Multiple Carbon–Carbon Bond Cleavage on a Heptaosmium Cluster: Synthesis and Structural Characterisation of $[Os_7(CO)_{18}(\mu_3\text{-}CPh)_2]$ and $[Os_7(CO)_{15}(\mu_3\text{-}CPh)_4]$†

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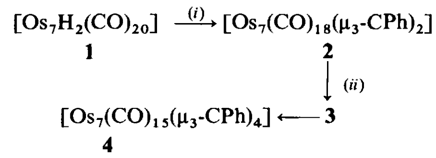
The cluster $[Os_7H_2(CO)_{20}]$ reacts with excess of Ph_2C_2 in refluxing toluene to produce first the brown species $[Os_7(CO)_{18}(\mu_3\text{-}CPh)_2]$ **2** and then, over a longer period, the purple cluster $[Os_7(CO)_{15}(\mu_3\text{-}CPh)_4]$ **4**. These clusters have been shown by X-ray crystallography to possess monocapped octahedral and unprecedented bicapped square-pyramidal metal cores, respectively. In each case the crystallographic data clearly show that in the course of this reaction carbon–carbon multiple-bond cleavage has occurred and 'carbyne' (CPh) units have been generated and stabilised by interactions with *triangulo*-Os_3 structural units. Crystal data: for **2**, triclinic, space group $P\bar{1}$, $a = 11.379(5)$, $b = 18.525(5)$, $c = 9.886(2)$ Å, $\alpha = 106.43(2)$, $\beta = 113.61(3)$ and $\gamma = 82.22(3)°$; for **4**, monoclinic, space group $C2/c$, $a = 15.953(5)$, $b = 19.816(4)$, $c = 14.383(2)$ Å and $\beta = 94.51(6)°$.

We are currently exploring the interactions of alkynes (R_2C_2) with osmium clusters containing from three to eight metal atoms. Our purpose is simply to explore the reactions that alkynes undergo with clusters of different nuclearity and to establish and understand the bonding modes adopted by CR fragments and their dependence on the number and type of metal atoms present. In earlier reports[1,2] we discussed the derivatives obtained from Os_n (n = 3–6) precursors; we now report an extension of this work to the heptaosmium system, $[Os_7H_2(CO)_{20}]$ **1**. Some aspects of this work have been the subject of an earlier communication.[3]

Results and Discussion

The dihydrido heptaosmium cluster $[Os_7H_2(CO)_{20}]$ **1** reacts with diphenylacetylene in toluene under reflux to produce initially a brown compound **2**, then a green compound **3**, and finally, after an extended period, a purple compound **4**. These clusters may be separated and purified by thin-layer chromatography and, in a series of separate experiments, we have established that a pure sample of **2** undergoes reaction with excess of Ph_2C_2 to produce **3** and **4**, and that a pure sample of **3** undergoes further reaction with Ph_2C_2 to produce **4**. However, considerable difficulty was initially experienced in establishing the precise formulae of these derivatives by the usual analytical and spectroscopic methods. Neither mass spectrometry nor ^1H NMR spectroscopy was particularly informative save for verifying the presence of phenyl groups and indicating that no hydride ligands were present (see Table 1) in all these derivatives. Fortunately, however, in the case of compounds **2** and **4** we were able to obtain X-ray quality crystals (see Experimental section). The X-ray diffraction experiments identified compound **2** as $[Os_7(CO)_{18}(\mu_3\text{-}CPh)_2]$ and **4** as $[Os_7(CO)_{15}(\mu_3\text{-}CPh)_4]$. Thus the reaction sequence (see Scheme 1) has been established.

Unfortunately, we have been unable fully to characterise complex **3**. All attempts to grow crystals suitable for X-ray analysis have failed and the spectroscopic data, as indicated above, were not particularly informative. Given the course that the reaction sequence follows from compound **2** to **4** it seems quite reasonable to suggest that **3** is of the form $[Os_7(CO)_{17}(\mu_3\text{-}CPh)_2(Ph_2C_2)]$ which contains a diphenylacetylene ligand in the Chatt–Dewar bonding mode.



