(PPh$_3$)$_2$]$^+$ cation in the course of the thermal degradation process. The infared spectrum of the compound also indicated the presence of trianionic species. Furthermore, a signal at δ −13.8 in the ^{1}H NMR spectrum is indicative of the presence of a hydride ligand. The resonance multiplet structure of the [PPh$_3$H]$^+$ ion is identical to that observed for [PPh$_3$H]-[O$_3$SCF$_3$] prepared by reaction of triflic acid (CF$_3$SO$_3$H) with triphenylphosphine. On the basis of these data we formulated the cluster as [PPh$_3$H]$_3$[Os$_{18}$HgHC$_2$(CO)$_{42}$] **6**
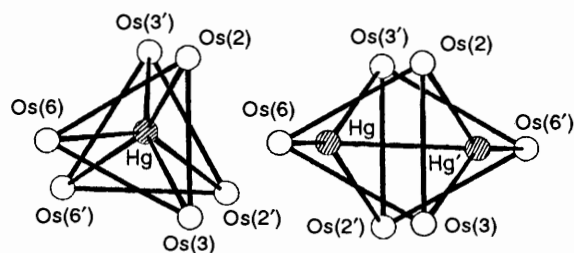
Although the crystals obtained of compound **6** diffracted only weakly, and in spite of the gross disorder of the phosphonium cations which precluded their structural determination, it was possible to establish the cluster structure from an X-ray crystallographic study. The molecular structure is shown in Fig. 2(a) along with the structure of the bare Os$_{18}$Hg core [Fig. 2(b)]. The principal bond distances and interbond angles are given in Table 2. The overall structural arrangement of **6** is as postulated above for the deprotonated tetraanionic analogue **5** on the basis of its spectroscopic data. The central Hg atom links the two Os$_9$C halves in a μ$_6$ arrangement as previously observed in [Hg{Pt$_3$(2,6-Me$_2$-C$_6$H$_3$NC)$_6$}$_2$][6] and in [{RuCo$_3$(CO)$_{12}$}$_2$Hg] (see below).[7] This generates a cluster geometry which bears close resemblance to the other known structures of Os$_{18}$Hg$_x$ clusters ($x = 2$ or 3).[1–4]

However, there are several notable differences in comparison
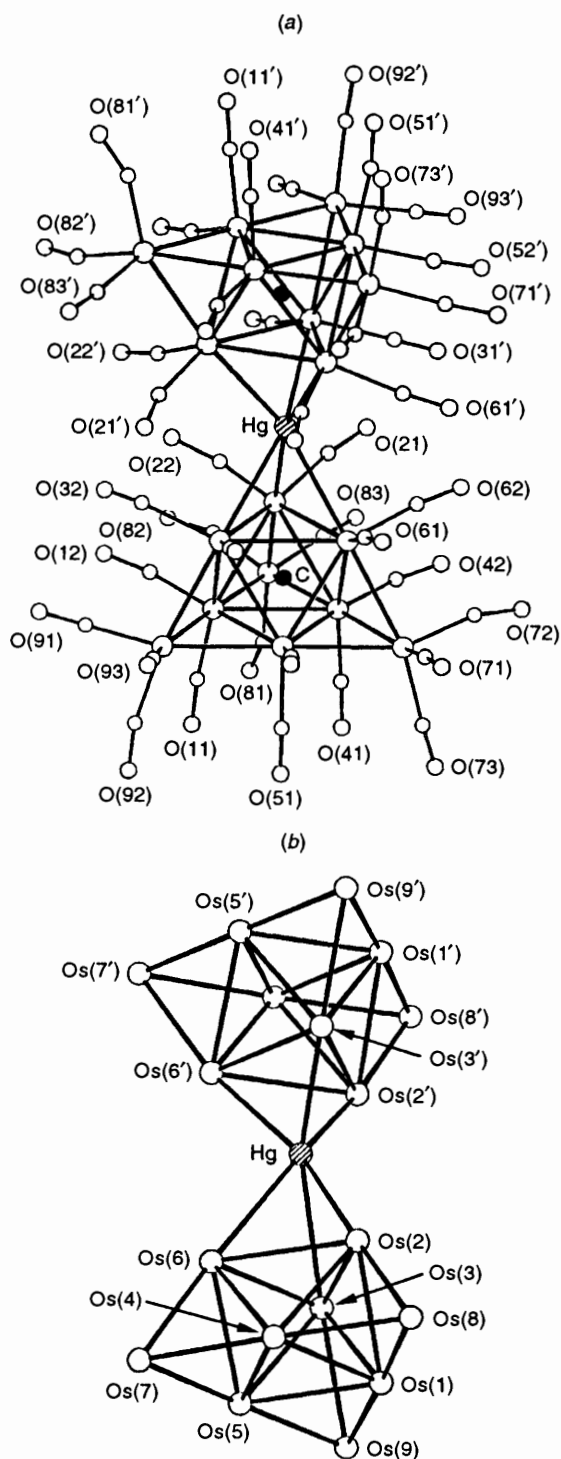
Fig. 2 Perspective diagrams of the cluster trianion $[Os_{18}HgHC_2$-$(CO)_{42}]^{3-}$ **6** showing: (*a*) the overall structure [for each carbonyl group the number of the carbon atom is the same as that of the attached oxygen atom and the number of each osmium atom is the first digit(s) of the relevant carbonyl atoms]; (*b*) the structure of the $Os_{18}Hg$ metal core in which the two Os_9 units are related by a crystallographic C_2 axis

