Some Reactions of Dodecacarbonyltetrahydridotetraosmium with Olefins; The Molecular Structure of 1,1,1,2,2,3,3,3,4,4,4-Undecacarbonyl-1,2-μ-(1′-σ,1′—2′-η-cyclohexenyl)-tri-μ-hydrido-*tetrahedro*-tetraosmium

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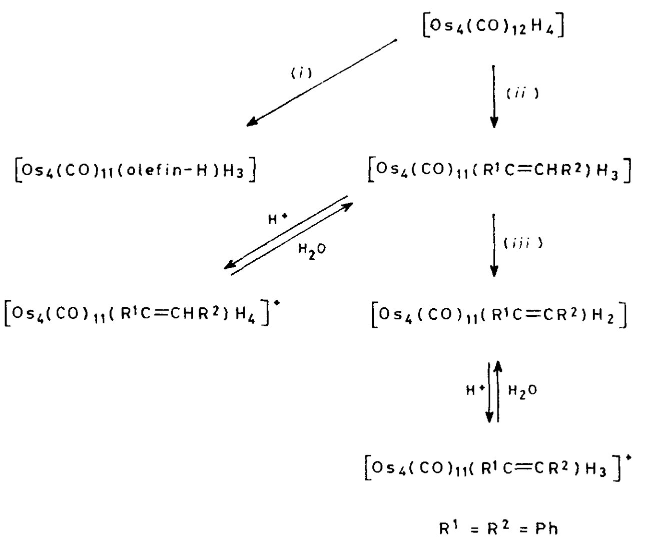
The complexes $[Os_4(CO)_{11}(\text{cyclo-olefin} - H)H_3]$ (cyclo-olefin = cyclo-octatetraene, cyclo-octa-1,5-diene, cyclohexene, or norbornene) have been identified as the products of reaction of $[Os_4(CO)_{12}H_4]$ with the appropriate cyclic olefin. The structures of these complexes are discussed in terms of available spectroscopic data and in the case of the title complex $[Os_4(CO)_{11}(C_6H_9)H_3]$ on the basis of a single-crystal *X*-ray analysis. This molecule crystallises in space group $P2_1/n$ with $a = 9.266(4)$, $b = 14.850(8)$, $c = 16.847(9)$ Å, $\beta = 93.39(3)°$, and $Z = 4$. The osmium atoms define a tetrahedron, with the cyclohexene ring σ-bonded to one metal and π-bonded to another. The complex $[Os_4(CO)_{12}H_4]$ also reacts with the acyclic olefins $CH_2{=}CH_2$, $CH_2{=}CHPh$, $CH_2{=}CHCMe_3$, $CH_2{=}CMeCMe_3$, and *cis*-CHPh=CHPh to give the related complexes $[Os_4(CO)_{11}(\text{olefin} - H)H_3]$. On heating, apart from the complex where the olefin is $CH_2{=}CMeCMe_3$, dehydrogenation occurs to produce the dihydrido-complexes $[Os_4(CO)_{11}(R^1C{=}CR^2)H_2]$ (R^1 = H, R^2 = H, Ph, or CMe_3; $R^1 = R^2$ = Ph). These complexes have been shown to contain a $R^1C{=}CR^2$ fragment bound *via* two σ and one π bond to one tetrahedral face of the Os_4 cluster unit.

In earlier papers methods for the preparation of $[Os_4(CO)_{12}H_4]$ were described [1, 2] but yields by these routes were low and precluded any detailed examination of the chemistry of this complex. Recently we devised a better preparative route involving the direct reaction of hydrogen with $[Os_3(CO)_{12}]$ under moderate pressures and temperatures and which gives $[Os_4(CO)_{12}H_4]$ in quantitative yield.[3] This has permitted a closer examination of this tetrahydrido-cluster and it would appear that, in general, its chemistry is different to that of $[Ru_4(CO)_{12}H_4]$ reported previously.[4] The present paper, one of a series concerned with the reactions of small organic molecules with metal clusters, reports a series of organometallic cluster compounds based on the tetrahedral Os_4 unit which have been prepared from the direct reaction of $[Os_4(CO)_{12}H_4]$ with a variety of olefins.



SCHEME (*i*) Cyclic olefin; (*ii*) $R^1CH{=}CHR^2$ (R^1=H, R^2=H, Ph, or CMe_3; $R^1 = R^2$=Ph); (*iii*) heat, $-H_2$

As discussed in the Experimental section, the cluster compounds $[Os_4(CO)_{11}(\text{olefin} - H)H_3]$ are readily prepared from the direct reaction of $[Os_4(CO)_{12}H_4]$ with the appropriate olefin. In reactions with cyclic olefins yields are very low (*ca.* 10%) and as a consequence the products of these reactions are the more poorly characterised. Reaction with acyclic olefins proceeds more effectively allowing a more detailed examination of the reaction products. Significantly, in all these reactions the tetrahedral M_4 unit is maintained. This is in contrast to the behaviour exhibited by $[Ru_4(CO)_{12}H_4]$ which undergoes Ru–Ru bond cleavage to produce both *triangulo* Ru_3 and butterfly Ru_4 derivatives.[4]

RESULTS AND DISCUSSION

The complexes prepared together with some of their reactions are shown in the Scheme and Tables 1 and 2 provide some useful spectroscopic data. All the complexes are yellow-orange and were obtained as well defined tablets which are readily soluble in a range of organic solvents. They were identified largely on the basis of their mass spectra supported by analytical data and where possible ^1H n.m.r. and i.r. spectra. The probable structure of the co-ordinated organo-group has been established (where possible) by ^1H n.m.r. data and the hydride ligands have been detected in the same way. An *X*-ray structural analysis has established the important structural features of $[Os_4(CO)_{11}(C_6H_9)H_3]$ (Figure 1).