Scheme 1 (*i*) PhC_2Ph, toluene reflux, 110 °C; (*ii*) PhC_2Ph, toluene reflux, 110 °C, 3 d

The molecular structures of compounds **2** and **4** (Figs. 1 and 2) are closely related and will be discussed together. The compound $[Os_7(CO)_{18}(\mu_3\text{-}CPh)_2]$ possesses the familiar monocapped octahedral framework of metal atoms (see Fig. 1) a geometry shared by $[Os_7(CO)_{21}]$[1a] and $[Os_7(CO)_{20}\{P(OMe)_3\}]$.[1b]

Relevant bond distances and angles for compound **2** are reported in Table 2. The two benzylidyne ligands are μ_3-capping triangular faces of the metal core, one in association with the μ_3-capping Os atom [Os(7)] and the other located on the central octahedral hexaosmium core. It is noteworthy that the two CPh ligands occupy positions which are farthest away from each other on the metal framework; this is almost certainly compatible with their μ_3 co-ordination requirements. Comparison of the Os–Os bond lengths of **2** with those of the parent $[Os_7(CO)_{21}]$[1a] reveals that both the octahedral core and the tetrahedral cap are smaller in **2** than in the latter species [mean 2.824(2), 2.854(6) and 2.789(2), 2.819(6) Å for the two moieties, respectively]. The presence of the μ_3-capping benzylidyne groups is responsible for this shrinkage, causing contraction of the triangular faces to which they are co-ordinated [mean 2.803(2) and 2.719(2) Å for octahedral and tetrahedral faces, respectively]. The two ligands are asymmetrically bound to the osmium triangles, both showing two 'short' [mean 2.05(2) Å] and one 'long' [2.22(2) Å] Os–C distances. The average Os–C–Os angle of 82(1)° is within the range expected for these ligands. Considering a three-electron donation from each benzylidyne ligand, compound **2** possesses the same number of electrons (98) as the parent $[Os_7(CO)_{21}]$. The two benzylidyne ligands donating a total of six electrons formally replace three CO ligands from the metal core of this latter species. It is

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Spectroscopic data for new heptaosmium clusters

Cluster	Colour	IR(ν_{CO}) (cm^{-1})[a]	Mass spectrum (*m*/*z*)[b]	^{1}H NMR[c]		
				δ	Intensity	Assignment
2 $[Os_7(CO)_{18}(\mu_3\text{-}CPh)_2]$	Brown	2072vs, 2061s, 2058m, 2028s, 2013m, 1939w	2026 (2026)	7.53 (m)	—	2 Ph
4 $[Os_7(CO)_{15}(\mu_3\text{-}CPh)_4]$	Purple	2101vw, 2072w, 2063s, 2048s, 2029vs, 2011ms, 1980w, 1945w	2120 (2120)	7.57 (m)	—	4 Ph
3 $[Os_7(CO)_{17}(\mu_3\text{-}CPh)_2(Ph_2C_2)]$	Green	2099vw, 2067s, 2061s, 2029s, 2014m, 1989w, 1941w	2120[d]	7.55	10	2 Ph
				6.58	10	2 Ph

[a] In CH_2Cl_2; v = very, s = strong, m = medium and w = weak. [b] Based on ^{192}Os; calculated values in parentheses. [c] In CD_2Cl_2. [d] It would appear that decomposition occurs in the course of the experiment to produce compound **3**.

