Synthesis and Structural Characterisation of Heptaosmium Alkyne Clusters†

Dario Braga,[a] **Fabrizia Grepioni,***[,a] **Brian F. G. Johnson,**[b] **Jack Lewis***[,c] **and Julie A. Lunniss**[c]
[a] *Dipartimento di Chimica 'G. Ciamician', University of Bologna, Via F. Selmi 2, 40126 Bologna, Italy*
[b] *Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK*
[c] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK*

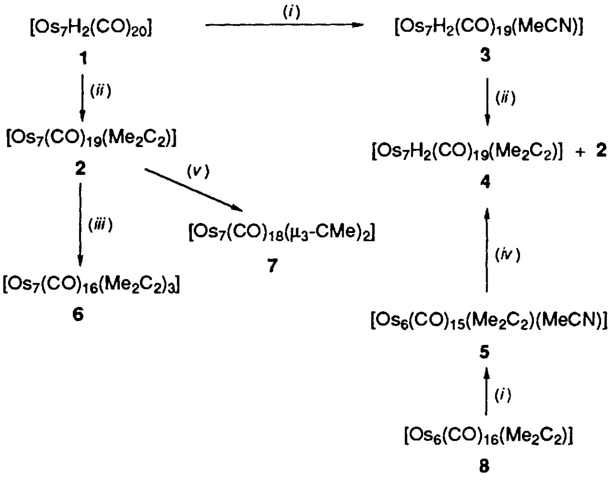
Reaction of the cluster $[Os_7H_2(CO)_{20}]$ **1** with Me_2C_2 in toluene at 90–100 °C gives $[Os_7(CO)_{19}(Me_2C_2)]$ **2** in moderate yield. The more reactive species $[Os_7H_2(CO)_{19}(MeCN)]$ **3** reacts with the same alkyne at room temperature to yield **2** together with $[Os_7H_2(CO)_{19}(Me_2C_2)]$ **4**. Cluster **4** is also the only product from the reaction of $[Os_6(CO)_{15}(Me_2C_2)(MeCN)]$ **5** with $[OsH_2(CO)_4]$. On further heating with excess of Me_2C_2, cluster **2** reacts to produce the species $[Os_7(CO)_{16}(Me_2C_2)_3]$ **6**. On prolonged heating, cluster **2** loses CO to form $[Os_7(CO)_{18}(\mu_3\text{-CMe})_2]$ **7**. Compounds **2**, **4** and **6** have been characterised on the basis of their ^1H NMR, IR, and electron-impact mass spectral data. The molecular structure of cluster **2** has been determined by a single-crystal X-ray diffraction study.

Over the past decade or so we have been concerned with an investigation into the nature of the products of the reactions of alkynes with osmium clusters having nuclearities ranging from three to six, in order to establish the nature of the bonding interaction of alkyne units with varying numbers of metal atoms.[1] Given the structural versatility shown by these cluster units, we were keen to extend these studies to larger metal clusters with seven or more metal atoms. In an earlier paper[2] we reported studies of the reaction of $[Os_7H_2(CO)_{20}]$ **1** with Ph_2C_2 in which a major feature was cleavage of the alkyne to generate μ_3- and μ_4-PhC fragments. We now report similar studies of the reactions of $[Os_7H_2(CO)_{20}]$ **1** or $[Os_7H_2(CO)_{19}(MeCN)]$ **3** with Me_2C_2 which, in contrast, yield products in which the integrity of the alkyne unit is predominantly retained, although under more forcing conditions cleavage to produce CMe fragments is also observed.

Results and Discussion

Reaction of compound **1** with excess of Me_2C_2 in toluene at 90–100 °C for 1–2 h affords **2** as major product. This brown material was identified initially on the basis of its spectroscopic and analytical data (see Table 1 and Experimental section) and fully characterised by single-crystal X-ray diffraction (see below). Prolonged thermolysis of either **1** or **2** with excess of Me_2C_2 produces a new green compound **6** in high yield. The highest peak recorded in the mass spectrum appears at m/z = 1954 corresponding to the molecular formula $[Os_7(CO)_{16}(Me_2C_2)_3]$. Further confirmation that six inequivalent methyl groups are present in this compound comes from its ^1H NMR spectrum in $CDCl_3$, which exhibits six singlets of equal intensity in the region δ 3.01–4.02 (see Table 1).

