Sequential Synthesis of Some Tetraosmium–Arene Clusters†

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On activation with Me_3NO the tetrahydrido-tetranuclear cluster $[Os_4(\mu\text{-}H)_4(CO)_{12}]$ **1** underwent reaction with cyclohexa-1,3-diene in CH_2Cl_2 under ambient conditions to give, as the major products, the four organometallic clusters $[Os_4(\mu\text{-}H)_3(CO)_{11}(\eta^3\text{-}C_6H_9)]$ **2**, $[Os_4(\mu\text{-}H)_2(CO)_{12}(\eta^2\text{-}C_6H_8)]$ **3**, $[Os_4(\mu\text{-}H)_2(CO)_{11}(\eta^4\text{-}C_6H_8)]$ **4** and $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ **5**. On heating in hexane, **3** is converted into **4** and subsequently **4** into **5**. Compound **5** underwent further reaction with Me_3NO in CH_2Cl_2 in the presence of cyclohexa-1,3-diene to produce $[Os_4(CO)_9(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ **6** and $[Os_4(\mu\text{-}H)_2(CO)_8(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ **7**. Structural analyses of **4** and **7** by single-crystal X-ray diffraction have shown that the C_6H_8 ligand is bonded through two alkene bonds and that the benzene ligand in **7** is co-ordinated in an η^6 fashion. In each case the ligands are bonded to single osmium atoms only. Compound **5** was also found to react with Me_3NO in CH_2Cl_2 in the presence of benzene yielding $[Os_4(CO)_8(\eta^6\text{-}C_6H_6)_2]$ **8**, whilst with either toluene or mesitylene it undergoes arene displacement to produce $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_5Me)]$ **9** or $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_4Me_2\text{-}1,3)]$ **10** respectively.

We are currently involved in a detailed and systematic study of the interactions of arenes with cluster units of differing nuclearity and have established that, in general, arene moieties tend to adopt one of the two dominant bonding arrangements, *viz.* the η^6-terminal or $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$-face capping modes. In some clusters, *e.g.* $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$,[1] both bonding types co-exist. There are also several compounds where the interconversion of these bonding types readily occurs, leading to the formation of a number of isomeric forms as for $[Ru_5C(CO)_{12}(C_6H_6)]$.[2] To date, we have been unable to identify specifically the factors which control these bonding arrangements; however, we and others have observed that for tetrahedral clusters of osmium and cobalt the η^6 mode is apparently the only bonding type observed.[3,4]

In this paper we report a more extended appraisal of the reactions of $[Os_4(\mu\text{-}H)_4(CO)_{12}]$ **1** with cyclohexa-1,3-diene which lead ultimately to the formation of η^6-benzene products.

Results and Discussion

Chemical Synthesis, Characterisation and Mechanistic Proposals.—The tetranuclear cluster $[Os_4(\mu\text{-}H)_4(CO)_{11}(MeCN)]$ **1a**, together with small amounts of the disubstituted derivative $[Os_4(\mu\text{-}H)_4(CO)_{10}(MeCN)_2]$ **1b**, were prepared from the reaction of $[Os_4(\mu\text{-}H)_4(CO)_{12}]$ **1** with Me_3NO in MeCN at room temperature. Reaction of this mixture with cyclohexa-1,3-diene in CH_2Cl_2 at room temperature for 6 h, or the direct reaction of **1** with Me_3NO in CH_2Cl_2 in the presence of cyclohexa-1,3-diene, gives several products, of which four major compounds have been identified on the basis of their spectroscopic properties (see Table 1) and crystal structure determinations as $[Os_4(\mu\text{-}H)_3(CO)_{11}(\eta^3\text{-}C_6H_9)]$ **2**, $[Os_4(\mu\text{-}H)_2(CO)_{12}(\eta^2\text{-}C_6H_8)]$ **3**, $[Os_4(\mu\text{-}H)_2(CO)_{11}(\eta^4\text{-}C_6H_8)]$ **4** and $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ **5**. Other minor products have not yet been identified, although their IR spectroscopic data appear consistent with their formulation as derivatives containing a basic Os_4 cluster unit. In a series of separate experiments we have further established that on heating in hexane compound **3** undergoes conversion into **4**, which in turn undergoes conversion into **5** (see Scheme 1) in low yield.