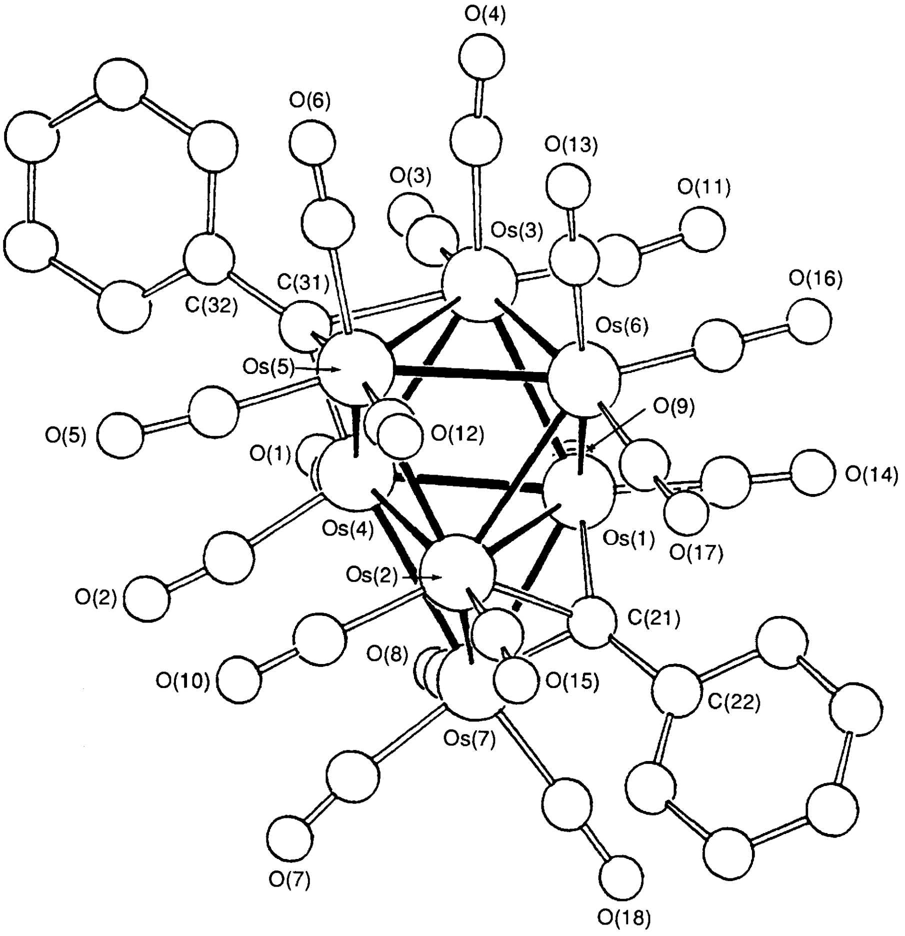

Fig. 1 The molecular structure of compound **2**

interesting that one CO ligand is 'removed' from each Os atom of the osmium-capped triangular face of the octahedral core, where the osmium atoms have the highest connectivity.

The molecular structure of compound **4** is shown in Fig. 2. The Os_7 metal core in this case is of a novel type consisting of a square pyramid which is μ_3-capped on opposite triangular faces by two Os atoms. Four μ_3-benzylidyne ligands are found μ_3-capping triangular faces of the metal framework: two are situated on the two opposite faces of the square pyramid, while the remaining two occupy the outer triangular faces generated by the capping Os atoms. All fifteen CO ligands are terminally bonded, with three on each capping atom, two on the Os atoms of the square base and one on the pyramid axis. The resulting idealised molecular symmetry is C_{2v} which is remarkable for a high-nuclearity cluster of such complexity. In the crystal the molecule lies on a crystallographic two-fold axis passing through the pyramid vertex, the middle of the square base and comprising the single CO group bound to Os(1). The phenyl group orientation strictly conforms to the idealised symmetry. Relevant bond distances and angles for compound **4** are in Table 3.

To the best of our knowledge compound **4** represents the first example of a cluster possessing more than two μ_3-CR groups derived from the cleavage of the C–C bonds of metal-co-ordinated alkyne ligands. This may be attributed to the large surface area offered by such a high-nuclearity cluster. Note too that the logical precursor of **4** would either be the bis(alkyne) cluster $[Os_7(CO)n(PhC_2Ph)_2]$ (n = 16 or 17) analogous to the predicted, but as yet unobserved, intermediate in the conversion of $[Os_7(CO)_{19}(MeC_2Me)]$ into $[Os_7(CO)_{16}(MeC_2Me)_3]$, or a mixed benzylidyne–alkyne cluster of the type $[Os_7(CO)_{17}(CPh)_2(PhC_2Ph)]$ discussed above, especially as it precedes the formation of **4**. The polyhedral electron count for **4** is 98 electrons and the observed structure thus obeys the eighteen-electron rule. Furthermore, the bicapped, square-pyramidal geometry of **4** represents a third of many alternative polyhedra