Fig. 3 Comparison of the central Os_6Hg unit of $[Os_{18}HgHC_2$-$(CO)_{42}]^{3-}$ **6**, where the Os_3 triangles are related by C_2 symmetry, with the centrosymmetric Os_6Hg unit in $[Os_{18}Hg_2C_2(CO)_{42}]^{2-}$ **3**

Hg atom. In the centrosymmetric structures their planes are strictly parallel and twisted relative to each other by 60° (although permitting 'slippage' along one of the bisecting vectors of the triangles, as for instances observed in **3**). The two planes are no longer exactly parallel in **6** (tilt angle 1.4°) and the twist angle is reduced to 27.7° (Fig. 3).

In the structure of compounds **1–3** the Os_3 triangle adjacent to the central mercury subunit $[Os(2)–Os(3)–Os(6)]$ is significantly expanded relative to the other Os_3 triangles in the osmium domains of the clusters $\{1, d_{av}[(Os–Os)_{triang}] = 3.062;$ **2**, 3.036; **3**, 3.016 Å, in comparison to an average Os–Os distance of *ca.* 2.84 Å in all these species [1] [4]$\}$. The same situation is found in the structure of **6** $\{d_{av}[(Os–Os)_{triang}] = 2.954$, compared with $d_{av}(Os–Os) = 2.830$ Å$\}$, however somewhat less pronounced than in the other species.

The location of the mercury atom extremely close to the crystallographic C_2 axis prevented full refinement of its parameters. This situation therefore precludes detailed discussion of the Os–Hg bond lengths.

Direct location of a hydride ligand in a high-nuclearity osmium cluster is not possible from X-ray data, and an assignment based on indirect methods is also ruled out where the possibility of disorder exists.[8] That **6** is indeed a mono hydride was shown by protonation of **5** with 1 equivalent of triflic acid which generated a cluster with identical spectroscopic properties to those of **6**.

