Reaction of $[Os_5(CO)_{19}]$ with Acetylenes: the *X*-Ray Crystal Structure of $[Os_5(CO)_{17}(HCCH)]$ [†]

Brian F. G. Johnson, Jack Lewis,* Paul R. Raithby, and Maria J. Rosales
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The carbonyl cluster $[Os_5(CO)_{19}]$ reacts with acetylene in heptane, under reflux, to give $[Os_5(CO)_{17}(HCCH)]$ (1) and the known complex $[Os_4(CO)_{12}(HCCH)]$ (2) as the major products. The cluster (1) crystallises in the monoclinic space group $P2_1/c$ with a = 20.255(11), b = 9.391(7), c = 28.227(15) Å, β = 91.62(3)°, and Z = 8. The structure was solved by a combination of direct methods and Fourier difference syntheses, and refined by blocked-cascade least squares to R = 0.060 and R' = 0.060 for 5 496 unique diffractometer data. In the two independent, but structurally similar molecules the Os atom skeleton consists of two triangles sharing a common vertex to give the ' bow-tie ' conformation. The acetylene ligand caps one of the triangles, and is σ-bonded to the Os atom involved in bonding in the other triangle and to one of the peripheral Os atoms, and π-bonded to the other peripheral metal atom. The complex $[Os_5(CO)_{19}]$ also reacts with mono- and di-substituted acetylenes. With HCCR (R = Me or Ph), in heptane, the major products were characterised as $[Os_5(CO)_{17}(HCCR)]$ [R = Me (3) or Ph (4)] and $[Os_4(CO)_{12}(HCCR)]$ [R = Me (5) or Ph (6)]. With R^1CCR^2 [$R^1 = R^2$ = Ph or MeO(O)C] decarbonylation to $[Os_5(CO)_{16}]$ occurred before there was any reaction with the acetylene.

The novel pentanuclear binary carbonyl $[Os_5(CO)_{19}]$ has recently been obtained by the reaction of $[Os_6(CO)_{18}]$ with CO, in heptane, under the specific reaction conditions of 90 atm (*ca.* 9.12×10^6 Pa), 160 °C, and 1.5 h.[1] This cluster exhibits an open ' bow-tie ' metal geometry where two Os_3 triangles share a common vertex.[2] This is in marked contrast to the previously known pentanuclear osmium binary carbonyl $[Os_5(CO)_{16}]$, where the metal atoms display a closed trigonal-bipyramidal geometry.[3] The latter complex has been obtained in low yields from the pyrolysis of $[Os_3(CO)_{12}]$,[4] and appears to be fairly unreactive under moderate conditions. Hitherto, most of the chemistry of Os_5 clusters has developed from the hydrido-complex $[Os_5H_2(CO)_{15}]$.[5] It is hoped that $[Os_5(CO)_{19}]$ will more readily undergo substitution and addition reactions. In view of the current interest in the interactions between unsaturated organic molecules and clusters we have treated this ' bow-tie ' cluster with acetylenes, and we now report the results of these reactions, and the molecular structure of $[Os_5(CO)_{17}(HCCH)]$.

Results and Discussion

The reaction of $[Os_5(CO)_{19}]$ with free acetylene (HC≡CH) in refluxing heptane for 0.5 h results in the conversion of 80% of the starting material. The major products were isolated from the reaction mixture, and were purified by t.l.c. The two complexes were initially characterised by i.r. and mass spectroscopy as $[Os_5(CO)_{17}(HCCH)]$ (1) and the known[6] complex $[Os_4(CO)_{12}(HCCH)]$ (2) (Table 1).

With longer reaction times the only product isolated from the reaction mixture was (2). This implies that under the reaction conditions the pentanuclear cluster (1) loses an $Os(CO)_5$ fragment to give the tetranuclear cluster. In fact, with the $[Os_5(CO)_{19}]$–HCCH system this transformation is rapid, and when there is still some unreacted $[Os_5(CO)_{19}]$ the product $[Os_5(CO)_{17}(HCCH)]$ (1) starts to break down to $[Os_4(CO)_{12}(HCCH)]$ (2). The reaction was closely monitored by i.r. spectroscopy in order to stop the reaction so as to obtain the maximum yield of (1), and it was observed that the two reactions are simultaneous. The degradation of solutions of the pentanuclear cluster also takes place at room temperature and at −20 °C, and complete decomposition occurs after several weeks.