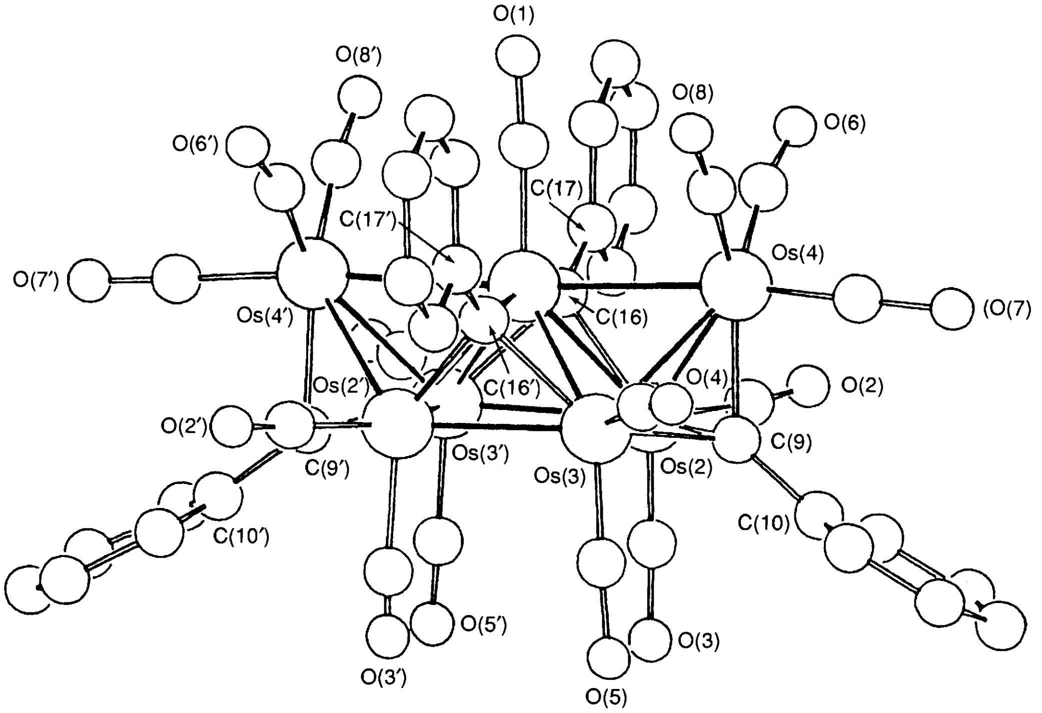

Fig. 2 The molecular structure of compound **4**

Table 2 Relevant bond distances (Å) for compound **2**

Os(1)–Os(2)	2.754(2)	Os(4)–C(1)	1.88(4)	C(1)–O(1)	1.18(4)	Os(1)–C(21)	2.02(3)
Os(1)–Os(4)	2.781(2)	Os(4)–C(2)	1.89(3)	C(2)–O(2)	1.15(3)	Os(2)–C(21)	2.01(3)
Os(1)–Os(7)	2.703(2)	Os(3)–C(3)	1.89(4)	C(3)–O(3)	1.16(4)	Os(7)–C(21)	2.22(3)
Os(2)–Os(5)	2.842(2)	Os(3)–C(4)	1.92(3)	C(4)–O(4)	1.11(4)	Os(3)–C(31)	2.19(3)
Os(2)–Os(7)	2.700(2)	Os(5)–C(5)	1.88(4)	C(5)–O(5)	1.18(4)	Os(4)–C(31)	1.99(3)
Os(3)–Os(5)	2.821(2)	Os(5)–C(6)	1.95(3)	C(6)–O(6)	1.08(3)	Os(5)–C(31)	2.23(3)
Os(4)–Os(5)	2.794(2)	Os(7)–C(7)	1.93(3)	C(7)–O(7)	1.13(4)	C(21)–C(22)	1.49(4)
Os(5)–Os(6)	2.847(2)	Os(7)–C(8)	1.91(4)	C(8)–O(8)	1.10(4)	C(22)–C(23)	1.42(4)
Os(1)–Os(3)	2.854(2)	Os(1)–C(9)	1.89(4)	C(9)–O(9)	1.16(4)	C(23)–C(24)	1.32(4)
Os(1)–Os(6)	2.875(2)	Os(2)–C(10)	1.93(3)	C(10)–O(10)	1.13(3)	C(24)–C(25)	1.37(5)
Os(2)–Os(4)	2.752(2)	Os(3)–C(11)	1.82(3)	C(11)–O(11)	1.22(4)	C(25)–C(26)	1.38(5)
Os(2)–Os(6)	2.910(2)	Os(5)–C(12)	1.91(4)	C(12)–O(12)	1.19(4)	C(26)–C(27)	1.34(4)
Os(3)–Os(4)	2.795(2)	Os(6)–C(13)	1.87(3)	C(13)–O(13)	1.11(3)	C(27)–C(22)	1.34(4)
Os(3)–Os(6)	2.868(2)	Os(1)–C(14)	1.91(3)	C(14)–O(14)	1.11(3)	C(31)–C(32)	1.46(4)
Os(4)–Os(7)	2.965(2)	Os(2)–C(15)	1.92(4)	C(15)–O(15)	1.15(4)	C(32)–C(33)	1.40(4)
		Os(6)–C(16)	1.84(3)	C(16)–O(16)	1.18(3)	C(33)–C(34)	1.41(5)
		Os(6)–C(17)	1.90(3)	C(17)–O(17)	1.15(4)	C(34)–C(35)	1.42(4)
		Os(7)–C(18)	1.87(4)	C(18)–O(18)	1.18(4)	C(35)–C(36)	1.42(4)
						C(36)–C(37)	1.38(4)
						C(37)–C(32)	1.39(4)