Conclusion

This work has shown that the reductive removal of mercury atoms from high-nuclearity clusters may be achieved very selectively by the appropriate choice of the reducing agent. With the characterisation of **5** and **6** we are now able to present the complete series of $Os_{18}Hg_x$ ($x = 1$–3) clusters which are mutually interconvertible. The thermal degradation of the electron-deficient cluster **3** to yield, among other unidentified products, the more highly charged species **2** and **6** is an indication of the tendency of such species to undergo redox disproportionations. This observation complements the conproportionation reactions of $[Os_{18}Hg_2C_2(CO)_{42}]^{y-}$ ($y = 2$–4) and $[Os_{20}(CO)_{40}]^{z-}$ ($z = 0$–4) we reported recently.[4,9]

Experimental

All manipulations were performed under an inert-gas atmosphere of dried argon in standard (Schlenk) glassware. Schlenk tubes and other reaction vessels were evacuated and flame-dried with a bunsen burner prior to use. Solvents and solutions were transferred from one reaction vessel to another with the aid of stainless-steel cannulae under complete exclusion of air and moisture ('cannula/septa technique'). The compounds $[N(PPh_3)_2][Os_{18}Hg_3C_2(CO)_{42}]$ **1** and $[N$-$(PPh_3)_2]_2[Os_{18}Hg_2C_2(CO)_{42}]$ **3** were prepared as described in refs. 2 and 3. All other reagents were obtained commercially and used without further purification. The ^{13}C-enriched sample of **5** was synthesised from ^{13}C-enriched $[Os_3(CO)_{12}]$.[3]

to these previously established cluster structures. Whereas the two tricapped octahedral Os_9C moieties in compounds **1–3** are related by a crystallographic centre of symmetry, the structure of **6** is non-centrosymmetric. The central mercury atom is located slightly off the two-fold crystallographic axis (orthogonal to the two virtual three-fold axes of the Os_9C units) which relates the two halves of the cluster. This different situation also manifests itself in the relative arrangement of the two Os_3 triangles $[Os(2)–Os(3)–Os(6)]$ which are linked by the

Table 2 Selected bond lengths (Å) and angles (°) for the cluster trianion $[Os_{18}HgHC_2(CO)_{42}]^{3-}$

Os(1)–Os(2)	2.862(6)	Os(1)–Os(3)	2.906(6)	Os(4)–Os(6)	2.879(6)	Os(4)–Os(7)	2.786(6)
Os(1)–Os(4)	2.863(5)	Os(1)–Os(5)	2.862(5)	Os(4)–Os(8)	2.776(6)	Os(5)–Os(6)	2.878(6)
Os(1)–Os(8)	2.772(5)	Os(1)–Os(9)	2.788(5)	Os(5)–Os(7)	2.756(5)	Os(5)–Os(9)	2.778(5)
Os(2)–Os(3)	2.961(5)	Os(2)–Os(4)	2.888(6)	Os(6)–Os(7)	2.788(6)	Os(6)–Hg	3.026
Os(2)–Os(6)	2.960(5)	Os(2)–Os(8)	2.783(6)	Os(2)–Hg	2.893	Os(3)–Hg	3.067
Os(3)–Os(5)	2.865(5)	Os(3)–Os(9)	2.942(5)	Hg–Os(2')	2.882	Hg–Os(3')	2.593
Os(3)–Os(9)	2.793(5)	Os(4)–Os(5)	2.864(5)	Hg–Os(6')	2.884		