Very little can be said about the mechanism by which compound **6** is formed from **2**. It is likely that compound **6** retains the cluster structure of **2** (see below), though it is difficult to say how the three Me_2C_2 groups are bound to the metal framework. To date, no evidence for any intermediate containing two Me_2C_2 moieties has been found despite repeated efforts. The reaction of **3** with Me_2C_2 (see below) was monitored by following the ^1H NMR spectrum of the reaction mixture over the conversion period. No ^1H NMR signals, other than those due to either **2** or **6**, were observed at any time.



Scheme 1 Preparation of the new alkyne derivatives. (*i*) Me_2NO–MeCN; (*ii*) excess of Me_2C_2 in toluene at 90–100 °C; (*iii*) excess of Me_2C_2 over longer periods; (*iv*) $[OsH_2(CO)_4]$; (*v*) prolonged heating (≈3 d) in dichloromethane

The acetonitrile derivative $[Os_7H_2(CO)_{19}(MeCN)]$ **3** can be prepared readily from **1** (see Scheme 1). At room temperature this derivative readily reacts with excess of Me_2C_2 to produce compound **2** together with a second orange product **4**. Compound **4** displays a molecular ion in its mass spectrum at m/z = 1932 which corresponds to the molecular formula $[Os_7H_2(CO)_{19}(Me_2C_2)]$. The ^1H NMR spectrum, which exhibits three signals (all singlets) at δ 2.65, −18.91 and −22.33 of relative intensity 6:1:1, is consistent with this formulation. Variable-temperature ^1H NMR studies over the temperature range 25 °C to −85 °C showed no evidence for fluxionality, the spectrum remaining virtually unchanged. The same compound **4** has also been obtained by an alternative route from the hexaosmium cluster $[Os_6(CO)_{16}(Me_2C_2)]$ **8**. First, compound **8** was converted into $[Os_6(CO)_{15}(Me_2C_2)(MeCN)]$ **5** by reaction with Me_3NO in MeCN, and then to **4** by further

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Spectroscopic data for compounds **2**, **4**, **6** and **7**

Compound		Colour	IR[a] (ν_{CO}/cm^{-1})	Mass[b] (m/z)	¹H NMR[c]		
					δ	Integration	Assignment
2	$[Os_7(CO)_{19}(Me_2C_2)]$	Brown	2102vw, 2079ms, 2068vs, 2039s, 2018m, 1944vw	1930 (1930)	3.23(s)		Me
4	$[Os_7H_2(CO)_{19}(Me_2C_2)]$	Orange	2105w, 2083vs, 2053w, 2045ms, 2025m, 1985m	1932 (1932)	2.65(s) −18.91(s) −22.23(s)	6 1 1	2 × Me H H
6	$[Os_7(CO)_{16}(Me_2C_2)_3]$	Green	2089m, 2064vs, 2043s, 2027s, 2007m, 2000m, 1963w, 1946w	1954 (1954)	4.02(s) 3.81(s) 3.58(s) 3.32(s) 3.10(s) 3.01(s)	1 1 1 1 1 1	Me Me Me Me Me Me
7	$[Os_7(CO)_{18}(\mu_3\text{-}CMe)_2]$	Brown	2068vs, 2058s, 2055m, 2027s, 2011m, 1935w	1902 (1902)	4.45(s) 3.82(s)	1 1	Me Me

[a] In CH_2Cl_2. [b] Based on ^{192}Os; calculated value in parentheses, v = very, s = strong, m = medium, and w = weak. [c] In CD_2Cl_2.