The cluster $[Os_4(CO)_{12}(HCCH)]$ (2) has been obtained previously from the reaction of $[Os_3(CO)_{12}]$ with ethylene.[6] In this complex the four Os atoms adopt a ' butterfly ' configuration with three terminal carbonyl groups associated with each metal. The acetylenic ligand lies over the ' butterfly ' with the organic C–C bond parallel to the Os–Os ' hinge ' bond. This acetylenic fragment is π-bonded to the two ' wing-tip ' metal atoms and σ-bound to the ' hinge ' atoms.

With monosubstituted acetylenes, HCCR (R = Me or Ph), the reaction of $[Os_5(CO)_{19}]$ in refluxing heptane led to total conversion of the starting material after 1 h. The main products were characterised spectroscopically (Table 1) as $[Os_5(CO)_{17}(HCCR)]$ [R = Me (3) or Ph (4)] and $[Os_4(CO)_{12}(HCCR)]$ [R = Me (5) or Ph (6)]. The latter complex, as in the case of the reaction with acetylene, may be considered as a decomposition product of $[Os_5(CO)_{17}(HCCR)]$ formed by the loss of an $Os(CO)_5$ molecule. The rate of transformation of the pentanuclear to the tetranuclear cluster is considerably faster for the phenyl derivative (4) than for the methyl derivative (3). It is, therefore, possible that steric factors may be important in the stability of the pentanuclear complexes relative to the loss of $Os(CO)_5$. An examination of the i.r. carbonyl-stretching frequencies (Table 1) for the pentanuclear clusters indicates that there is a significant difference in position and intensity of the bands for (1) compared to those for (3) and (4). This difference is consistent with the replacement of one of the α-acetylenic hydrogens by a methyl or phenyl group, thus reducing the molecular symmetry. However, this change in symmetry may indicate a change in bonding mode of the acetylenic ligand. A variety of bonding modes for a monosubstituted acetylene have been observed in cluster complexes of the iron triad,[7,8] ranging from the ' end-on ' co-ordination of one acetylenic carbon to a metal–metal edge or a trimetal unit to the symmetric π interaction observed in a number of tetrametal butterfly complexes.

The reaction of $[Os_5(CO)_{19}]$, in refluxing octane, with the

---

[†] 1-[Bis(tetracarbonylosmio)(*Os*–*Os*)]-μ_3-vinylene-C^1(Os^1)-C^2(Os^2)C^{1-2}(Os^3)-*cyclo*-tris(tricarbonylosmium)(5*Os*–*Os*).

Supplementary data available (No. SUP 23728, 42 pp.): thermal parameters, complete bond lengths and angles, least-squares planes, structure factors. See Instructions for Authors, Section 4.0, *J. Chem. Soc., Dalton Trans.*, 1983, Issue 3, p. xvii.

Table 1. Spectroscopic data for the products of the reaction between [$Os_5(CO)_{19}$] and acetylenes

Compound	I.r., $\tilde{\nu}_{CO}/cm^{-1}$ (CH_2Cl_2 solution)	Mass spectrum, m/e (M^+ ^{192}Os)
(1) [$Os_5(CO)_{17}(HCCH)$]	2 127w, 2 076m, 2 051s, 2 007w	1 482[a]
(2) [$Os_4(CO)_{12}(HCCH)$]	2 074s, 2 047m, 2 037m, 2 013w[b]	1 123
(3) [$Os_5(CO)_{17}(HCCMe)$]	2 108w, 2 069s, 2 056w, 2 035m, 1 999 (sh)	1 470
(4) [$Os_5(CO)_{17}(HCCPh)$]	2 109w, 2 072s, 2 049w, 2 037m, 1 999 (sh)	1 530
(5) [$Os_4(CO)_{12}(HCCMe)$]	2 073s, 2 045m, 2 036m, 2 011w	1 140
(6) [$Os_4(CO)_{12}(HCCPh)$]	2 073s, 2 048m, 2 037w, 2 013w	1 200

[a] The highest peak corresponds to $Os_5(CO)_{18}(HCCH)$. [b] The carbonyl-stretching frequencies are in close agreement with the value reported for this compound in ref. 6.