The two compounds **2** and **5** have been previously observed and their molecular structures determined by single-crystal X-ray diffraction analysis.[3,5] We have attempted to determine the molecular structure of **3** in the solid state by X-ray diffraction. However, the crystal was found to be affected by some rather unpleasant disorder which could not be fully rationalised. From the information currently available, together with spectroscopic data (see Table 1), the most probable structure corresponds to that shown in Scheme 1, *i.e.* a tetrahedron of osmium atoms containing eleven terminal and one bridging carbonyl ligand and an η^2-bonded diene ligand. Compound **4** has also been examined by spectroscopic and X-ray diffraction methods and its molecular structure determined from crystals grown from a toluene solution at −5 °C (see below). The mass spectrum of **4** exhibits a parent peak at *m*/*z* 1150 (calc. 1151) followed by the loss of eleven CO groups in succession. The ^1H NMR spectrum contains a broad resonance at δ −19.70 typical of a hydride and three resonances at δ 5.58, 3.96 and 2.02 with relative intensities 2:2:4. The former two signals can be assigned to the olefinic protons of the diene, the latter to the aliphatic ring protons. As anticipated, the compound consists of an Os_4 tetrahedron and contains a C_6H_8 ligand bonded to a single osmium atom in the η^4 mode. The compounds **3**–**5** emerge as a closely related series. As a CO ligand is lost, additional electron-pair donation from the C_6 organic fragment is observed, paralleling the change from an η^2- to an η^4- and then to an η^6-bonding configuration. The conversion of **4** into **5** necessitates not only the loss of a CO ligand, but also the concomitant cleavage of two C–H bonds and loss of H_2. We have no evidence to suggest that hydrogenation of the $\eta^6\text{-}C_6H_6$ in **5** occurs.

We have also investigated the photochemistry of these derivatives. On irradiation in toluene and in the presence of cyclohexa-1,3-diene, cluster **1b** reacts to produce more or less the same range of derivatives **2**, **4** and **5** (Scheme 2). Another activated cluster, $[Os_4(\mu\text{-}H)_4(CO)_{11}(NMe_3)]$ **1c**, reacts similarly. Again, in a separate experiment, we have established that on

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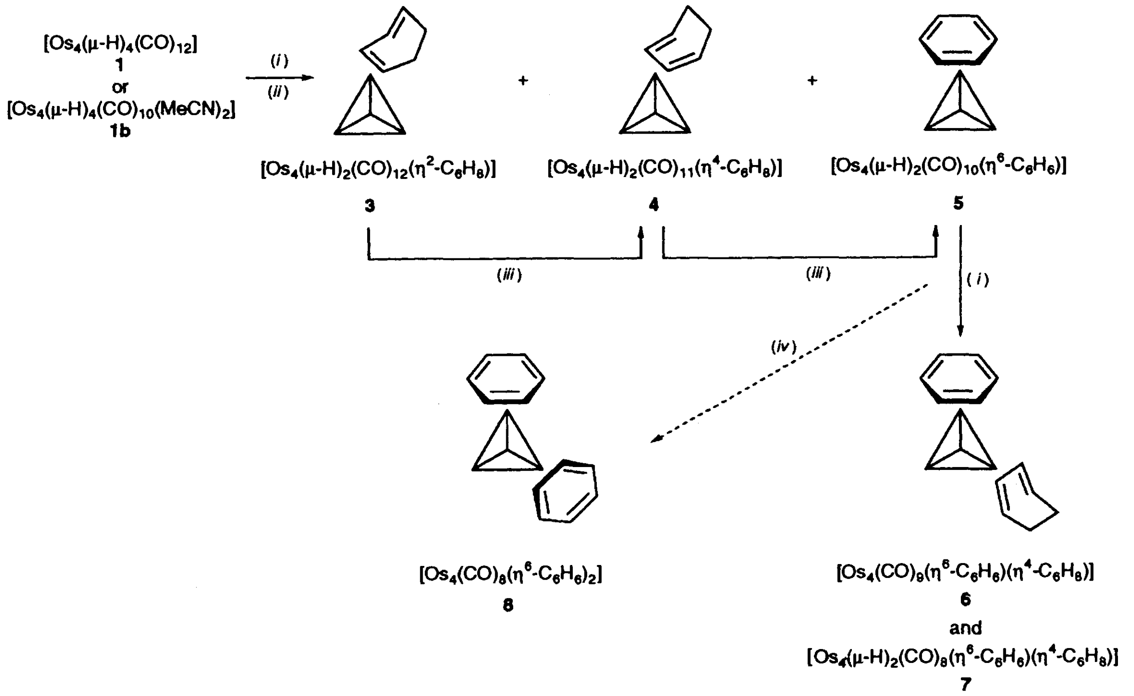
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



Scheme 1 Sequential formation of clusters 3–8. (*i*) 3.2 equivalents Me_3NO–CH_2Cl_2–1,3-C_6H_8; (*ii*) CH_2Cl_2–1,3-C_6H_8; (*iii*) heat, hexane; (*iv*) 3.2 equivalents Me_3NO–CH_2Cl_2–C_6H_6

irradiation **4** is smoothly converted into **5**. These observations lead us to believe that the same process, *viz*. ejection of CO, is the primary step for both the thermal and photolytic reactions; by this means 58-electron co-ordinatively unsaturated intermediate compounds are formed, and these then undergo reaction with the appropriate substrate.