The complexes $[Os_4(CO)_{11}(R^1C{=}CHR^2)H_3]$ (R^1 = H, R^2 = H, Ph, or CMe_3; $R^1 = R^2$ = Ph) were the easiest to identify and characterise. On the basis of mass-spectroscopic and ^1H n.m.r. data the presence of three hydride ligands per cluster was clearly indicated. The i.r. spectra of the complexes in the metal-carbonyl region [ν(CO)] are similar and largely independent of the nature of R^1 and R^2. From their formulae and spectroscopic properties, these complexes are obviously related to the *triangulo*-clusters $[Os_3(CO)_9(HC{=}CHR)H]$.[5] A large number of possible structures may be considered, differing only in the arrangement of the hydride ligands about the Os_4 cluster unit. However, on the basis of their ^1H n.m.r. spectra which exhibit three hydride resonances of relative intensity 1 : 1 : 1 in the high-field region combined with the suggested location of the H ligands in $[Os_4(CO)_{11}(C_6H_9)H_3]$ from *X*-ray analysis (see below), we suggest that the correct structure is that shown in Figure 2.

TABLE 1

Infrared spectra (1 600—2 200 cm^{-1}) and molecular-ion value (*m*/*e* of M^+) of $[Os_4(CO)_{12}H_4]$ and its vinyl complexes

Complex *	ν(CO) (in cyclohexane)	*m*/*e* of M^+
$[Os_4(CO)_{12}H_4]$	2 085m, 2 068s, 2 021s, 1 998m	1 108
$[Os_4(CO)_{11}(CH{=}CH_2)H_3]$	2 102m, 2 069vs, 2 053vs, 2 042vs, 2 026m, 2 016m, 2 006s, 1 996m, 1 987m, 1 975(sh)	1 106
$[Os_4(CO)_{11}(HC{=}CHPh)H_3]$	2 100m, 2 069vs, 2 051vs, 2 040vs, 2 025m, 2 015m, 2 005s, 1 994m, 1 986m, 1 979w, 1 975w	1 182
$[Os_4(CO)_{11}(HC{=}CHCMe_3)H_3]$	2 099m, 2 068vs, 2 052vs, 2 038vs, 2 025m, 2 013m, 2 005s, 1 994m, 1 982m, 1 978w	1 162
$[Os_4(CO)_{11}(PhC{=}CHPh)H_3]$	2 098m, 2 068vs, 2 053vs, 2 042vs, 2 025m, 2 013m, 2 005m, 1 992m, 1 984m, 1 975w	1 258
$[Os_4(CO)_{11}(HC{=}CMeCMe_3)H_3]$	2 099m, 2 065vs, 2 052vs, 2 037vs, 2 020m, 2 013w, 2 005m, 1 995m, 1 983m, 1 977w	1 176
$[Os_4(CO)_{11}(C_6H_9)H_3]$	2 097m, 2 065vs, 2 040vs, 2 035vs, 2 021m, 2 010m, 2 004m, 1 993m, 1 981m, 1 975w	1 154
$[Os_4(CO)_{11}(cot - H)H_3]$	2 098m, 2 067vs, 2 052vs, 2 038vs, 2 025m, 2 011m, 2 003m, 1 992m, 1 982m, 1 975w	1 180
$[Os_4(CO)_{11}(cod - H)H_3]$	2 098m, 2 066vs, 2 050vs, 2 038vs, 2 021m, 2 011m, 2 003m, 1 992m, 1 982m, 1 975w	1 178
$[Os_4(CO)_{11}(nor - H)H_3]$	2 098m, 2 066vs, 2 050vs, 2 036vs, 2 019m, 2 010m, 2 002m, 1 992m, 1 981m, 1 975w	1 166

* cot = Cyclo-octatetraene, cod = cyclo-octa-1,5-diene, and nor = norbornene.

The complexes derived from cyclic olefins were easily identified from their mass spectra, but because of the small amounts available and the low H content per cluster, reliable ^1H n.m.r. spectra could not be obtained. Their i.r. spectra (Table 1) are similar to those of the acyclic derivatives described above and there can be little doubt that they possess a similar structure. The *X*-ray analysis of $[Os_4(CO)_{11}(C_6H_9)H_3]$ (see below) supports this view.

Dehydrogenation.—On heating, the complexes $[Os_4(CO)_{11}(R^1C{=}CHR^2)H_3]$ undergo H_2 elimination to yield the dihydrido-complexes $[Os_4(CO)_{11}(R^1C{=}CR^2)H_2]$. This dehydrogenation presumably takes place first by H transfer from the vinylic group to the Os_4 core followed by H_2 ejection from the Os_4H_4 unit. The ^1H n.m.r. spectra of all these dihydrido-complexes exhibit two high-field resonances (see Table 3). No coupling between the two olefinic protons in the parent complex $[Os_4(CO)_{11}(C_2H_2)H_2]$ is observed indicating a 1,2- rather than a 1,1-bonding mode for the C_2H_2 unit (see Figure 3). The appearance of two hydride resonances in the spectrum of this parent species indicates that the hydride ligands occupy non-equivalent sites. Given the structure of the vinyl derivative (Figure 2) and the fact that no ^1H–^1H coupling is observed, we conclude that the structure illustrated in Figure 3 is the most likely for this series of dihydrido-organometallic clusters.