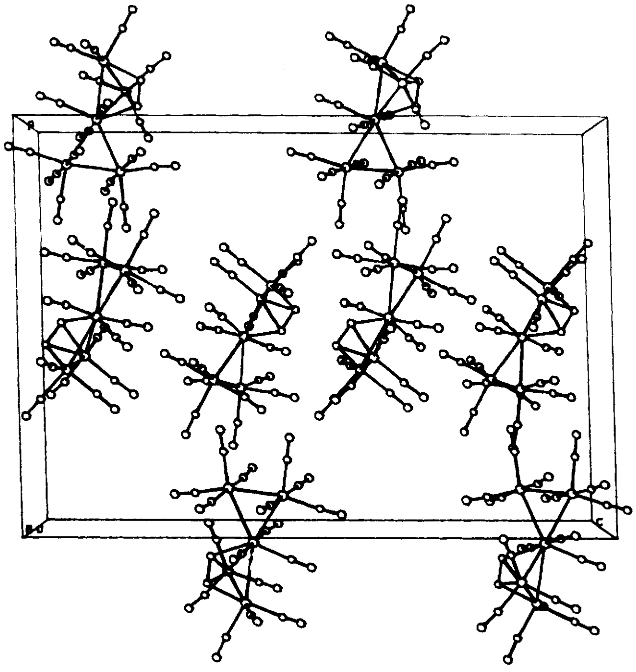

Figure 1. The unit-cell contents for [$Os_5(CO)_{17}(HCCH)$] viewed down the crystallographic *b* axis

disubstituted acetylenes PhC≡CPh and MeO(O)C≡C(O)OMe, in 1 : 10 and 1 : 1 cluster : acetylene ratios, did not result in the formation of cluster acetylene products. In both cases, the predominant reaction was the elimination of carbon monoxide with the resultant production of [$Os_5(CO)_{16}$]. In heptane the decarbonylation was slower but still occurred before any reaction with the alkyne. Previously, [$Os_5(CO)_{19}$] has been shown to lose CO readily under similar reaction conditions to give [$Os_5(CO)_{16}$].[2] Once formed, [$Os_5(CO)_{16}$] reacts with diphenylacetylene to give [$Os_5(CO)_{13}(PhCCPh)_2$] as the major product, which has also been obtained from the reaction of [$Os_5H_2(CO)_{15}$] with PhC≡CPh.[8]

The mechanism for the attack of acetylenes upon the [$Os_5(CO)_{19}$] cluster is not known but, from the results reported above, it is possible that the presence of a hydrogen atom α to at least one of the acetylenic carbon atoms aids the reaction. Although electronic factors are probably of major importance, steric factors also play a role. In this context it is interesting to note that there is no reaction between the phosphite-substituted complex [$Os_5(CO)_{16}\{P(OMe)_3\}_3$] and acetylene after 3 h.

Although spectroscopic evidence for the nature of the acetylenic cluster complexes gave an idea of their molecular formula there was little evidence as to the geometry of the metal framework or to the mode of bonding of the acetylenic unit. In order to establish the molecular geometry of the acetylene cluster [$Os_5(CO)_{17}(HCCH)$] a single-crystal *X*-ray analysis was undertaken.

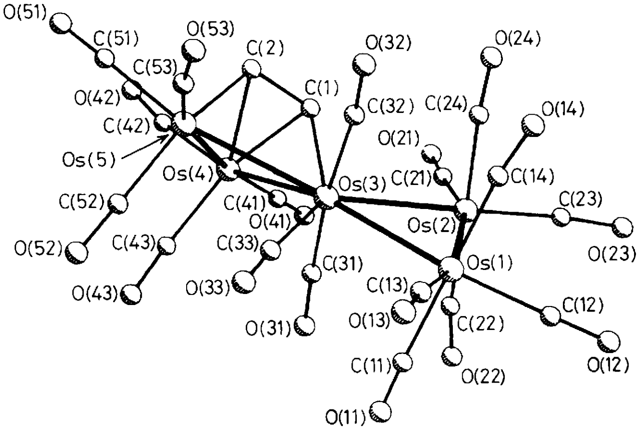

Figure 2. A single molecule of [$Os_5(CO)_{17}(HCCH)$]

There are two independent but structurally equivalent molecules in the asymmetric unit; the unit-cell contents are illustrated in Figure 1. The molecules are separated by normal van der Waals distances, and there are no abnormally short intermolecular contacts. One molecule of [$Os_5(CO)_{17}(HCCH)$] is shown in Figure 2, together with the atom numbering scheme adopted, while selected interatomic bond lengths and bond angles are presented in Table 2.