Os(3)–Os(1)–Os(2)	61.8(1)	Os(4)–Os(1)–Os(2)	60.6(1)	Os(7)–Os(4)–Os(5)	58.4(1)	Os(7)–Os(4)–Os(6)	58.9(1)
Os(4)–Os(1)–Os(3)	90.6(2)	Os(5)–Os(1)–Os(2)	91.0(2)	Os(8)–Os(4)–Os(1)	58.9(1)	Os(8)–Os(4)–Os(2)	58.8(1)
Os(5)–Os(1)–Os(3)	59.6(1)	Os(5)–Os(1)–Os(4)	60.0(1)	Os(8)–Os(4)–Os(5)	118.8(2)	Os(8)–Os(4)–Os(6)	120.6(2)
Os(8)–Os(1)–Os(2)	59.2(1)	Os(8)–Os(1)–Os(3)	120.9(2)	Os(8)–Os(4)–Os(7)	177.2(2)	Os(3)–Os(5)–Os(1)	61.0(1)
Os(8)–Os(1)–Os(4)	59.0(1)	Os(8)–Os(1)–Os(5)	119.0(2)	Os(4)–Os(5)–Os(1)	60.0(1)	Os(4)–Os(5)–Os(3)	91.5(1)
Os(9)–Os(1)–Os(2)	120.5(2)	Os(9)–Os(1)–Os(3)	58.7(1)	Os(6)–Os(5)–Os(1)	90.9(2)	Os(6)–Os(5)–Os(3)	61.6(1)
Os(9)–Os(1)–Os(4)	118.9(2)	Os(9)–Os(1)–Os(5)	58.9(1)	Os(6)–Os(5)–Os(4)	60.2(1)	Os(7)–Os(5)–Os(1)	119.4(2)
Os(9)–Os(1)–Os(8)	177.9(2)	Os(3)–Os(2)–Os(1)	59.8(1)	Os(7)–Os(5)–Os(3)	120.9(2)	Os(7)–Os(5)–Os(4)	59.4(1)
Os(4)–Os(2)–Os(1)	59.7(1)	Os(4)–Os(2)–Os(3)	89.1(1)	Os(7)–Os(5)–Os(6)	59.3(1)	Os(9)–Os(5)–Os(1)	59.2(1)
Os(6)–Os(2)–Os(1)	89.3(1)	Os(6)–Os(2)–Os(3)	59.6(1)	Os(9)–Os(5)–Os(3)	59.3(1)	Os(9)–Os(5)–Os(4)	119.2(2)
Os(6)–Os(2)–Os(1)	59.0(1)	Os(8)–Os(2)–Os(1)	58.8(1)	Os(9)–Os(5)–Os(6)	120.9(2)	Os(9)–Os(5)–Os(7)	178.5(2)
Os(8)–Os(2)–Os(3)	118.6(2)	Os(8)–Os(2)–Os(4)	58.6(1)	C(51)–Os(5)–Os(9)	90(3)	C(52)–Os(5)–Os(1)	149(3)
Os(8)–Os(2)–Os(6)	117.6(2)	Hg–Os(2)–Os(1)	123.0(2)	Os(3)–Os(6)–Os(2)	60.2(1)	Os(4)–Os(6)–Os(2)	59.3(1)
Hg–Os(2)–Os(3)	63.2(1)	Hg–Os(2)–Os(4)	121.2(2)	Os(4)–Os(6)–Os(3)	89.6(1)	Os(5)–Os(6)–Os(2)	88.7(1)
Hg–Os(2)–Os(6)	62.3(2)	Hg–Os(2)–Os(8)	178.0(2)	Os(5)–Os(6)–Os(3)	59.0(1)	Os(5)–Os(6)–Os(4)	59.7(1)
C(21)–Os(2)–Os(1)	145(4)	Os(2)–Os(3)–Os(1)	58.4(1)	Os(7)–Os(6)–Os(2)	118.1(2)	Os(7)–Os(6)–Os(3)	117.1(2)
Os(5)–Os(3)–Os(1)	59.5(1)	Os(5)–Os(3)–Os(2)	89.0(1)	Os(7)–Os(6)–Os(4)	58.9(1)	Os(7)–Os(6)–Os(5)	58.2(1)
Os(6)–Os(3)–Os(1)	88.8(1)	Os(6)–Os(3)–Os(2)	60.2(1)	Hg–Os(6)–Os(2)	57.8(2)	Hg–Os(6)–Os(3)	61.8(1)
Os(6)–Os(3)–Os(5)	59.4(1)	Os(9)–Os(3)–Os(1)	58.5(1)	Hg–Os(6)–Os(4)	117.0(3)	Hg–Os(6)–Os(5)	120.6(2)
Os(9)–Os(3)–Os(2)	116.9(2)	Os(9)–Os(3)–Os(5)	58.8(1)	Hg–Os(6)–Os(7)	175.9(3)	Os(5)–Os(7)–Os(4)	62.2(1)
Os(9)–Os(3)–Os(6)	118.2(2)	Hg–Os(3)–Os(1)	115.7(3)	Os(6)–Os(7)–Os(4)	62.2(2)	Os(6)–Os(7)–Os(5)	62.5(1)
Hg–Os(3)–Os(2)	57.3(3)	Hg–Os(3)–Os(5)	119.7(3)	Os(2)–Os(8)–Os(1)	62.0(1)	Os(4)–Os(8)–Os(1)	62.1(1)
Hg–Os(3)–Os(6)	60.4(2)	Hg–Os(3)–Os(9)	174.2(3)	Os(4)–Os(8)–Os(2)	62.6(1)	Os(3)–Os(9)–Os(1)	62.8(1)
Os(2)–Os(4)–Os(1)	59.7(1)	Os(5)–Os(4)–Os(1)	60.0(1)	Os(5)–Os(9)–Os(1)	61.9(1)	Os(5)–Os(9)–Os(3)	61.9(1)
Os(5)–Os(4)–Os(2)	90.5(2)	Os(6)–Os(4)–Os(1)	90.9(2)	Os(3)–Hg–Os(2)	59.5(2)	Os(6)–Hg–Os(2)	60.0(3)
Os(6)–Os(4)–Os(2)	61.8(1)	Os(6)–Os(4)–Os(5)	60.2(1)	Os(6)–Hg–Os(3)	57.7(2)		
Os(7)–Os(4)–Os(1)	118.3(2)	Os(7)–Os(4)–Os(2)	120.7(2)				