TABLE 2

Hydrogen-1 n.m.r. data for $[Os_4(CO)_{12}H_4]$ and its vinyl complexes [a]

Complex	τ [b]	Assignment	*J*/Hz
$[Os_4(CO)_{12}H_4]$	30.35(s)		
$[Os_4(CO)_{11}(H^aC{=}CH_2{}^{bc})H_3]$	1.17 (1, dd)	H^a	$J(H^a–H^b)$ 8.7 $J(H^a–H^c)$ 12.3
	5.04 (1, d)	H^b	
	6.65 (1, d)	H^c	
	24.15 (1, s)	OsH	
	29.30 (1, s)	OsH	
	31.00 (1, s)	OsH	
$[Os_4(CO)_{11}(H^aC{=}CH^bPh)H_3]$	0.94 (1, d)	H^a	$J(H^a–H^b)$ 12.1
	2.75 (5, m)	Ph	
	5.18 (1, d)	H^b	
	24.65 (1, s)	OsH	
	28.87 (1, s)	OsH	
	30.80 (1, s)	OsH	
$[Os_4(CO)_{11}(H^aC{=}CH^bCMe_3)H_3]$	1.32 (1, d)	H^a	$J(H^a–H^b)$ 12.3
	5.82 (1, d)	H^b	
	8.90 (9, s)	Bu^t	
	24.77 (1, s)	OsH	
	29.52 (1, s)	OsH	
	31.08 (1, s)	OsH	
$[Os_4(CO)_{11}(PhC{=}CHPh)H_3]$	2.75 (10, m)	2 Ph	
	5.39 (1, s)	CH	
	24.65 (1, s)	OsH	
	28.51 (1, s)	OsH	
	30.13 (1, s)	OsH	

[a] In $CDCl_3$, at ambient probe temperature (35 °C). s = Singlet, d = doublet, m = multiplet. [b] The relative intensity and multiplicity are given in parentheses.

There are two points of note. First, the formation of the 1,2- rather than the 1,1-derivative differs from the behaviour observed for the *triangulo* Os_3 derivatives. Secondly, the elimination of H_2 rather than CO from the proposed tetrahydrido-intermediate ' $Os_4(CO)_{11}(HC{=}CH)H_4$ ' is also in contrast to the behaviour shown by the corresponding *triangulo*-intermediate ' $Os_3(CO)_{10}(C{=}CH_2)H_2$ '.[6]

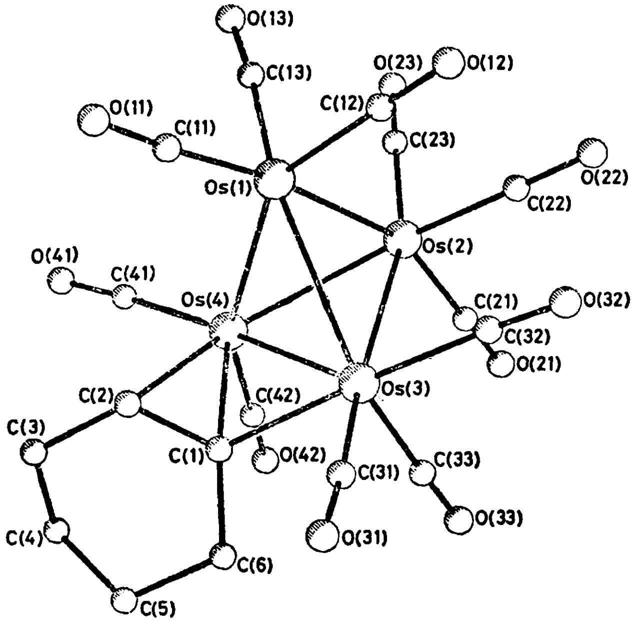


FIGURE 1 The molecular structure of $[Os_4(CO)_{11}(C_6H_9)H_3]$

The ' parent complex ' $[Os_4(CO)_{11}(HC{=}CH)H_2]$ cannot be hydrogenated to yield $[Os_4(CO)_{11}(HC{=}CH_2)H_3]$. On passing H_2 through a solution of $[Os_4(CO)_{11}(HC{=}CH)H_2]$ (*ca.* 80 °C), $[Os_4(CO)_{12}H_4]$ and Os metal are produced. Similar results were obtained for the other related derivatives $[Os_4(CO)_{11}(R^1C{=}CR^2)H_2]$. No attempt was made to identify the organic products of these reactions.

Protonation.—The protonation of a series of alkene and alkyne complexes of Os_3 was reported earlier.[7] That study provided information about the ability of H atoms to migrate within the *triangulo*-cluster system. We have now examined some corresponding reactions of the new Os_4 species. None of the complexes $[Os_4(CO)_{11}(R^1C{=}CHR^2)H_3]$ underwent protonation in CF_3CO_2H; however, on addition of $HSFO_3$ to a solution of the complex in $CDCl_3$ at −20 °C four signals of relative intensity 1 : 1 : 1 : 1 were observed in the high-field region (see Table 5; R^1 = H, R^2 = CMe_3; R^1 = R^2 = Ph) clearly indicating that H^+ addition to the tetrahedral Os_4 unit had occurred. No evidence for the attack on the co-ordinated organo-group was found. In contrast to the *triangulo*-system, no evidence for diprotonation was found. In all cases, on quenching with water, deprotonation occurred and the original complex was regenerated. For these cationic species the ^1H n.m.r. spectra indicate that: (*i*) the four hydride ligands occupy non-equivalent sites around the tetraosmium cluster; and (*ii*) there is no coupling between the hydride protons and the protons of the organic ligand (see Figures 4 and 5).

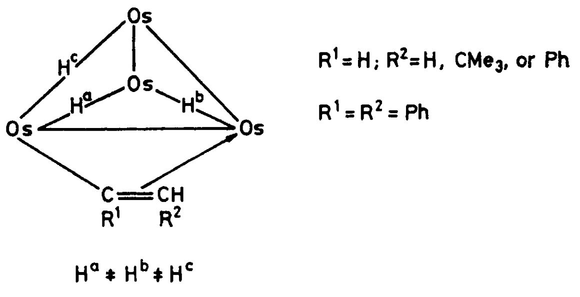


FIGURE 2 Probable structure of $[Os_4(CO)_{11}(R^1C{=}CHR^2)H_3]$ complexes (carbonyl groups omitted for clarity)

TABLE 3

Hydrogen-1 n.m.r. data * for complexes with a 1,2-alkene linkage

Complex	τ	Assignment
$[Os_4(CO)_{11}(HC{=}CH)H_2]$	0.20 (2, s)	C_2H_2
	19.33 (1, s)	OsH
	31.60 (1, s)	OsH
$[Os_4(CO)_{11}(HC{=}CPh)H_2]$	0.07 (1, s)	CH
	2.75 (5, m)	Ph
	20.18 (1, s)	OsH
	31.22 (1, s)	OsH
$[Os_4(CO)_{11}(HC{=}CCMe_3)H_2]$	0.10 (1, s)	CH
	8.59 (9, s)	Bu^t
	20.21 (1, s)	OsH
	31.69 (1, s)	OsH
$[Os_4(CO)_{11}(PhC{=}CPh)H_2]$	2.92 (10, m)	2 Ph
	20.32 (1, s)	OsH
	31.46 (1, s)	OsH

* Details as in Table 2.