The 'bow-tie' arrangement of the metal atoms observed in the parent [$Os_5(CO)_{19}$] cluster[2] is retained in this acetylene derivative, [$Os_5(CO)_{17}(HCCH)$] (1). The acetylene ligand sits over the Os(3)Os(4)Os(5) [Os(8)Os(9)Os(10) in the second molecule] triangle, and is σ-bonded to Os(3)[Os(8)] and Os(5)[Os(10)] and π-bonded to Os(4)[Os(9)]. A similar mode of bonding of the acetylenic ligand has been observed for the diphenylacetylene group in the trinuclear cluster [$Os_3(CO)_{10}(PhCCPh)$].[9,10] Indeed the two structures show some marked similarities, and if the [$Os_3(CO)_{10}(RCCR)$] formula is re-written as [$Os_3(CO)_9(RCCR)L$] (where L represents an equatorial CO group on an Os atom which is σ-bonded to the acetylene) replacement of L by a '$(OC)_4Os$–$Os(CO)_4$' unit gives the [$Os_5(CO)_{17}(RCCR)$] structure. The acetylenic C–C bond in the trinuclear cluster, at 1.439(10) Å,[10] is slightly longer than the average value of 1.36(5) Å for the equivalent bonds in (1), but the latter distance is similar to the value of 1.39(4) Å for the acetylenic bond capping an Os_3 triangle in another Os_5 cluster, [$Os_5(CO)_{13}(PhCCPh)_2$].[8] In all three clusters there is a significant increase in the C–C bond distance over that in the free acetylene which is consistent with the donation of π-electron density to the cluster, and all formally act as four-electron donors. The Os–C linkages in complex (1)

Table 2. Selected bond parameters for $[Os_5(CO)_{17}(HCCH)]$ (1); distances in Å, angles in °

Molecule 1		Molecule 2		Molecule 1		Molecule 2	
Os(1)–Os(2)	2.833(3)	Os(6)–Os(7)	2.832(2)	Os(3)–C(1)	2.23(3)	Os(8)–C(3)	2.19(3)
Os(1)–Os(3)	2.933(3)	Os(6)–Os(8)	2.938(3)	Os(4)–C(1)	2.13(3)	Os(9)–C(3)	2.24(3)
Os(2)–Os(3)	2.921(3)	Os(7)–Os(8)	2.937(3)	Os(4)–C(2)	2.29(3)	Os(9)–C(4)	2.30(4)
Os(3)–Os(4)	2.908(3)	Os(8)–Os(9)	2.888(3)	Os(5)–C(2)	2.09(3)	Os(10)–C(4)	2.12(3)
Os(3)–Os(5)	2.957(3)	Os(8)–Os(10)	2.976(3)	C(1)–C(2)	1.39(4)	C(3)–C(4)	1.33(4)
Os(4)–Os(5)	2.715(3)	Os(9)–Os(10)	2.718(3)				

Molecule 1		Molecule 2		Molecule 1		Molecule 2	
Os(2)–Os(1)–Os(3)	60.8(1)	Os(7)–Os(6)–Os(8)	61.2(1)	Os(1)–Os(3)–C(1)	138.2(8)	Os(6)–Os(8)–C(3)	137.1(8)
Os(1)–Os(2)–Os(3)	61.3(1)	Os(6)–Os(7)–Os(8)	61.2(1)	Os(2)–Os(3)–C(1)	86.7(8)	Os(7)–Os(8)–C(3)	84.0(8)
Os(1)–Os(3)–Os(2)	57.9(1)	Os(6)–Os(8)–Os(7)	57.6(1)	Os(4)–Os(3)–C(1)	46.7(8)	Os(9)–Os(8)–C(3)	50.0(8)
Os(1)–Os(3)–Os(4)	158.9(1)	Os(6)–Os(8)–Os(9)	154.5(1)	Os(5)–Os(3)–C(1)	66.8(8)	Os(10)–Os(8)–C(3)	64.9(8)
Os(2)–Os(3)–Os(4)	108.9(1)	Os(7)–Os(8)–Os(9)	108.6(1)	Os(3)–Os(4)–C(1)	49.6(8)	Os(8)–Os(9)–C(3)	48.5(7)
Os(1)–Os(3)–Os(5)	143.5(1)	Os(6)–Os(8)–Os(10)	147.4(1)	Os(5)–Os(4)–C(1)	72.9(9)	Os(10)–Os(9)–C(3)	69.4(8)
Os(2)–Os(3)–Os(5)	153.3(1)	Os(7)–Os(8)–Os(10)	148.5(1)	Os(3)–Os(4)–C(2)	68.8(8)	Os(8)–Os(9)–C(4)	69.8(8)
Os(4)–Os(3)–Os(5)	55.1(1)	Os(9)–Os(8)–Os(10)	55.2(1)	Os(5)–Os(4)–C(2)	48.5(9)	Os(10)–Os(9)–C(4)	49.1(8)
Os(3)–Os(4)–Os(5)	63.4(1)	Os(8)–Os(9)–Os(10)	64.1(1)	Os(3)–Os(5)–C(2)	69.9(8)	Os(8)–Os(10)–C(4)	70.1(8)
Os(3)–Os(5)–Os(4)	61.5(1)	Os(8)–Os(10)–Os(9)	60.7(1)	Os(4)–Os(5)–C(2)	55.0(9)	Os(9)–Os(10)–C(4)	55.2(11)