The product **2** is commonly observed under all reaction conditions studied. For this product to be formed the cyclohexa-1,3-diene is required to undergo partial hydrogenation and C–H bond formation, and also C–H cleavage and Os–C σ-bond formation. This cluster does not appear to be an active intermediate in the formation of **3**–**5**, instead it appears to be an intermediate on route to the formation of a σ, σ, π complex related to the benzyne derivative $[Os_3(\mu\text{-}H)_2(CO)_9(C_6H_4)]$.[6] Further studies of this compound are in progress.[7]

The η[6]-benzene product, **5**, undergoes further reaction with Me_3NO in CH_2Cl_2 in the presence of cyclohexa-1,3-diene to produce the compounds $[Os_4(CO)_9(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ **6** and $[Os_4(\mu\text{-}H)_2(CO)_8(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ **7**. If benzene is used in the place of cyclohexa-1,3-diene a new product, tentatively characterised as $[Os_4(CO)_8(\eta^6\text{-}C_6H_6)_2]$ **8**, results in low yield (Scheme 1). Compound **6** has previously been reported as one of the products of the reaction of $[Os_4(\mu\text{-}H)_2(CO)_{10}(MeCN)_2]$ with cyclohexa-1,3-diene under rather more vigorous conditions and characterised by X-ray analysis.[3] The second compound, **7**, has been prepared for the first time and identified by spectroscopic techniques and X-ray diffraction analysis on crystals obtained by the slow evaporation of a $CDCl_3$ solution at room temperature. Again the compound adopts a tetrahedron of osmium atoms with a C_6H_8 ligand bound in an η^4 mode and the benzene ligand in an η^6 mode, both to single osmium atoms (see Fig. 2). The mass spectrum of **7** contains a strong parent peak at *m*/*z* 1144 (calc. 1145). This is followed by the successive loss of several CO groups. At room temperature the ^1H NMR spectrum exhibits two broad resonances in the hydride region at δ −15.72 and −19.44. A singlet resonance is observed at δ 5.74 with a relative intensity of 6 which is consistent with a terminally bound benzene ligand. The diene gives rise to four broad signals at δ 5.04, 3.55, 2.16 and 1.67 with relative intensities 2:2:2:2; the first two are probably derived from the olefinic protons and the last two from the aliphatic ring protons. On cooling these broad signals are each resolved into a series of multiplet resonances. The low-temperature spectrum is very complicated and has not been fully resolved, although the change in broadness with temperature does indicate a degree of fluxionality. Inspection of the crystal structure indicates that each proton of the diene ring should be chemically inequivalent, and therefore give eight signals. Clearly this is not the case and rapid rotation/flexing of the ring may be responsible. Compound **8** has also been prepared for the first time and identified on the basis of its spectroscopic properties. A molecular ion is observed at *m*/*z* 1140 (calc. 1140) in the mass spectrum, followed by the sequential loss of several carbonyl ligands, and its ^1H NMR spectrum in $CDCl_3$ reveals a singlet at δ 5.75 (12 H), which is consistent with two apically bound benzene molecules. This value is comparable to that observed for related systems such as $[Os_3(CO)_9(R_2C_2)(\eta^6\text{-}C_6H_6)]$ (δ 5.94),[9] compound **6** (δ 5.75),[3] and **7** (δ 5.74). The presence of a single benzene resonance requires a plane of symmetry in the molecule (or some benzene movement to generate a plane of symmetry) and, as expected, the benzene must undergo free rotation.