Table 2 Relevant bond distances (Å) and angles (°) for compound **2**

Os(1)–Os(2)	2.611(1)	Os(2)–Os(5)	2.749(1)
Os(1)–Os(3)	2.846(2)	Os(2)–Os(7)	2.740(2)
Os(1)–Os(4)	2.821(1)	Os(3)–Os(4)	2.747(2)
Os(1)–Os(6)	2.762(2)	Os(3)–Os(5)	2.842(1)
Os(1)–Os(7)	2.740(2)	Os(3)–Os(6)	2.837(1)
Os(2)–Os(3)	2.850(1)	Os(4)–Os(5)	2.866(1)
Os(2)–Os(4)	2.804(2)	Os(4)–Os(6)	2.864(1)
Os(1)–C(20)	2.08(3)	C(20)–C(21)	1.39(3)
Os(2)–C(21)	2.14(3)	C(20)–C(22)	1.54(4)
Os(7)–C(20)	2.18(3)	C(21)–C(23)	1.53(4)
Os(7)–C(21)	2.14(3)	C–O	1.16(4) (average)
Os–C_{CO}	1.90(3) (average)		
C(22)–C(20)–C(21)	118(2)	Os–C–O	175(3) (average)
C(23)–C(21)–C(20)	124(3)		

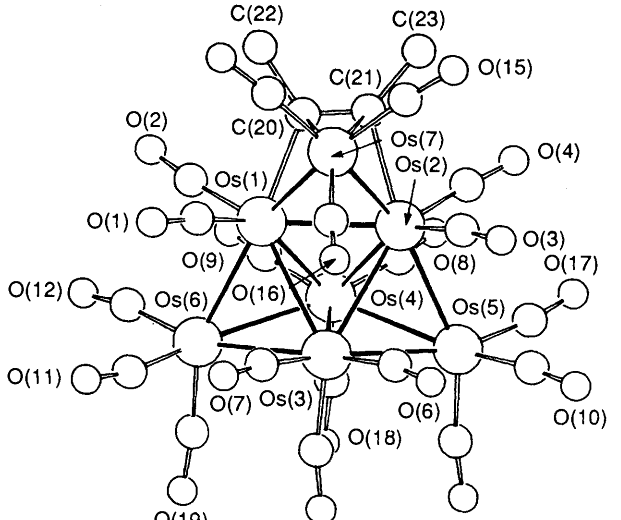


Fig. 1 Molecular structure of $[Os_7(CO)_{19}(\mu_3{:}\eta^2\text{-}Me_2C_2)]$ **2**. The C atoms of the CO groups bear the same numbering as the corresponding O atoms; H atoms of the methyl groups are omitted for clarity

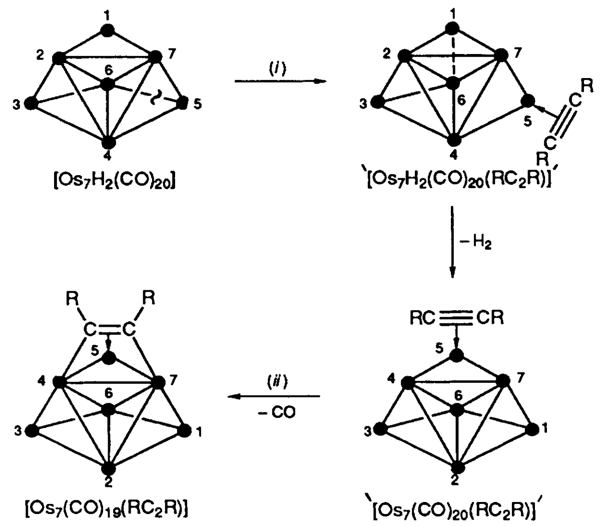
reaction with the monomeric dihydrido species $[OsH_2(CO)_4]$. In solution, cluster **4** readily ejects H_2 on heating to form cluster **2**. This process may be reversed by the sequential reaction of **2** first with $NaBH_4$ in tetrahydrofuran (thf) to form the anion $[Os_7H(CO)_{19}(Me_2C_2)]^-$, which was not isolated, and then with HBF_4 in CH_2Cl_2 to yield the dihydride **4**.

On heating cluster **2** over a prolonged period (≈3 d) a further reaction occurs: carbon monoxide is evolved and a new brown cluster $[Os_7(CO)_{18}(\mu_3\text{-}CMe)_2]$ **7** is produced. This cluster was identified by the usual spectroscopic techniques (see Table 1) and, on the basis of the spectroscopic data, it would appear to possess the same structure as that of the previously reported[2] cluster $[Os_7(CO)_{18}(\mu\text{-}CPh)_2]$. Thus, the metal polyhedron in **7** is the familiar monocapped octahedron, a geometry also shared by $[Os_7(CO)_{21}]$[3a] and $[Os_7(CO)_{20}\{P(OMe)_3\}]$.[3b] It would appear that in this reaction the ejection of CO produces an unsaturated intermediate, which causes cleavage of the C–C bond to generate the new 'saturated' compound **7**.