are similar to the Os–C σ bonds [2.070(9) and 2.182(8) Å] and the Os–C π interactions [2.188(8) and 2.293(9) Å] in $[Os_3(CO)_{10}(PhCCPh)]$.[10] A projection of the acetylenic C–C bond makes an angle of 8.9° with an extension of the Os(3)–Os(5) bond, showing a slight twist of the acetylene relative to the metal framework. The introduction of the acetylene into the ' bow-tie ' cluster is concomitant with an electron imbalance in the capped triangle; Os(3)[Os(8)] is formally electron-rich with 19 electrons while Os(5)[Os(10)] has only 17 electrons. This imbalance may be partially negated by the short Os(4)–Os(5)[Os(9)–Os(10)] bond, since a bond of similar length [2.771(1) Å] in $[Os_3(CO)_{10}(PhCCPh)]$ has been described as dative,[10] donating electron density to the electron-poor Os(5)[Os(10)] atom. However, it is probably better to describe the bonding in this ' $Os_3(RCCR)$ ' unit in terms of multicentre molecular orbitals rather than in terms of individual metal–metal bonds. Also consistent with the electron imbalance is the presence of an incipient bridging carbonyl between the electron-rich Os(3)[Os(8)] atom and Os(4)[Os(9)] with dimensions Os(3)–C(31) 1.85(3) Å [Os(8)–C(81) 1.88(3) Å] and Os(4)–C(31) 2.79(3) Å [Os(9)–C(81) 2.81(3) Å].

The bonding within the metal framework in $[Os_5(CO)_{17}(HCCH)]$ (1) is somewhat different from that in $[Os_5(CO)_{19}]$.[2] The central metal atom, Os(3)[Os(8)], in (1) is formally eight-co-ordinate and there is an increase in dihedral angle between the two linked Os_3 triangles from 21.2° in $[Os_5(CO)_{19}]$ to 34.5° [43.7° for the second molecule] in (1). This increase in twist between the two planes is presumably a consequence of the greater steric constraints on Os(3)[Os(8)] and the requirement of incipient carbonyl bridge-bond formation to Os(4)-[Os(9)]. Coupled with this is a widening of the Os(2)–Os(3)–Os(4)[Os(7)–Os(8)–Os(9)] angle from the value of 95.2(1)° in the parent carbonyl,[2] and a redistribution of the Os(3)-[Os(8)]–Os bond lengths. A comparison of these parameters is illustrated in Figure 3. The metal–metal distances within the acetylene-capped triangle in (1) show similar trends to those in $[Os_3(CO)_{10}(PhCCPh)]$.[10] The Os–Os bonds in the uncapped triangle more closely resemble those in $[Os_5(CO)_{19}]$,[2] but show significant variations from the average Os–Os bond length of 2.877(3) Å for the equilateral triangle in $[Os_3(CO)_{12}]$.[11] In complex (1) the Os–Os bond between these two six-co-ordinate Os atoms is *ca.* 0.1 Å shorter than the bonds between the six- and eight-co-ordinate metal atoms.

The carbonyl groups, other than those involved in the incipient bridge bonds, are essentially linear with an average Os–C–O angle of 175(3)°. The rather high estimated standard deviations on the Os–C and C–O bond lengths make difficult an accurate assessment of the bonding. The average Os–C and C–O distances are 1.94(4) and 1.15(6) Å, respectively.

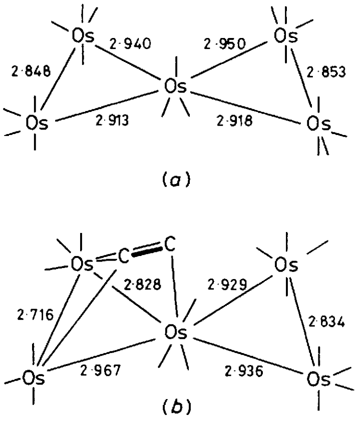

Figure 3. The structures of $[Os_5(CO)_{19}]$ (*a*) and $[Os_5(CO)_{17}(HCCH)]$ (*b*) showing the metal–metal bond lengths (Å) [in (*b*) the distances are averaged over the two independent molecules]

Experimental

All operations were performed with the exclusion of air, except for chromatography. Reaction solvents were purified, dried, and deoxygenated by distillation under N_2 over appropriate drying agents. These solvents were stored under N_2.