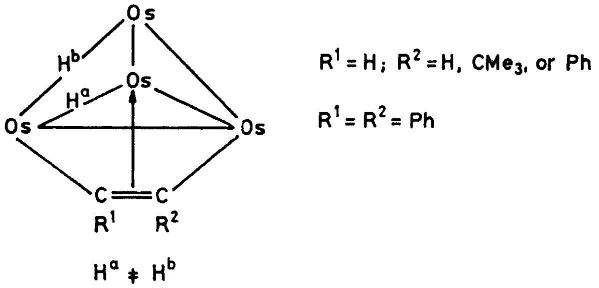


FIGURE 3 Probable structure of $[Os_4(CO)_{11}(R^1C{=}CR^2)H_2]$ complexes (carbonyl groups omitted for clarity)

TABLE 4

Infrared spectra (1 600—2 200 cm^{-1}) and molecular-ion value (m/e of M^+) of complexes with a 1,2-alkene linkage

Complex	ν(CO) (in cyclohexane)	m/e of M^+
$[Os_4(CO)_{11}(HC{=}CH)H_2]$	2 101w, 2 067vs, 2 062s, 2 026vs, 2 019s, 2 006w, 1 996w, 1 981w, 1 960m	1 104
$[Os_4(CO)_{11}(HC{=}CPh)H_2]$	2 100m, 2 068vs, 2 060s, 2 025vs, 2 020s, 2 005w, 1 996w, 1 981w, 1 960m	1 180
$[Os_4(CO)_{11}(HC{=}CCMe_3)H_2]$	2 101m, 2 067vs, 2 059vs, 2 024vs, 2 021s, 2 014m, 2 007m, 1 994m, 1 956m	1 160
$[Os_4(CO)_{11}(PhC{=}CPh)H_2]$	2 100m, 2 069vs, 2 061s, 2 024vs, 2 018s, 2 009m, 1 996m, 1 960m	1 256

Structure of $[Os_4(CO)_{11}(C_6H_9)H_3]$.—A single molecule of $[Os_4(CO)_{11}(C_6H_9)H_3]$ is shown in Figure 1 and includes the atom-numbering scheme adopted. Interatomic bond distances and interbond angles for the non-hydrogen atoms appear in Tables 6 and 7, with, in each case, the estimated standard deviations in parentheses.

TABLE 5

Hydrogen-1 n.m.r. data for $[Os_4(CO)_{11}(R^1C=CHR^2)H_4]^+$ and $[Os_4(CO)_{11}(PhC=CPh)H_3]^+$

Complex	τ *
$[Os_4(CO)_{11}(HC=CHCMe_3)H_4]^+$	24.93
	28.88
	30.38
	31.60
$[Os_4(CO)_{11}(PhC=CHPh)H_4]^+$	24.96
	28.76
	29.56
	30.51
$[Os_4(CO)_{11}(PhC=CPh)H_3]^+$	20.21
	28.22
	32.31

* All resonances have a relative intensity of 1.

The molecule has no crystallographically imposed symmetry. The four osmium atoms define a tetrahedron where three of the Os–Os bonds are significantly shorter (mean 2.801 Å) than the other three (mean 2.958 Å). In addition to Os–Os bond formation, atoms Os(1) and Os(2) are each co-ordinated to three terminal carbonyls. If Os–H(hydride) bonds are neglected, distortions from the regular, six-co-ordinate, octahedral geometry at the two metals are caused by the necessity to form close-packed triangular units in the Os_4 cluster, as is illustrated by the Os–Os–Os angles (mean 60.0°). Os(3) may be considered as seven-co-ordinate since it is σ bonded to atom C(1) of the cyclohexene ring, and to three terminal carbonyls. Os(4) has only two terminal carbonyls, but is involved in π bonding with the unsaturated fragment of the cyclohexene ring.

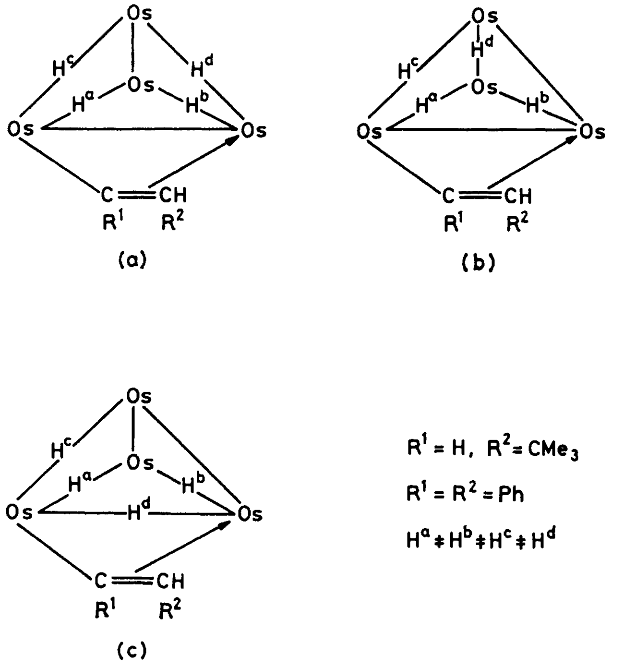


FIGURE 4 Possible structures for the cation $[Os_4(CO)_{11}(R^1C=CHR^2)H_4]^+$
Structure (c) is regarded as unlikely (see text), carbonyl ligands are omitted for clarity