Solution infrared spectra were recorded in NaCl or CaF$_2$ cells (path length 0.5 mm) on Perkin-Elmer PE 983 and PE 1710 spectrometers, and fast atom bombardment (FAB) mass spectra were obtained on a Kratos MS50 spectrometer. The matrix used was 3-nitrobenzyl alcohol and the calibrant CsI. The isotope distributions of parent ions were simulated with a computer program implemented on the DS90 data system of a Kratos MS890 mass spectrometer. The NMR spectra were recorded on a Bruker AM 400 Fourier-transform spectrometer. Deuteriated solvents were used in all experiments, and the resonance of the residual protons or the natural-abundance ^{13}C were used as internal secondary chemical shift reference (vs. tetramethylsilane).

[N(PPh$_3$)$_2$]$_4$[Os$_{18}$HgC$_2$(CO)$_{42}$] 5

(a) The compound [N(PPh$_3$)$_2$]$_2$[Os$_{18}$Hg$_3$C$_2$(CO)$_{42}$] 1 (50 mg, 7.9 × 10^{-6} mol) was dissolved in thf (15 cm^3). Upon titration with a solution of sodium–benzophenone (ca. 10 mg Na, 80 mg Ph$_2$CO in 15 cm^3 thf) and monitoring the reaction by IR spectroscopy, the initial formation of the tetraanionic cluster 2 was observed. Further addition {total amount: 1.8 cm^3 of the Na[Ph$_2$CO] solution} yielded a cluster hexaanion 4 [IR: ν(CO) 2030m, 2008vs, 1960s and 1945m (sh) cm^{-1}]. After addition of [N(PPh$_3$)$_2$]Cl (50 mg) to the brown solution, silica was added and the solvent was removed in vacuo. The silica with the absorbed cluster was packed on top of a 25 cm silica column (diameter 2.5 cm). Elution with acetone–hexane (3:1) yielded a major green-brown fraction which was collected and recrystallised from acetone–hexane (2:1, 5 cm^3): yield 48%. IR (CH$_2$Cl$_2$): ν(CO) 2029vs, 1979m and 1973m (sh) cm^{-1}. ^{13}C NMR [100.6 MHz, 50% ^{13}C-enriched sample in (CD$_3$)$_2$CO at 295 K]: δ 192.0 (6 CO), 190.9 [12 CO, $^2J(^{199}Hg-^{13}C) = 53$ Hz], 185.6 (6 CO) and 179.9 (18 CO); the resonance of the interstitial carbide was not observed. Most abundant

isotopomer of the molecular ion in the negative-ion FAB mass spectrum: m/z 4827 (simulated 4828).