Product separation was achieved using thin-layer chromatography (t.l.c.) with plates precoated to a thickness of 0.25 mm with Merck Kieselgel $60F_{254}$.

Infrared spectra between 2 150 and 1 600 cm^{-1} were recorded on a Perkin-Elmer 257 spectrometer with the absorption of CO(g) at 2 143 cm^{-1} as calibrant. Mass spectra were recorded on an A.E.I. MS12 spectrometer with *ca.* 70 eV (1.12×10^{-17} J) ionising potential at 100 ± 30 °C. Tris(perfluoroheptyl)-*s*-triazine was used as a reference.

Preparations.—$[Os_5(CO)_{17}(HCCH)]$ (1). In a typical reaction

Table 3. Atom co-ordinates (× 10^4)

Atom	*X/a*	*Y/b*	*Z/c*
Os(1)	3 681(1)	4 291(1)	3 183(1)
Os(2)	3 462(1)	1 640(2)	3 631(1)
Os(3)	4 766(1)	2 948(1)	3 730(1)
Os(4)	5 718(1)	786(2)	4 029(1)
Os(5)	6 032(1)	3 527(2)	4 241(1)
Os(6)	9 058(1)	3 270(1)	623(1)
Os(7)	8 918(1)	2 217(1)	1 555(1)
Os(8)	10 239(1)	2 267(1)	1 152(1)
Os(9)	11 050(1)	159(2)	1 633(1)
Os(10)	11 694(1)	2 486(2)	1 308(1)
C(1)	4 903(15)	1 667(37)	4 389(9)
C(2)	5 439(15)	2 213(41)	4 649(10)
C(3)	10 581(15)	2 158(35)	1 893(9)
C(4)	11 225(16)	2 369(43)	1 968(10)
C(11)	4 120(16)	3 404(37)	2 614(10)
O(11)	4 326(11)	2 965(25)	2 298(6)
C(12)	2 824(19)	4 425(41)	2 853(11)
O(12)	2 314(12)	4 375(36)	2 670(9)
C(13)	3 982(17)	6 148(40)	3 021(10)
O(13)	4 145(12)	7 232(31)	2 894(8)
C(14)	3 268(17)	5 071(38)	3 737(11)
O(14)	2 970(13)	5 579(33)	4 026(8)
C(21)	3 631(18)	−221(41)	3 935(11)
O(21)	3 715(12)	−1 224(24)	4 141(8)
C(22)	3 618(17)	812(40)	2 996(11)
O(22)	3 600(13)	174(27)	2 649(7)
C(23)	2 556(18)	1 451(41)	3 556(11)
O(23)	1 970(11)	1 391(31)	3 463(9)
C(24)	3 338(18)	2 522(41)	4 246(11)
O(24)	3 225(14)	3 089(32)	4 599(8)
C(31)	4 927(16)	1 644(36)	3 257(10)
O(31)	5 013(11)	877(25)	2 914(7)
C(32)	4 494(18)	4 334(41)	4 204(12)
O(32)	4 402(12)	5 243(24)	4 476(7)
C(33)	5 256(16)	4 377(36)	3 364(10)
O(33)	5 476(10)	5 224(28)	3 155(7)
C(41)	5 275(15)	−1 011(36)	3 864(9)
O(41)	5 022(11)	−2 044(22)	3 763(7)
C(42)	6 375(16)	−123(38)	4 425(10)
O(42)	6 705(14)	−679(31)	4 700(9)
C(43)	6 319(18)	796(41)	3 517(11)
O(43)	6 665(12)	786(38)	3 193(8)
C(51)	6 750(19)	3 368(43)	4 709(12)
O(51)	7 161(14)	3 220(34)	4 971(9)
C(52)	6 613(16)	3 928(37)	3 725(10)
O(52)	6 976(12)	4 081(35)	3 421(8)
C(53)	5 961(19)	5 361(45)	4 408(12)
O(53)	5 828(14)	6 505(31)	4 547(9)
C(61)	8 170(15)	3 952(34)	529(9)
O(61)	7 634(12)	4 271(32)	481(8)
C(62)	8 883(16)	1 379(37)	364(10)
O(62)	8 733(16)	283(30)	177(9)
C(63)	9 222(14)	5 138(33)	831(9)
O(63)	9 286(11)	6 337(26)	978(7)
C(64)	9 354(14)	3 761(32)	−3(9)
O(64)	9 483(12)	4 060(27)	−370(6)
C(71)	8 011(15)	2 672(34)	1 623(9)
O(71)	7 477(10)	2 973(26)	1 664(6)
C(72)	8 714(16)	358(37)	1 316(10)
O(72)	8 509(14)	−796(30)	1 172(9)
C(73)	9 067(17)	1 347(39)	2 150(11)
O(73)	9 126(12)	695(33)	2 520(7)
C(74)	9 177(14)	4 037(34)	1 825(9)
O(74)	9 311(11)	5 048(24)	2 010(6)
C(81)	10 029(15)	411(34)	943(9)
O(81)	9 904(13)	−701(25)	736(9)
C(82)	10 628(16)	2 691(36)	506(10)
O(82)	10 811(12)	2 872(28)	164(6)
C(83)	10 416(13)	4 184(31)	1 338(8)
O(83)	10 502(10)	5 354(23)	1 458(7)
C(91)	10 335(16)	−1 102(38)	1 838(10)
O(91)	9 939(13)	−1 733(28)	1 976(8)
C(92)	11 693(16)	−691(36)	2 064(10)
O(92)	12 046(12)	−1 063(42)	2 359(8)
C(93)	11 389(16)	−986(38)	1 110(11)
O(93)	11 572(15)	−1 597(29)	789(8)
C(101)	11 873(27)	4 352(64)	1 208(17)
O(101)	11 945(19)	5 573(43)	1 088(12)
C(102)	12 083(20)	1 730(45)	689(12)
O(102)	12 264(16)	1 253(45)	376(9)
C(103)	12 536(28)	2 421(51)	1 662(17)
O(103)	13 039(16)	2 234(40)	1 840(13)