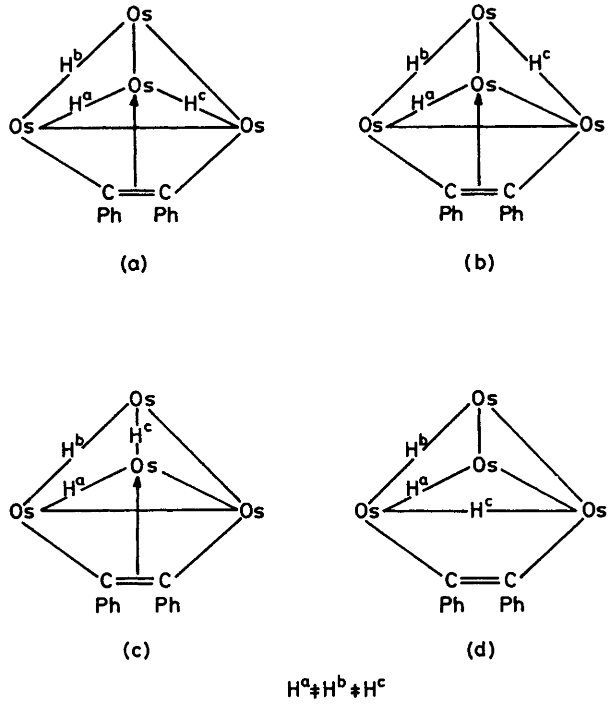


FIGURE 5 Possible structures for the cation $[Os_4(CO)_{11}(PhC=CPh)H_3]^+$

The hydridic hydrogens could not be located directly, but an examination of the Os–Os–C(carbonyl) angles, in the light of observations made on other hydrido-osmium clusters, suggests that the hydrides edge-bridge the Os(1)–Os(3), Os(1)–Os(4), and Os(2)–Os(4) bonds. The average *cis* Os–Os–C angle involving these bonds is 106.1° compared with 94.1° for the remainder. The lengths of the two longest bridged metal–metal bonds are typical of values assigned to bonds with hydride bridges.[8,9] The third bridged bond [Os(2)–Os(4)] is of

TABLE 6

Bond lengths (Å)

Os(1)–Os(2)	2.794(1)	Os(4)–C(2)	2.311(11)
Os(1)–Os(3)	2.984(1)	Os(1)–C(11)	1.901(12)
Os(1)–Os(4)	2.953(1)	Os(1)–C(12)	1.921(11)
Os(2)–Os(3)	2.937(2)	Os(1)–C(13)	1.866(12)
Os(2)–Os(4)	2.817(1)	Os(2)–C(21)	1.908(9)
Os(3)–Os(4)	2.793(1)	Os(2)–C(22)	1.859(12)
Os(3)–C(1)	2.170(9)	Os(2)–C(23)	1.862(13)
Os(4)–C(1)	2.188(10)	Os(3)–C(31)	1.909(13)
C(11)–O(11)	1.158(15)	Os(3)–C(32)	1.954(10)
C(12)–O(12)	1.154(14)	Os(3)–C(33)	1.887(10)
C(13)–O(13)	1.163(15)	Os(4)–C(41)	1.889(10)
C(21)–O(21)	1.137(12)	Os(4)–C(42)	1.890(10)
C(22)–O(22)	1.160(15)	C(1)–C(2)	1.394(13)
C(23)–O(23)	1.160(17)	C(2)–C(3)	1.520(15)
C(31)–O(31)	1.144(17)	C(3)–C(4)	1.506(15)
C(32)–O(32)	1.121(13)	C(4)–C(5)	1.485(17)
C(33)–O(33)	1.139(12)	C(5)–C(6)	1.525(15)
C(41)–O(41)	1.141(12)	C(6)–C(1)	1.575(14)
C(42)–O(42)	1.129(13)		

intermediate length, while the other two ' short ' unbridged Os–Os bonds are *ca.* 0.07 Å shorter than the unbridged M–M distances of 2.884(2) (mean of two) and 2.876 (1) Å in $[Os_3(CO)_{11}H_2]$ [8] and $[Os_4(CO)_{12}H_3I]$, respectively. These hydride positions require one of the ' long ' metal–metal bonds [Os(2)–Os(3)] to remain unbridged, which suggests that the Os–Os distances in this cluster are influenced by factors such as metal co-ordination number and electron distribution as well as by the presence of bridging hydrides. Each of the metal atoms obeys the ' 18-electron rule ' and with cyclohexene acting as a three-electron donor the complex may be considered as a 60-electron system.

TABLE 7

Bond angles (°)