(b) Compound 3 (30 mg, 4.9 × 10^{-6} mol) was dissolved in thf (10 cm^3). After addition of a solution (1.1 cm^3) of sodium–benzophenone (ca. 10 mg Na, 80 mg Ph$_2$CO in 15 cm^3 thf) and monitoring the reaction by IR spectroscopy, the red-brown product was worked up as described above to yield a compound with identical spectroscopic data to those cited above: yield 51%.

[PPh$_3$H]$_3$[Os$_{18}$HgHC$_2$(CO)$_{42}$] 6

The compound [N(PPh$_3$)$_2$]$_2$[Os$_{18}$Hg$_2$C$_2$(CO)$_{42}$] 3 (50 mg, 7.8 × 10^{-6} mol) was dissolved in CH$_2$Cl$_2$ (10 cm^3) and refluxed for 24 h at which time the IR spectrum indicated complete disappearance of the bands attributable to the starting material. The red-brown solution was concentrated to ca. 1 cm^3 and the product mixture separated by TLC on silica. Elution with CH$_2$Cl$_2$ gave two bands (apart from the black baseline): R_f = 0.3 (ca. 5 mg), violet, identified by IR and mass spectrometry as containing 2; R_f = 0.4, red-brown (14 mg) containing the previously unknown cluster 6. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 295 K): δ 7.6–7.5 (m, PPh$_3$H$^+$) and −13.8 (s, hydride). IR (CH$_2$Cl$_2$): ν(CO) 2044vs, 2002m and 1991m cm^{-1}. Most abundant isotopomers of the ion peak distribution in the negative-ion FAB mass spectrum: $m/z = 2412$, dianion (simulated 2412); 4827, monoanion (simulated 4828); 5090, dianion + [PPh$_3$H]$^+$ (simulated 5092); 5353, trianion + 2[PPh$_3$H]$^+$ (simulated 5355).

Protonation of compound 5

The compound [N(PPh$_3$)$_2$]$_4$[Os$_{18}$HgC$_2$(CO)$_{42}$] 5 (25 mg, 3.8 × 10^{-6} mol) was dissolved in CH$_2$Cl$_2$ (10 cm^3). Addition of a solution (0.6 cm^3) of CF$_3$SO$_3$H (10 mg) in CH$_2$Cl$_2$ (10 cm^3)

and subsequent purification of the product by TLC on silica (eluent CH_2Cl_2) yielded a single fraction (red-brown, $R_f = 0.4$) which was spectroscopically identified as compound **6**.

Reaction of compound 5 with Hg^{2+}

To a solution of compound **5** (25 mg, 3.8×10^{-6} mol in 10 cm³ of CH_2Cl_2) was added $Hg(O_3SCF_3)_2$ (1.9 mg, 3.8×10^{-6} mol). An immediate change from brown-red to purple was observed. After removal of the solvent, the reaction product was identified as compound **3**.

Crystal structure determination of [PPh₃H]₃[Os₁₈HgHC₂-(CO)₄₂] 6

Crystal data. $C_{98}H_{49}HgO_{42}Os_{18}P_3$, $M = 5615.55$, monoclinic, space group $C2/c$, $a = 28.935(7)$, $b = 16.495(4)$, $c = 27.219(7)$ Å, $\beta = 105.47(3)°$, $U = 12\,520.5$ Å³, $D_c = 2.979$ g cm⁻³, $F(000) = 9864$, $Z = 4$, $\mu(Mo-K\alpha) = 195$ cm⁻¹.