$[Os_5(CO)_{19}]$ (20 mg) was dissolved in n-heptane (25 cm^3) and heated to reflux. Acetylene was bubbled through the solution for 1 h. The solvent was evaporated under vacuum and the residue separated by t.l.c. using a solution of 2% ethyl acetate–hexane as eluant. The two yellow bands were identified as $[Os_5(CO)_{17}(HCCH)]$ (1) (yield 3 mg, 15%) and $[Os_4(CO)_{12}(HCCH)]$ (yield 11 mg, 55%) (2).

$[Os_5(CO)_{17}(HCCMe)]$ (3). The complex $[Os_5(CO)_{19}]$ (10 mg) was dissolved in n-heptane (25 cm^3) and HCCMe was bubbled through the solution while it was heated to reflux for 2 h. The solvent was removed under vacuum and the residue separated by t.l.c. (2% ethyl acetate–hexane). The orange-yellow products were characterised spectroscopically.

$[Os_5(CO)_{17}(HCCPh)]$ (4). The complex $[Os_5(CO)_{19}]$ (25 mg) was dissolved in n-heptane (20 cm^3) and a solution of HCCPh (3 cm^3, 1% w/v) in n-heptane added. The solution was heated to reflux for 2.5 h. The solvent was evaporated under vacuum and the residue separated by t.l.c. (2% ethyl acetate–hexane). The two main orange products were characterised spectroscopically.

Reaction of $[Os_5(CO)_{19}]$ *with* PhCCPh *or* $MeO(O)CC_2C(O)OMe$.—The complex $[Os_5(CO)_{19}]$ (15 mg) and RCCR [R = Ph (20 mg) or MeO(O)C (0.02 cm^3)] in n-octane (25 cm^3) were heated to reflux for 0.5 h. At this time the i.r. spectrum showed that all the $[Os_5(CO)_{19}]$ had been converted into $[Os_5(CO)_{16}]$.

X-Ray Crystal Structure Determination of $[Os_5(CO)_{17}(HCCH)]$ (1).—Orange single crystals of complex (1) in the shape of elongated rectangular blocks were obtained by recrystallisation from CH_2Cl_2 solution. A single crystal with dimensions *ca.* 0.31 × 0.27 × 0.11 mm was mounted on the end of a glass fibre with epoxy-resin, and the space group and approximate cell dimensions determined *via* Weissenberg (Cu-K_α) *X*-ray photography.