Os(2)–Os(1)–Os(3)	61.0(1)	Os(2)–Os(1)–C(11)	173.0(3)
Os(2)–Os(1)–Os(4)	58.6(1)	Os(3)–Os(1)–C(11)	115.6(4)
Os(3)–Os(1)–Os(4)	56.1(1)	Os(4)–Os(1)–C(11)	114.4(3)
Os(1)–Os(2)–Os(3)	62.7(1)	Os(2)–Os(1)–C(12)	91.7(3)
Os(1)–Os(2)–Os(4)	63.5(1)	Os(3)–Os(1)–C(12)	98.5(3)
Os(3)–Os(2)–Os(4)	58.0(1)	Os(4)–Os(1)–C(12)	147.0(3)
Os(1)–Os(3)–Os(2)	56.3(1)	Os(2)–Os(1)–C(13)	86.2(3)
Os(1)–Os(3)–Os(4)	61.4(1)	Os(3)–Os(1)–C(13)	145.6(3)
Os(2)–Os(3)–Os(4)	58.8(1)	Os(4)–Os(1)–C(13)	99.1(3)
Os(1)–Os(4)–Os(2)	57.9(1)	Os(1)–Os(2)–C(21)	158.1(3)
Os(1)–Os(4)–Os(3)	62.5(1)	Os(3)–Os(2)–C(21)	96.9(3)
Os(2)–Os(4)–Os(3)	63.1(1)	Os(4)–Os(2)–C(21)	99.7(3)
Os(1)–C(11)–O(11)	175.9(11)	Os(1)–Os(2)–C(22)	98.0(3)
Os(1)–C(12)–O(12)	178.8(10)	Os(3)–Os(2)–C(22)	99.3(4)
Os(1)–C(13)–O(13)	174.3(8)	Os(4)–Os(2)–C(22)	155.0(4)
Os(2)–C(21)–O(21)	179.3(9)	Os(1)–Os(2)–C(23)	101.9(3)
Os(2)–C(22)–O(22)	177.5(11)	Os(3)–Os(2)–C(23)	163.3(3)
Os(2)–C(23)–O(23)	179.0(10)	Os(4)–Os(2)–C(23)	110.5(3)
Os(3)–C(31)–O(31)	175.1(9)	Os(1)–Os(3)–C(31)	119.8(3)
Os(3)–C(32)–O(32)	174.4(9)	Os(2)–Os(3)–C(31)	170.2(3)
Os(3)–C(33)–O(33)	177.2(9)	Os(4)–Os(3)–C(31)	128.9(3)
Os(4)–C(41)–O(41)	174.7(9)	Os(1)–Os(3)–C(32)	88.8(3)
Os(4)–C(42)–O(42)	177.6(10)	Os(2)–Os(3)–C(32)	79.0(3)
C(11)–Os(1)–C(12)	94.9(4)	Os(4)–Os(3)–C(32)	136.8(3)
C(11)–Os(1)–C(13)	95.7(5)	Os(1)–Os(3)–C(33)	144.3(3)
C(12)–Os(1)–C(13)	92.4(4)	Os(2)–Os(3)–C(33)	89.1(3)
C(21)–Os(2)–C(22)	92.9(4)	Os(4)–Os(3)–C(33)	94.9(3)
C(21)–Os(2)–C(23)	97.2(4)	Os(1)–Os(4)–C(41)	109.4(3)
C(22)–Os(2)–C(23)	88.9(5)	Os(2)–Os(4)–C(41)	126.8(3)
C(31)–Os(3)–C(32)	92.1(4)	Os(3)–Os(4)–C(41)	163.3(3)
C(31)–Os(3)–C(33)	95.7(4)	Os(1)–Os(4)–C(42)	157.4(3)
C(32)–Os(3)–C(33)	93.3(4)	Os(2)–Os(4)–C(42)	100.4(3)
C(41)–Os(4)–C(42)	88.1(4)	Os(3)–Os(4)–C(42)	103.9(3)
C(31)–Os(3)–C(1)	79.9(4)	Os(1)–Os(3)–C(1)	93.6(2)
C(32)–Os(3)–C(1)	171.8(4)	Os(2)–Os(3)–C(1)	108.8(2)
C(33)–Os(3)–C(1)	89.4(3)	Os(4)–Os(3)–C(1)	50.4(2)
C(41)–Os(4)–C(1)	120.1(4)	Os(1)–Os(4)–C(1)	94.0(2)
C(42)–Os(4)–C(1)	88.9(4)	Os(2)–Os(4)–C(1)	112.5(2)
C(41)–Os(4)–C(2)	89.3(4)	Os(3)–Os(4)–C(1)	49.8(2)
C(42)–Os(4)–C(2)	107.0(4)	Os(1)–Os(4)–C(2)	87.9(2)
C(1)–Os(4)–C(2)	36.0(3)	Os(2)–Os(4)–C(2)	135.2(2)
Os(3)–C(1)–Os(4)	79.7(3)	Os(3)–Os(4)–C(2)	76.2(2)
Os(3)–C(1)–C(2)	124.3(6)	C(2)–C(1)–C(6)	117.8(7)
Os(4)–C(1)–C(2)	76.8(6)	C(1)–C(2)–C(3)	123.0(8)
Os(3)–C(1)–C(6)	117.3(5)	C(2)–C(3)–C(4)	113.1(8)
Os(4)–C(1)–C(6)	124.1(5)	C(3)–C(4)–C(5)	107.3(8)
Os(4)–C(2)–C(1)	67.2(5)	C(4)–C(5)–C(6)	114.2(10)
Os(4)–C(2)–C(3)	122.1(6)	C(1)–C(6)–C(5)	113.6(8)

The co-ordination mode of the cyclohexene ligand in this complex is similar to that proposed, from i.r. and n.m.r. data, for a number of substituted triosmium clusters.[5, 10] Recent structural studies on $[Os_3(CO)_{10}(HC{=}CHEt)H]$ [11] and $[Os_3(CO)_{10}(C_2H_3)H]$ [12] have also confirmed this type of bonding. The Os(3)–C(1) distance is in good agreement with the single-bond values of 2.15(2) Å in the but-1-enyl complex,[11] but significantly longer than the value [2.109(2) Å] in the ethylene complex,[12] which was determined by a combined *X*-ray- and neutron-diffraction study. It should, however, be considered as an Os–C σ bond. The C(1)–C(2) unit is unsymmetrically co-ordinated to the Os(4) atom, C(2) being *ca.* 0.128 Å further away. Both the Os(4)–C(1) and Os(4)–C(2) distances are significantly shorter than the comparable bonds in the other two complexes {2.28(2) and 2.46(3) Å for $[Os_3(CO)_{10}(HC{=}CHEt)H]$ [11]}. This suggests a stronger π donation from the ring system. The C(1)–C(2) distance is *ca.* 0.06 Å longer than the theoretical double-bond value (1.33 Å),[13] showing that electron density has been donated to the metal atom from this bond. The two π-bonded carbons are planar, and may be considered as sp^2 hybridised. The remaining bond distances and angles in the cyclohexene ring do not deviate greatly from the expected values. The π system [Os(4), C(1), C(2)] makes an angle of 45.7° with the basal Os_3 plane [Os(2), Os(3), Os(4)].