Data collection. Data were collected in the range θ 3–21° with a weakly diffracting dark crystal of size $0.38 \times 0.24 \times 0.11$ mm, using a scan width of 0.90°, by the technique previously described.[10] Equivalent reflections were merged to give 2668 unique data and 2646 with $I/\sigma(I) > 3.0$.

Structure solution and refinement.[11] The coordinates of six osmium atoms defining an octahedron in the unique half of the trianion were deduced from a Patterson synthesis and the remaining metal atoms were located in a Fourier synthesis. The maximum for the mercury atom extended about 0.5 Å on either side of the crystallographic C_2 axis. Refinement with the mercury on the C_2 axis led to a very high thermal parameter, consistent with its true position being slightly off the axis. After many attempts the most satisfactory refinement was obtained by assigning the Hg atom a site *ca.* 0.3 Å from the symmetry axis with half occupancy and its x and y coordinates and an isotropic thermal parameter were refined. Only thirty seven of the carbonyl ligands and one phosphorus atom were located in an initial Fourier-difference map. After initial refinement of the available atoms with isotropic thermal parameters, a preliminary empirical absorption correction[12] facilitated location of the remaining carbonyl atoms. Considerable difficulty was encountered in locating the [PPh₃H]⁺ counter ions. These problems were attributed to severe disorder and only the phosphorus atoms were located; one phosphorus atom is disordered in equal population over two sites related by the two-fold axis and the remaining phosphorus of the asymmetric unit is disordered over two general sites in equal population giving a total of three phosphorus atoms per cluster. All attempts to locate the disordered phenyl-ring carbon atoms of the cation were unsuccessful. Final absorption corrections were applied to the original data after refinement with isotropic thermal parameters for all the atoms located.[12] Satisfactory refinement was only obtained when the final cycles of full-matrix least-squares refinement were heavily damped, blocked and individual reflections were assigned unit weights. The osmium atoms were assigned anisotropic thermal parameters and refinement converged at $R = 0.0924$ for a total of 273 parameters.

Complete 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.*, 1996, Issue 1.

References

1 L. H. Gade, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 24.
2 L. H. Gade, B. F. G. Johnson, J. Lewis, M. McPartlin and H. R. Powell, *J. Chem. Soc., Chem. Commun.*, 1990, 110; *J. Chem. Soc., Dalton Trans.*, 1992, 921.
3 L. H. Gade, B. F. G. Johnson, J. Lewis, M. McPartlin, T. Kotch and A. J. Lees, *J. Am. Chem. Soc.*, 1991, **113**, 8698; E. Charalambous, L. H. Gade, B. F. G. Johnson, J. Lewis, M. McPartlin, T. Kotch and A. J. Lees, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1137.
4 L. H. Gade, B. F. G. Johnson, J. Lewis, G. Conole and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1992, 3249.
5 See, for example, A. Vogler and H. Kunkeley, *J. Organomet. Chem.*, 1988, **355**, 1.
6 Y. Yamamoto, H. Yamazaki and T. Sakurai, *J. Am. Chem. Soc.*, 1982, **104**, 2329; Y. Yamamoto, K. Takahashi, K. Matsuda and H. Yamazaki, *J. Chem. Soc., Dalton Trans.*, 1987, 1833.
7 P. Braunstein, J. Rosé, A. Tiripicchio and M. Tiripicchio-Camellini, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 767.
8 L. H. Gade, B. F. G. Johnson and J. Lewis, *Croat. Chem. Acta*, in the press; A. Bashall, L. H. Gade, J. Lewis, B. F. G. Johnson, G. McIntyre and M. McPartlin, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1164.
9 L. H. Gade, B. F. G. Johnson, J. Lewis, M. McPartlin, H. R. Powell, P. R. Raithby and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1994, 521.
10 M. K. Cooper, P. J. Guerney and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1982, 757.
11 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.
12 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.