The Structure of Compound **2**.—The molecular structure of compound **2** (see Fig. 1) was determined by single-crystal X-ray diffraction. Relevant bond distances and angles are listed in Table 2. The molecule possesses an Os_7 metal framework consisting of three fused tetrahedra which bear an extra Os atom [Os(7)] linked to the Os_6 core by two Os–Os bonds. The resulting outer Os_3 triangle forms angles of 114.2 and 169.2° with the two contiguous triangular faces of the Os_6 core. This is the main structural difference between the metal-atom polyhedron in **2** and in the parent species $[Os_7H_2(CO)_{20}]$ **1**[4a] where the outer 'flap' lies symmetrically in the molecular mirror plane comprising four Os atoms of the Os_6 core. Metal–metal bond lengths [range 2.611(1)–2.866(1) Å], though conforming to a pattern similar to that observed in **1** with the shortest bond μ-bridged by the external Os atom [2.611(1), 2.665(4) Å in **2** and **1**, respectively], show slightly smaller mean values both within the Os_6 core [2.800(1) *versus* 2.842(4) Å] and within the outer 'flap' [2.740(1) *versus* 2.800(4) Å]. This general shrinkage of the metal framework can be ascribed to the removal of the two H(hydride) atoms from **1**, whose presence is likely to cause metal–metal bond lengthening (no unambiguous location of the two H atoms was, however, possible for this species).

The Me_2C_2 ligand is found $\mu_3{:}\eta^2$-bonded to the outer flap, thus being responsible for the mentioned displacement of the μ_2-Os atom. The idealised molecular symmetry is reduced, with respect to **1**, to C_s-m with the mirror plane bisecting both the Os_6 core and the Me_2C_2 system and including Os(7). The Me_2C_2 plane forms an angle of 54.9° with the bridged Os_3 triangle (the outer flap), and almost comprises Os(1) and Os(2) (mean elevation *ca.* 0.5 Å).

On the basis of electron counting the organic ligand is required to supply four electrons to the cluster orbitals having formally replaced one CO group [on Os(7)] and the two H



Scheme 2 Proposed mechanism for the formation of [Os$_7$(CO)$_{19}$(Me$_2$C$_2$)]. (*i*) RC$_2$R (R = Me); (*ii*) alkyne rearrangement

(hydride) atoms with respect to **1**. The bonding of the Me$_2$C$_2$ ligand can be formally depicted as occurring *via* two σ interactions with the Os$_6$ core [mean Os–C 2.11(3) Å] and one π interaction with the outer Os atom [mean Os–C 2.18(3) Å] which has undergone CO loss. The Me–C–C, Me–C and C=C structural parameters [mean 121(1)°, mean 1.53(4), and 1.39(3) Å, respectively] conform to a sp^2 bonding system and appear to be in agreement with the values found in related species containing other μ$_3$:η ligands such as [Os$_6$C(CO)$_{16}$(MeCCMe)][4b] [Me–C 1.57(3), C=C 1.36(2) Å], [Os$_3$(CO)$_{10}$(PhCCPh)][5] [Ph–C 1.50(1), C=C 1.44(1) Å] and [Os$_6$(CO)$_{16}$(MeCCEt)][6] [C–C 1.54(7), C=C 1.35(6) Å].

It is worth pointing out that the Me$_2$C$_2$ ligand co-ordination involves the most electron-rich Os atom in **2** [Os(7)] and occurs with minimum perturbation of the Os$_6$ core by taking advantage of the considerable structural flexibility of the outer 'flap'.

Conclusion

Formally, the conversion of cluster **2** into cluster **7** does not result in a change in the polyhedral electron count of 98 electrons; however, it does entail a reorganisation of the Os$_7$ metallic framework from an edge-bridged, bicapped tetrahedron to a monocapped octahedron. A possible mechanistic pathway is shown in Scheme 2.