which can be derived by face-capping aggregation (+12 electrons) on 86-electron clusters,[4] such as the related [$Os_6(CO)_{16}(CPh)_2$] (a monocapped square pyramid), see above.[5]

It is also noteworthy that the square base of the square-pyramidal core in compound **4** is not supported by any ligand. In general, most square-pyramidal clusters (or square-pyramidal cores) have the square base bridged by ligands. This is the case of [$Os_6(CO)_{16}(CPh)_2$],[5] of the carbide [$Os_5C(CO)_{15}$][6] and of many others, including [$Os_7H_2(CO)_{21}$][7] where the presence of two bridging hydrides in the square base has been inferred on the basis of potential-energy calculations. The square-pyramidal core of **4** appears to be slightly 'squeezed' along its axis with shorter base–vertex bonds [mean 2.647(1) Å] and longer intrabasal bonds [mean 2.792(1) Å]. The opposite effect was observed in the related species [$Os_6(CO)_{16}(\mu_4\text{-CPh})(\mu_3\text{-CPh})$][5] [2.859(3) and 2.743(3) Å, respectively], where the square base bears a μ_4-CPh ligand. Structural parameters involving the μ_3-CPh groups [mean Os–C 2.12(1), μ_3-C–CPh 1.45(1) Å] agree with those discussed above for **2**, although the asymmetry observed in this latter species is less noticeable in **4** [Os–C ranges: C(9) 2.13(1)–2.16(1); C(16) 2.09(1)–2.17(1) Å]. These data can also be compared with those reported for other species containing μ_3-CPh groups such as [$Os_3(CO)_9(\mu_3\text{-CPh})$][8] [2.13(1), 1.46(2) Å] and [$Os_6(CO)_{16}(\mu_4\text{-CPh})(\mu_3\text{-CPh})$][5] [for the μ_3 ligand, 2.09(3) and 1.46(4) Å]. It appears that steric factors play an essential role in determining the stability of **4**: there is no simple and regular way of distributing twenty-one terminal carbonyl ligands {as in the isoelectronic [$Os_7(CO)_{21}$]}[1a] over a bicapped square-pyramidal framework. The μ_3-CPh ligands not only allow a lower ligand/electron donation ratio, but also allow optimisation of ligand–ligand interactions *via* occupation of face centres (edge- and face-bridging carbonyls are rarely observed in third-row metal clusters). These considerations indicate that three-electron donor benzylidyne (or alkylidyne) ligands may offer alternative ways to building large and compact metal cores, at least in cases where stabilisation might be prevented by excessive carboxyl crowding.

Conclusion

In this work we have again observed that the higher-nuclearity clusters show a marked tendency to bring about atom–atom multiple alkyne bond cleavage and to generate 'carbyne' fragments (CR) stabilised by combination with *triangulo*-osmium faces. To a large extent this chemistry closely parallels that found for boron clusters in the formation of carboranes, and this close relationship will be considered in a further report in which the comprehensive chemistry developed for the reactions of alkynes with clusters of nuclearities ranging from three to eight will be discussed.

Experimental

Reaction of $[Os_7H_2(CO)_{20}]$ *with* Ph_2C_2.—In a typical reaction, $[Os_7H_2(CO)_{20}]$ (20 mg, 0.11 mmol) and Ph_2C_2 (0.5 mmol) were heated under reflux in toluene (40 cm^3) for 3 d. During the course of the reaction, the colour changed from red to dark brown. The solvent was removed under a stream of nitrogen, after which the solid was redissolved in the minimum amount of dichloromethane and subjected to thin-layer chromatography using dichloromethane–hexane (15:85) as eluent. Three bands were detected: in order of decreasing R_f $[Os_7(CO)_{18}(PhC)_2]$ **2**, brown, 15–20% (Found: C, 13.95; H, 0.50. Calc. for $C_{32}H_{10}O_{18}Os_7$: C, 14.10; H, 0.50%); $[Os_7(CO)_{15}(CPh)_4]$ **4**, purple, 20–30%; and unidentified **3**, khaki-green, 30–50%. The yields quoted are after recrystallisation from dichloromethane–hexane. Crystals of **2** and **4** suitable for X-ray analysis were grown from dichloromethane–hexane.