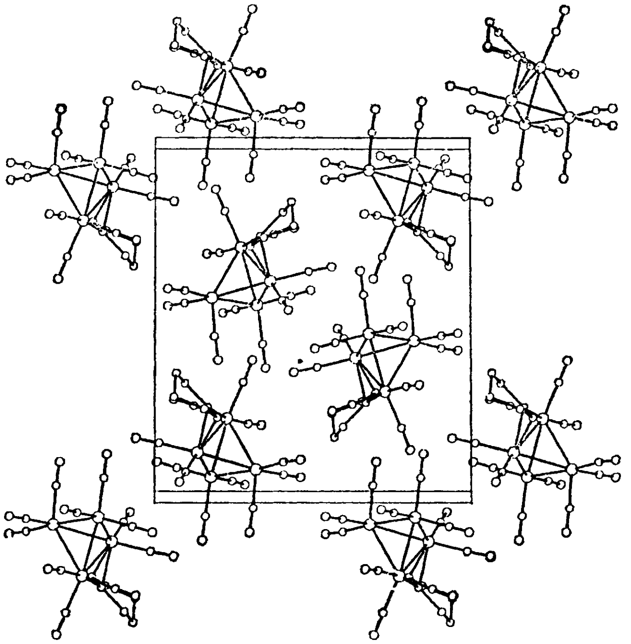


FIGURE 6 Crystal packing diagram for $[Os_4(CO)_{11}(C_6H_9)H_3]$

All the carbonyl ligands are approximately linear, with a maximum angular deviation at the carbons from 180° of *ca.* 6°. These small distortions are probably due to the packing effect of the hydride ligands. This tends to be confirmed by the C–Os–Os bond angles, which are generally more obtuse when the Os–Os bond is considered to be hydride-bridged. There is a maximum deviation of 5.3σ from the mean distance of 1.895 Å for Os–C(carbonyl) bonds, a value which agrees well with the average Os–C bond length (1.901 Å) in $[Os_4(CO)_{12}H_3I]$.[9] There are no significant deviations from the mean C–O distance of 1.146 Å, and this also in good agreement with the value of 1.145 Å in the iodo-complex.

Figure 6 shows a molecular packing diagram of

$[Os_4(CO)_{11}(C_6H_9)H_3]$. There are no abnormally short intramolecular contacts, and the closest approach between an osmium atom and a cyclohexene hydrogen is 2.399 Å, between Os(4) and H(21), the hydrogen on the π-bonded carbon C(2). The molecules are separated by van der Waals distances, and there is only one short intermolecular contact of 2.55 Å, between H(32) and O(13) (at $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$).

Conclusions.—In this work we have demonstrated that the reactions of olefins with cluster species give products which, to some extent, depend on the nature of the clusters. Thus, whereas olefins react with Os_3 clusters to yield, amongst other products, 1,1-derivatives of the olefinic group, the tetranuclear clusters yield specifically the 1,2-complex. This work is now being extended to Os_5 and Os_6 clusters.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer. Carbon monoxide was used as calibrant. Hydrogen-1 n.m.r. spectra were obtained on Varian Associates HA 100 (100 MHz) or XL 100 spectrometers, ^{13}C on the XL 100 operating at 25.2 MHz and equipped with an internal deuterium lock. Mass spectra were recorded on an A.E.I. M.S.12 spectrometer using tris(perfluoroheptyl)-1,3,5-triazine as calibrant. Microanalytical data were obtained by the microanalytical department of this laboratory. Thin-layer chromatography plates were prepared in this laboratory using glass plates (20 cm^2) coated with a 0.3-mm layer of silica gel/CT (Reeves Angel Scientific, type code S13FTLC).

The complexes $[Os_3(CO)_{12}]$ and $[Os_4(CO)_{12}H_4]$ were prepared by previously reported methods. All the reactions were carried out under an atmosphere of dry nitrogen, using dry freshly distilled solvents. Carbon-13 monoxide (91.8 atom % ^{13}C) was purchased from the British Oxygen Company Ltd. Osmium tetraoxide was generously supplied on loan by Johnson, Matthey and Co. Ltd.

General Procedure for Irradiations.—In all cases photolyses were carried out with a HPK 125 lamp in an efficiently cooked Pyrex apparatus of standard design operating at *ca.* 30 °C. The complex $[Os_4(CO)_{12}H_4]$ (0.1 g) was dissolved in benzene (150 cm^3) and the olefin added or passed through this solution for *ca.* 4 h. After removal of solvent *in vacuo* the residual solid was chromatographed on silica using 2% CH_2Cl_2–light petroleum (b.p. 40—60 °C). Two major bands were observed, the upper being unchanged $[Os_4(CO)_{12}H_4]$ and the lower the appropriate product. Yields were in the range 5—50%.

Pyrolysis of the $[Os_4(CO)_{11}(\text{olefin} - H)H_3]$ *Products.*—Typically, a solution of the appropriate complex in n-octane was heated under nitrogen for *ca.* 1 h. Chromatography of the resulting solution using 2% CH_2Cl_2–light petroleum (b.p. 40—60 °C) as eluent gave the $[Os_4(CO)_{11}(\text{olefin} - 2H)H_2]$ complex in *ca.* 70% yield.

X-*Ray Structural Analysis.*—Crystals of $[Os_4(CO)_{11}(C_6H_9)H_3]$ were deposited as elongated rectangular blocks from cyclohexane solution. A single crystal with dimensions *ca.* 0.263 × 0.175 × 0.123 mm was mounted on a Philips PW1100 four-circle diffractometer, and cell constants were derived from the angular measurements of 25 strong reflections ($20 < 2\theta \leqslant 30°$). 8 481 Intensities were then measured out to a $2\theta_{max.}$ of 60°, using graphite-monochromated Mo-K_α radiation and a θ—2θ scan procedure. Weak reflections which gave $I_t - 2(I_t)^{\frac{1}{2}} < I_b$ on the first scan were omitting, I_t being the intensity at the top of the reflection peak and I_b the mean of the two preliminary 5-s background measurements on either side of the peak. The background measuring time was proportional to I_b/I_i, where I_i is the total intensity recorded in the first scan of the reflection peak. A constant scan speed of 0.05° s^{-1} and a variable scan width [θ range $(0.60 + 0.20 \tan \theta)°$] were used. Three standard reflections were measured at regular intervals throughout the data collection and showed no significant variation in intensity.