In summary, the reaction of the heptanuclear cluster with Me$_2$C$_2$ under a variety of conditions produces the series of alkyne clusters [Os$_7$(CO)$_{19}$(Me$_2$C$_2$)], [Os$_7$H$_2$(CO)$_{19}$(Me$_2$C$_2$)], [Os$_7$(CO)$_{16}$(Me$_2$C$_2$)$_3$] and [Os$_7$(CO)$_{18}$(μ$_3$-CMe)$_2$]. Although the mechanisms by which these clusters undergo interconversion have not been completely established, the polyhedral rearrangements they undergo may be simply explained.

Experimental

All reactions were performed under dry nitrogen using conventional vacuum-line techniques. Solvents were freshly distilled under nitrogen and over the appropriate drying agent before use. Dimethylacetylene was of commercial grade and used without further purification. The compound Me$_3$NO was freshly sublimed before use. The heptaosmium clusters [Os$_7$H$_2$(CO)$_{20}$] and [Os$_7$H$_2$(CO)$_{19}$(MeCN)] were prepared by the established literature methods as were [Os$_6$(CO)$_{15}$(Me$_2$C$_2$)(MeCN)] and [OsH$_2$(CO)$_4$].

Preparative TLC was performed using pre-coated Merck thin-layer silica plates (0.25 mm, Kieselgel 60F$_{254}$).

Solution IR spectra were recorded on a Perkin-Elmer FTIR spectrometer, mass spectra on an AEI MS 12 spectrometer, and ^{1}H NMR spectra on a Bruker WM 250 MHz spectrometer, chemical shifts being recorded relative to SiMe$_4$. Microanalyses were carried out in The University Chemical Laboratory, Cambridge.

Reaction of [Os$_7$H$_2$(CO)$_{20}$] *with* Me$_2$C$_2$.—The cluster **1** (20 mg, 0.011 mmol) and Me$_2$C$_2$ (3 cm^3) were heated in toluene (40 cm^3) at 90–100 °C for 3 h. After removing the solvent under vacuum, the products were redissolved in CH$_2$Cl$_2$ and separated by TLC using CH$_2$Cl$_2$–hexane (15:85) as eluent. Product **2** (20% yield) was crystallised from tetrahydrofuran (Found: C, 14.95; H, 0.55. Calc.: C, 14.40; H, 0.30%).

Reaction of Compound **1** *or* **3** *with Excess of* Me$_2$C$_2$.—The cluster **3** (40 mg, 0.022 mmol) was dissolved in CH$_2$Cl$_2$ (25 cm^3) and a large excess of Me$_2$C$_2$ (3 cm^3) added. The reaction mixture was stirred for 28 h under nitrogen and the solvent then removed under vacuum. After separation by TLC using CH$_2$Cl$_2$–hexane (15:85), brown **2** (15% yield) and orange **4** (50% yield) were separated. Cluster **1** (20 mg, 0.011 mmol) was dissolved in toluene (40 cm^3) and treated with excess of Me$_2$C$_2$ (6 cm^3) at 90–100 °C for 12 h. Removal of the solvent under vacuum followed by TLC on silica gave cluster **6** (23%) and some unreacted **1**.

Reaction of Compound **2** *with* (*i*) NaBH$_4$ *and then* (*ii*) HBF$_4$.—Cluster **2** (10 mg, 0.005 mmol) was dissolved in tetrahydrofuran (20 cm^3) and the solution treated with NaBH$_4$ (0.010 mmol) with stirring for $\approx$10 min. The solvent was removed under vacuum and the brown residue {presumably Na[Os$_7$H(CO)$_{19}$(Me$_2$C$_2$)]} redissolved in CH$_2$Cl$_2$ (20 cm^3). The acid HBF$_4$ (two drops) was added to the solution which was stirred for 10 min under nitrogen. The solvent was then removed under vacuum. After TLC using CH$_2$Cl$_2$–hexane (15:85) as eluent green crystals of cluster **4** were obtained.