Table 3 Relevant bond distances (Å) for compound **4**

Os(1)–Os(2)	2.645(1)	Os(1)–Os(3)	2.650(1)
Os(2)–Os(3′)	2.729(1)	Os(2)–Os(4)	2.780(1)
Os(3)–Os(4)	2.775(1)		
Os(1)–C(1)	1.89(2)	Os(4)–C(8)	1.90(2)
Os(2)–C(2)	1.85(1)	Os(2)–C(9)	2.13(1)
Os(2)–C(3)	1.90(2)	Os(3)–C(9)	2.14(2)
Os(3)–C(4)	1.91(2)	Os(4)–C(9)	2.11(1)
Os(3)–C(5)	1.91(2)	Os(1)–C(16)	2.10(1)
Os(4)–C(6)	1.90(2)	Os(2)–C(16)	2.07(1)
Os(4)–C(7)	1.92(2)	Os(3′)–C(16)	2.17(1)
C(1)–O(1)	1.17(2)	C(5)–O(5)	1.12(2)
C(2)–O(2)	1.16(2)	C(6)–O(6)	1.14(2)
C(3)–O(3)	1.12(2)	C(7)–O(7)	1.14(2)
C(4)–O(4)	1.12(2)	C(8)–O(8)	1.16(2)
C(9)–C(10)	1.44(2)	C(16)–C(17)	1.47(2)
C(10)–C(11)	1.37(2)	C(17)–C(18)	1.41(2)
C(11)–C(12)	1.41(2)	C(18)–C(19)	1.40(2)
C(12)–C(13)	1.37(3)	C(19)–C(20)	1.38(2)
C(13)–C(14)	1.39(3)	C(20)–C(21)	1.39(2)
C(14)–C(15)	1.38(2)	C(21)–C(22)	1.38(2)
C(15)–C(16)	1.39(2)	C(22)–C(17)	1.40(2)

All manipulations were carried out under an inert atmosphere of nitrogen using standard Schlenk and vacuum-line techniques. Although the new compounds reported are not particularly air- or moisture-sensitive, reactions were regularly carried out under a dry nitrogen atmosphere. All solvents were dried by distillation over the appropriate drying agents.

The starting material $[Os_7H_2(CO)_{20}]$ **1** was prepared by the literature method.[2] All chromatographic separations and ensuing work-up were carried out in the open air. Thin-layer chromatography was carried out on either Merck 60F-254 0.25 mm precoated silica gel plates or 2 mm thick plates prepared in the University of Cambridge Chemical Laboratory.

Infrared spectra were recorded on a Perkin-Elmer 983 grating spectrometer or 1710 Fourier-transform spectrometer, ^{1}H NMR spectra using Bruker WP 80 SY, WM 250 and AM 400 Fourier-transform spectrometers. Fast atom bombardment mass spectra were recorded using a Kratos MS902 spectrometer with a matrix of dithioglycerol or 2-nitrobenzyl alcohol.

Structural Characterisation.—Crystal data for compound **2**. $C_{32}H_{10}O_{18}Os_7$, M = 2014, triclinic, space group $P\bar{1}$, a = 11.379(5), b = 18.525(5), c = 9.886(2) Å, α = 106.43(2), β = 113.61(3), γ = 82.22(3)°, U = 1830.9 Å^3, $F(000)$ = 1755, Z = 2, D_c = 3.65 g cm^{-3}, μ(Mo-Kα) = 233.2 cm^{-1}, R = 0.045 {R' =