The variance of the intensity I was calculated [14] as the sum of the variance due to counting statistics and $(0.03I)^{2}$, where the term in I^2 was introduced to allow for other sources of error.[15] I and $\sigma(I)$ were corrected for Lorentz polarization, and an empirical absorption correction was also applied. Equivalent reflections were averaged to give 4882 unique observed intensities [$I > 2.5\sigma(I)$].

Crystal data. $C_{17}H_{12}O_{11}Os_4$, $M = 1\,152.9$, Monoclinic, $a = 9.266(4)$, $b = 14.850(8)$, $c = 16.847(9)$ Å, $\beta = 93.39(3)°$, $U = 2\,314.1$ Å^3, $Z = 4$, $D_c = 3.32$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 219.4 cm^{-1}, space group $P2_1/n$ from systematic absences.

The four osmium atoms were located by multisolution Σ_2 sign expansion, and all the non-hydrogen atoms from a subsequent electron-density difference synthesis. The metal atoms were assigned anisotropic thermal parameters, the light atoms independent isotropic temperature factors, and the structure refined by blocked-cascade least squares to R 0.035. The cyclohexene hydrogen atoms were located from a Fourier difference map, and were included in further cycles of refinement, being assigned a common isotropic thermal parameter and constrained to lie 1.08 Å

TABLE 8

Atom co-ordinates (× 10^4)

	x/a	*y/b*	*z/c*
Os(1)	1 131(1)	3 202(1)	644(1)
Os(2)	3 061(1)	1 773(1)	503(1)
Os(3)	2 325(1)	2 282(1)	2 114(1)
Os(4)	363(1)	1 349(1)	1 095(1)
C(11)	−335(12)	4 071(7)	795(7)
O(11)	−1 239(10)	4 604(6)	837(6)
C(12)	2 640(11)	4 074(6)	540(6)
O(12)	3 552(9)	4 597(6)	492(6)
C(13)	784(10)	3 112(6)	−455(7)
O(13)	474(9)	3 007(6)	−1 128(6)
C(21)	4 103(9)	703(6)	792(6)
O(21)	4 729(8)	69(5)	971(5)
C(22)	4 740(12)	2 446(7)	433(7)
O(22)	5 788(10)	2 858(6)	360(6)
C(23)	3 009(11)	1 607(7)	−594(7)
O(23)	2 998(10)	1 506(6)	−1 277(6)
C(31)	2 033(11)	2 795(7)	3 131(7)
O(31)	1 761(10)	3 080(6)	3 735(6)
C(32)	4 126(10)	2 947(6)	2 021(6)
O(32)	5 139(8)	3 361(5)	2 024(5)
C(33)	3 283(10)	1 239(6)	2 510(6)
O(33)	3 865(8)	598(5)	2 717(5)
C(41)	−1 326(9)	987(5)	497(6)
O(41)	−2 405(8)	786(5)	185(5)
C(42)	668(9)	129(6)	1 375(6)
O(42)	861(9)	−606(5)	1 516(6)
C(1)	270(9)	1 672(5)	2 358(5)
C(2)	−1 066(9)	1 967(6)	2 033(6)
C(3)	−2 491(11)	1 544(7)	2 238(7)
C(4)	−2 316(11)	613(6)	2 584(7)
C(5)	−1 231(12)	674(7)	3 267(7)
C(6)	277(10)	946(6)	3 040(6)

from the relevant carbons in geometrically idealised positions. The hydride hydrogens were not located. At this stage eight reflections suffering from severe extinction effects were zero weighted, and an empirical extinction parameter x, where F_c is multiplied by $[1 - 0.000\,1 + (xF_c^2/\sin\theta)]$, introduced. This refined to a value 0.000 13(3). With the weighting scheme $w = 1/\sigma^2(F)$, $w\Delta^2$ was fairly independent of $|F_o|$ and sin θ. In the final cycle the mean shift-to-error of refined parameters was 0.005 and a final difference synthesis showed no areas of significant electron density. On 4 874 reflections the final residuals were R 0.034 and R' $(=\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|)$ 0.035.

Complex neutral-atom scattering factors[16] were employed, and were corrected for both parts of the anomalous dispersion. Tables 8 and 9 list the final atomic co-ordinates for the non-hydrogen and hydrogen atoms respectively. Details of anisotropic and isotropic thermal parameters, parameters involving hydrogen atoms, molecular planes, and observed and calculated structure factor amplitudes may be found in Supplementary Publication No. SUP 22402 (34 pp.).*

TABLE 9

Hydrogen-atom co-ordinates (× 10^4)

	x/a	y/b	z/c
H(21)	−1 089(9)	2 521(6)	1 617(6)
H(31)	−3 189(11)	1 504(7)	1 702(7)
H(32)	−2 985(11)	1 969(7)	2 666(7)
H(41)	−1 943(11)	155(6)	2 143(7)
H(42)	−3 336(11)	377(6)	2 785(7)
H(51)	−1 603(12)	1 166(7)	3 680(7)
H(52)	−1 157(12)	23(7)	3 553(7)
H(61)	858(10)	1 218(6)	3 560(6)
H(62)	826(10)	352(6)	2 843(6)

After preliminary data reduction on the I.C.L. computer of the Polytechnic of North London, all calculations were carried out on the IBM 370/165 computer at the University of Cambridge using programs written by Dr. G. M. Sheldrick. Figures 1 and 6 were drawn using the plotting program PLUTO written by Dr. W. D. S. Motherwell.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

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