Preparation of [Os$_7$(CO)$_{18}$(μ$_3$-CMe)$_2$] **7** *from the Thermolysis of* **2**.—Cluster **2** (10 mg, 0.005 mmol) was dissolved in dichloromethane (20 cm^3) and the solution heated at 60 °C under nitrogen for 3 h. After separation by TLC using CH$_2$Cl$_2$–hexane, the brown product **7** (18% yield) was separated and characterised (Found: C, 13.8; H, 0.50. Calc.: C, 13.9; H, 0.55%).

Crystallography.—*Crystal data.* C$_{23}$H$_6$O$_{19}$Os$_7$ **2**, M = 1917.7, monoclinic, space group $C2/c$, a = 37.99(1), b = 11.514(2), c = 16.68(1) Å, β = 107.25(4)°, U = 6986.1 Å^3, $F(000)$ = 6580, Z = 8, D_c = 3.65 g cm^{-3} Mo-Kα radiation, λ = 0.710 69 Å, μ(Mo-Kα) = 245.13 cm^{-1}, R = 0.056 (R' = 0.059) for 3710 independent reflections [$I_o > 2.5\sigma(I_o)$] collected in the range $2.5 < \theta < 25°$, crystal dimensions 0.11 × 0.15 × 0.14 mm, weighting scheme employed $w = k/[\sigma(F) + |g|F^2]$.

An absorption correction was applied by the method of Walker and Stuart[7a] (correction range 0.3–1.0). The structure was solved by direct methods which afforded the positions of the Os atoms. Light atoms were located by subsequent Fourier syntheses. The H atoms of the methyl groups were added in calculated positions (C–H 1.08 Å) and refined 'riding' on their corresponding C atoms; Os atoms were allowed to vibrate anisotropically.[7b] Attempts to apply full anisotropy to all light atoms yielded several non-positive-definite thermal parameters, probably because of an unsatisfactory absorption correction caused by the large transmission range (see above). The C and O atoms were therefore treated isotropically. The final Fourier maps showed the presence of a large residual peak which was treated as a small fraction of an Os atom [Os(8)] (<10%) being at reasonable distances from the neighbouring

Table 3 Atomic coordinates for compound **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.341 57(2)	0.284 38(9)	0.367 92(7)	C(10)	0.444 4(8)	0.074 8(31)	0.666 8(23)
Os(2)	0.401 45(2)	0.287 49(9)	0.495 16(7)	O(10)	0.450 8(7)	0.082 1(25)	0.742 1(17)
Os(3)	0.352 79(2)	0.095 50(10)	0.482 84(7)	C(11)	0.267 5(8)	0.061 4(30)	0.300 1(21)
Os(4)	0.395 12(2)	0.111 71(9)	0.375 35(6)	O(11)	0.236 4(7)	0.070 5(25)	0.292 4(17)
Os(5)	0.430 49(3)	0.073 16(10)	0.550 54(7)	C(12)	0.305 8(8)	0.078 3(29)	0.190 1(21)
Os(6)	0.317 85(3)	0.065 30(10)	0.308 49(7)	O(12)	0.299 7(5)	0.077 4(19)	0.116 4(14)
Os(7)	0.349 38(3)	0.455 64(11)	0.485 94(8)	C(13)	0.311 6(10)	0.569 0(37)	0.441 9(25)
C(1)	0.292 8(7)	0.322 2(26)	0.360 4(18)	O(13)	0.287 8(7)	0.627 4(27)	0.405 2(18)
O(1)	0.261 3(6)	0.341 7(22)	0.353 4(14)	C(14)	0.433 4(9)	−0.091 2(34)	0.553 9(23)
C(2)	0.328 8(9)	0.313 2(33)	0.253 1(23)	O(14)	0.436 0(6)	−0.190 5(24)	0.556 2(16)
O(2)	0.322 2(7)	0.336 0(25)	0.181 9(18)	C(15)	0.373 9(9)	0.558 6(34)	0.568 1(23)
C(3)	0.408 7(7)	0.328 8(29)	0.604 1(20)	O(15)	0.391 1(7)	0.625 7(28)	0.620 0(19)
O(3)	0.412 1(6)	0.337 2(23)	0.678 4(16)	C(16)	0.322 4(8)	0.388 9(29)	0.560 3(20)
C(4)	0.452 5(7)	0.322 6(27)	0.506 9(19)	O(16)	0.309 3(7)	0.351 0(26)	0.600 6(17)
O(4)	0.482 7(6)	0.348 3(22)	0.516 7(14)	C(17)	0.482 4(8)	0.098 4(29)	0.559 4(20)
C(5)	0.350 2(7)	−0.069 2(28)	0.489 1(19)	O(17)	0.512 1(5)	0.104 4(20)	0.565 3(14)
O(5)	0.348 1(6)	−0.169 4(22)	0.490 6(14)	C(18)	0.399 9(7)	−0.048 9(28)	0.366 7(19)
C(6)	0.362 3(7)	0.117 6(26)	0.603 9(18)	O(18)	0.402 5(5)	−0.156 3(20)	0.359 9(14)
O(6)	0.364 0(6)	0.122 2(21)	0.672 4(15)	C(19)	0.317 9(7)	−0.100 7(26)	0.302 3(18)
C(7)	0.302 1(7)	0.120 4(26)	0.475 3(18)	O(19)	0.316 1(7)	−0.197 4(26)	0.290 0(18)
O(7)	0.272 8(6)	0.123 0(22)	0.481 5(15)	C(20)	0.365 7(8)	0.447 5(23)	0.371 2(17)
C(8)	0.444 9(8)	0.142 5(30)	0.380 0(21)	C(21)	0.397 3(6)	0.455 8(22)	0.439 5(18)
O(8)	0.475 0(5)	0.156 1(20)	0.375 7(13)	C(22)	0.358 1(8)	0.545 8(25)	0.305 3(19)
C(9)	0.385 7(7)	0.139 1(28)	0.255 0(20)	C(23)	0.426 9(8)	0.548 4(27)	0.447 1(24)
O(9)	0.383 5(6)	0.143 3(22)	0.187 5(15)	Os(8)*	0.387 7(5)	0.459 9(17)	0.382 2(13)