Table 4 Fractional atomic coordinates for compound **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.856 02(11)	0.717 38(6)	0.132 97(15)	C(12)	0.793 9(33)	0.824 3(19)	0.606 0(46)
Os(2)	0.808 58(11)	0.691 97(6)	0.367 61(15)	O(12)	0.845 0(22)	0.829 6(13)	0.739 1(31)
Os(3)	0.725 59(11)	0.860 32(7)	0.162 88(16)	C(13)	0.948 8(26)	0.925 5(17)	0.548 7(38)
Os(4)	0.607 31(11)	0.729 33(6)	0.125 44(15)	O(13)	0.958 8(22)	0.983 4(13)	0.625 1(30)
Os(5)	0.682 65(11)	0.835 15(7)	0.407 68(16)	C(14)	1.009 2(28)	0.719 4(17)	0.099 3(39)
Os(6)	0.938 22(11)	0.828 28(7)	0.420 54(16)	O(14)	1.091 4(21)	0.722 1(12)	0.067 3(29)
Os(7)	0.757 89(11)	0.585 87(6)	0.101 37(16)	C(15)	0.924 5(31)	0.674 5(18)	0.559 5(43)
C(1)	0.520 3(36)	0.704 5(21)	−0.087 3(50)	O(15)	0.987 3(23)	0.658 2(14)	0.671 1(33)
O(1)	0.455 5(23)	0.698 9(13)	−0.217 5(32)	C(16)	1.071 0(24)	0.845 6(15)	0.372 8(33)
C(2)	0.481 6(29)	0.674 1(17)	0.130 9(40)	O(16)	1.155 8(22)	0.855 8(13)	0.341 7(30)
O(2)	0.401 5(22)	0.646 0(13)	0.139 4(30)	C(17)	1.070 3(29)	0.789 2(17)	0.575 6(40)
C(3)	0.607 9(33)	0.865 7(19)	−0.033 2(45)	O(17)	1.153 4(23)	0.769 3(13)	0.671 8(31)
O(3)	0.538 1(26)	0.867 0(15)	−0.156 1(37)	C(18)	0.862 5(33)	0.501 9(20)	0.066 3(45)
C(4)	0.729 3(30)	0.967 5(18)	0.247 8(41)	O(18)	0.930 2(24)	0.449 1(15)	0.049 9(34)
O(4)	0.735 3(23)	1.030 0(14)	0.289 9(31)	C(19)	0.934 4(24)	0.646 3(15)	0.268 8(34)
C(5)	0.542 2(34)	0.808 5(21)	0.436 8(47)	C(20)	1.060 4(26)	0.608 5(15)	0.335 9(36)
O(5)	0.447 2(23)	0.795 6(13)	0.445 3(31)	C(21)	1.176 2(30)	0.641 4(19)	0.362 8(42)
C(6)	0.657 8(27)	0.942 1(16)	0.489 5(37)	C(22)	1.286 2(29)	0.606 8(18)	0.423 2(39)
O(6)	0.638 8(21)	1.002 2(13)	0.517 9(30)	C(23)	1.291 9(38)	0.548 1(21)	0.484 5(49)
C(7)	0.650 6(30)	0.527 6(18)	0.137 6(41)	C(24)	1.179 1(29)	0.518 3(18)	0.463 5(41)
O(7)	0.596 6(24)	0.489 5(14)	0.161 7(33)	C(25)	1.065 8(27)	0.549 7(16)	0.391 4(37)
C(8)	0.661 2(34)	0.565 3(20)	−0.113 4(48)	C(26)	0.546 5(24)	0.836 0(14)	0.171 8(33)
O(8)	0.607 1(25)	0.551 6(15)	−0.236 9(35)	C(27)	0.420 2(26)	0.873 1(16)	0.129 9(36)
C(9)	0.781 8(34)	0.702 8(20)	−0.081 2(48)	C(28)	0.412 8(29)	0.951 2(17)	0.153 3(39)
O(9)	0.733 2(24)	0.696 3(14)	−0.212 3(33)	C(29)	0.293 0(33)	0.989 4(21)	0.117 2(46)
C(10)	0.680 1(28)	0.654 6(16)	0.410 8(38)	C(30)	0.181 3(33)	0.945 7(19)	0.035 9(43)
O(10)	0.610 6(20)	0.629 3(12)	0.438 8(28)	C(31)	0.188 4(33)	0.865 8(20)	−0.001 6(45)
C(11)	0.855 0(29)	0.868 8(17)	0.104 8(41)	C(32)	0.308 0(29)	0.832 4(18)	0.053 1(41)
O(11)	0.935 3(20)	0.883 5(12)	0.064 2(28)				