The crystal was transferred to a Syntex $P2_1$ diffractometer, and accurate cell dimensions determined from the angular measurement of 15 strong reflections in the range $15 < 2\theta < 25°$. 9 049 Intensity data were recorded in the range $3.0 < 2\theta \leqslant 50.0°$ using graphite-monochromated Mo-K_α radiation ($\lambda_{\alpha 1}$ 0.709 26, $\lambda_{\alpha 2}$ 0.713 54 Å) and a 96-step ω—2θ scan technique. The scan speed was varied from 3.0 to 29.3° min^{-1} depending upon the intensity measured in a 1-s prescan; reflections with intensities of less than 7 counts s^{-1} were not remeasured. The scan range was from 1° below 2θ $K_{\alpha 1}$ to 1° above 2θ $K_{\alpha 2}$. Two check reflections were monitored periodically throughout the course of data collection but showed no significant variation in intensity.

A semi-empirical absorption correction based on a pseudo-ellipsoid model and 332 azimuthal scan data from five independent reflections was applied. Transmission factors ranged from 0.441 to 0.993 for the full data set. The data set was profile fitted,[12] and Lorentz polarisation corrections were also applied. Equivalent reflections were averaged to give 5 496 unique observed data [$F > 5\sigma(F)$].

Crystal data. $C_{19}H_2O_{17}Os_5$, M = 1 485.21, Monoclinic, a = 20.255(11), b = 9.391(7), c = 28.227(15) Å, β = 91.62(3)°, U = 5 367(4) Å^3, D_m not measured, Z = 8, D_c = 3.67 g cm^{-3}, $F(000)$ = 5 166, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 236.66 cm^{-1}, space group $P2_1/c$ from systematic absences.

The ten unique Os atom positions were located by multi-solution Σ_2 sign expansion, and all the remaining non-hydrogen atoms from subsequent electron-density difference syntheses. The structure was refined by blocked-cascade least squares with the Os, O, and acetylenic C atoms assigned anisotropic thermal parameters, and the carbonyl C atoms individual isotropic thermal parameters. The acetylenic H atoms were not located. In the final cycles of refinement a weighting scheme of the form $w = [\sigma^2(F) + 0.0009|F|^2]^{-1}$ was introduced. The final residuals were R = 0.060 and $R' = [\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|]$ = 0.060. A difference map computed at this stage showed ripples of *ca.* 2 e Å^{-3} close to the Os atom positions but no other regions of significant electron density. The final atomic co-ordinates for complex (1) are presented in Table 3.

Complex neutral-atom scattering factors [13] were employed throughout structure solution and refinement. All computations were carried out on the University of Cambridge IBM 3081 computer using a modified version of SHELX.[14] The molecular plots were drawn using the PLUTO package.[15]

Acknowledgements

We thank the S.E.R.C. for financial support and the Universidad Nacional Autónoma de Mexico for a grant (to M. J. R.).

References

1 D. H. Farrar, B. F. G. Johnson, J. Lewis, J. N. Nicholls, P. R. Raithby, and M. J. Rosales, *J. Chem. Soc., Chem. Commun.*, 1981, 273.

2 D. H. Farrar, B. F. G. Johnson, J. Lewis, P. R. Raithby, and M. J. Rosales, *J. Chem. Soc., Dalton Trans.*, 1982, 2051.

3 B. E. Reichert and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1977, **33**, 173.

4 C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1975, 2606.

5 B. F. G. Johnson and J. Lewis, *Adv. Inorg. Chem. Radiochem.*, 1981, **24**, 225.

6 R. Jackson, B. F. G. Johnson, J. Lewis, P. R. Raithby, and S. W. Sankey, *J. Organomet. Chem.*, 1980, **193**, C1.

7 A. J. Carty, *Pure Appl. Chem.*, 1982, **54**, 113.

8 D. H. Farrar, G. R. John, B. F. G. Johnson, J. Lewis, P. R. Raithby, and M. J. Rosales, *J. Chem. Soc., Chem. Commun.*, 1981, 886.

9 M. Tachikawa, J. R. Shapley, and C. G. Pierpoint, *J. Am. Chem. Soc.*, 1975, **97**, 7172.

10 C. G. Pierpoint, *Inorg. Chem.*, 1977, **16**, 636.

11 M. R. Churchill and B. G. De Boer, *Inorg. Chem.*, 1977, **16**, 878.

12 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

13 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

14 G. M. Sheldrick, SHELX, a crystal structure solving package, University of Cambridge, 1976.

15 W. D. S. Motherwell, PLUTO, a molecular plotting package, University of Cambridge, 1976.

Received 6th *April* 1983; *Paper* 3/523