* See crystallography section for discussion of disorder.

Os atom [mean Os–Os 2.63(2) Å]. The metal framework of the resulting disorder model may be rationalised by assuming formation and cocrystallisation of a small quantity of the neutral [$Os_8H_2(CO)_{22}$], which is likely to possess the same metal core as the anionic species [$Os_8H(CO)_{22}$]$^-$.[8] Fractional atomic coordinates for compound **2** are reported in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

Financial support by Ministero dell'Universita' e della Ricerca Scientifica e Tecnologica (Italy) is acknowledged. D. B., F. G. and B. F. G. J. thank NATO for a collaborative research grant.

References

1 M. D. Vargas and J. N. Nicholls, *Adv. Inorg. Chem. Radiochem.*, 1986, **30**, 123.

2 D. Braga, F. Grepioni, B. F. G. Johnson, J. Lewis and J. A. Lunniss, *J. Chem. Soc., Dalton Trans.*, 1991, 2223.

3 (*a*) C. R. Eady, B. F. G. Johnson, R. Mason , H. B. Hitchcock and K. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1977, 385; (*b*) B. F. G. Johnson, J. Lewis, J. A. Lunniss, D. Braga and F. Grepioni, *J. Organomet. Chem.*, 1991, **401**, C46.

4 (*a*) E. J. Ditzel, H. D. Holden, B. F. G. Johnson, J. Lewis, A. Saunders and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1982, 1373; (*b*) C. R. Eady, J. M. Fernandez, B. F. G. Johnson, J. Lewis, P. R. Raithby and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 1978, 421.

5 C. G. Pierpont, *Inorg. Chem.*, 1977, **16**, 636.

6 M. P. Gomez-Sal, B. F. G. Johnson, R. A. Kamarudin, J. Lewis and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1985, 1622.

7 (*a*) N. Walker and D. Stuart, *Acta Crystallogr., Sect. B*, 1983, **39**, 158; (*b*) G. M. Sheldrick, SHELX 76, University of Cambridge, 1976.

8 B. F. G. Johnson, J. Lewis, W. J. H. Nelson, M. D. Vargas, D. Braga, K. Henrick and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1984, 2151.

Received 5*th July* 1991; *Paper* 1/03381F