Table 5 Fractional atomic coordinates for compound **4**

Atom	*x*	*y*	*z*
Os(1)	0.500 00	0.288 00(3)	0.250 00
Os(2)	0.401 71(3)	0.378 36(3)	0.322 07(4)
Os(3)	0.429 60(3)	0.375 61(3)	0.128 48(3)
Os(4)	0.322 77(3)	0.283 17(3)	0.203 23(4)
C(1)	0.500 0	0.192 6(9)	0.250 0
O(1)	0.500 0	0.133 8(7)	0.250 0
C(2)	0.324 2(9)	0.371 7(8)	0.411 1(10)
O(2)	0.274 4(8)	0.367 6(8)	0.465 5(9)
C(3)	0.396 3(13)	0.473 8(8)	0.335 4(11)
O(3)	0.392 3(11)	0.530 4(7)	0.340 2(12)
C(4)	0.383 9(10)	0.355 7(8)	0.004 8(12)
O(4)	0.352 8(7)	0.344 4(6)	−0.066 2(7)
C(5)	0.424 0(13)	0.469 4(7)	0.097 6(12)
O(5)	0.420 2(10)	0.524 3(6)	0.080 8(10)
C(6)	0.300 4(10)	0.220 8(9)	0.298 2(13)
O(6)	0.283 9(9)	0.184 7(8)	0.353 3(10)
C(7)	0.205 2(10)	0.289 3(7)	0.164 2(10)
O(7)	0.135 5(7)	0.293 5(6)	0.141 5(9)
C(8)	0.340 6(8)	0.210 6(8)	0.120 3(13)
O(8)	0.348 5(8)	0.168 2(8)	0.066 4(10)
C(9)	0.318 4(9)	0.389 4(6)	0.200 2(9)
C(10)	0.245 9(9)	0.431 9(7)	0.179 9(10)
C(11)	0.199 1(11)	0.455 3(9)	0.248 6(12)
C(12)	0.126 9(12)	0.494 5(10)	0.225 1(15)
C(13)	0.100 6(14)	0.511 1(10)	0.134 7(15)
C(14)	0.146 9(13)	0.485 8(10)	0.064 8(14)
C(15)	0.218 7(12)	0.448 5(9)	0.088 4(12)
C(16)	0.471 9(7)	0.302 3(6)	0.388 5(9)
C(17)	0.461 5(8)	0.264 0(7)	0.474 0(9)
C(18)	0.459 7(9)	0.192 8(7)	0.475 1(10)
C(19)	0.444 9(11)	0.155 8(8)	0.555 0(11)
C(20)	0.429 5(9)	0.190 2(8)	0.635 2(9)
C(21)	0.431 3(11)	0.260 3(9)	0.637 2(9)
C(22)	0.447 3(8)	0.296 1(7)	0.557 9(9)

$\Sigma[w^{\frac{1}{2}}(F_o - F_o)]/(w^{\frac{1}{2}}F_o) = 0.047\}$ for 2855 independent reflections $[F_o > 4\sigma(F_o)]$ collected in the range $2.5 < \theta < 25°$.

The structure was solved by direct methods; light atoms were located by subsequent Fourier difference syntheses. The Os atoms were allowed to vibrate anisotropically.

Crystal data for compound **4**. $C_{43}H_{20}O_{15}Os_7$, $M = 2108$, monoclinic, space group $C2/c$, $a = 15.953(5)$, $b = 19.816(4)$, $c = 14.383(2)$ Å, $\beta = 94.51(6)°$, $U = 4532.9$ Å^3, $Z = 4$, $D_c = 3.09$ g cm^{-3}, $F(000) = 3535$, μ(Mo-Kα) = 196.2, θ range 2.5–27°, final R 0.033 ($R' = 0.035$), for 2881 out of 4490 independent reflections $[F_o > 4\sigma(F_o)]$.

Details common to both species. Intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer by the ω–2θ scan method. An absorption correction was applied by the Walker and Stuart[9] method (correction range, 0.68–1.00 and 0.70–1.00 for **2** and **4**, respectively). The H atoms of the phenyl groups were added in calculated positions (C–H 1.08 Å) and refined 'riding' on their respective C atoms; a single isotropic thermal parameter was also refined [0.04(3) and 0.07(1) Å^2 for **2** and **4**, respectively]. The SHELX 76[10] package of crystallographic programs was used in all calculations. Fractional atomic coordinates for **2** and **4** are in Tables 4 and 5, respectively.

Additional material available in each case from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and remaining bond lengths and angles.

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