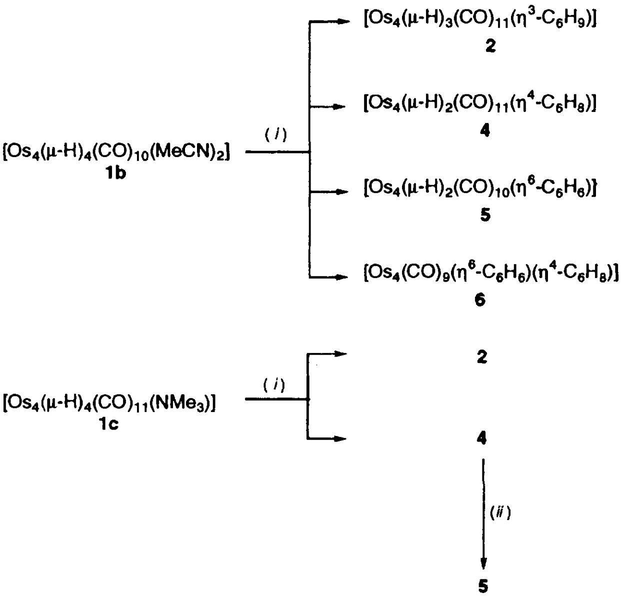
It is known that the tetranuclear cobalt cluster $[Co_4(CO)_9(\eta^6\text{-}C_6H_6)]$ readily undergoes arene exchange with C_6H_5Me, $C_6H_4Me_2$-1,3 and $C_6H_3Me_3$-1,3,5.[10] In contrast, it would appear from information currently available that the face-capping benzene moieties found in clusters based on Ru_3,[11] Os_3,[1] Ru_5C,[2] Ru_6C[1] and Os_6[12] units are far more resistant to exchange. In this work we have found that cluster **5** also undergoes arene exchange. On heating **5** in toluene the cluster $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_5Me)]$ **9** is produced and on heating **5** in octane in the presence of xylene the cluster $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_4Me_2\text{-}1,3)]$ **10** is slowly formed (see Scheme 3). There is no evidence to suggest that these substitutions are reversible. Both complexes **9** and **10** were identified by the usual spectroscopic methods (see Table 1) and their molecular structures confirmed by single-crystal X-ray diffraction studies.[13]

Complex **9** has also been prepared by an alternative route. Treatment of the activated clusters $[Os_4(\mu\text{-}H)_4(CO)_{11}(NMe_3)]$

Table 1 Spectroscopic data for complexes **2–11**

Compound	IR($\tilde{\nu}_{CO}$/cm^{-1})	Mass spectrum, obs. (calc.) *m/z*	^{1}H NMR ($CDCl_3$)
2 [$Os_4(\mu-H)_3(CO)_{11}(\eta^3-C_6H_9)$]	^{a} 2098w, 2066vs, 2051s, 2037s, 2022s, 2010vs, 1995ms, 1985m, 1954mw	1152 (1152)	4.19 (br s, 1 H), 3.33 (t of AB, q, 2 H), 2.75 (m, 1 H), 2.50 (br d, 1 H), 1.65 (m, 2 H), 1.30 (m, 2 H), −15.17 (s, 1 H), −19.25 (s, 1 H), −20.74 (s, 1 H)
3 [$Os_4(\mu-H)_2(CO)_{12}(\eta^2-C_6H_8)$]	^{a} 2080m, 2060w, 2038vs, 2021s, 1995m, 1984w, 1956w, 1880w	1179 (1178)	4.95 (m, 2 H), 3.26 (m, 1 H), 3.06 (m, 1 H), 2.45 (m, 1 H), 1.82 (m, 1 H), 1.28 (m, 1 H), 1.11 (m, 1 H), −19.62 (br s, 2 H)
4 [$Os_4(\mu-H)_2(CO)_{11}(\eta^4-C_6H_8)$]	^{a} 2092w, 2069s, 2049s, 2012s, 1998m, 1850vw ^{b} 2092m, 2066vs, 2044s, 2008s, 1842w	1150 (1151)	5.58 (m, 2 H), 3.96 (br s, 2 H), 2.02 (app. AB q, 4 H), −19.70 (br s, 2 H)
5 [$Os_4(\mu-H)_2(CO)_{10}(\eta^6-C_6H_6)$]	^{a} 2083w, 2063m, 2037s, 2005m, 1997m, 1956w ^{b} 2082m, 2060s, 2033s, 1993s (br), 1959w	1120 (1120)	5.95 (s, 6 H), −19.04 (br s, 1 H), −20.70 (br s, 1 H)
6 [$Os_4(CO)_9(\eta^6-C_6H_6)(\eta^4-C_6H_8)$]	^{b} 2080w, 2055s, 2018vs, 1976m, 1949w, 1850w	1170 (1170)	5.75 (s, 6 H), 5.46 (m, 1 H), 5.37 (m, 1 H), 4.49 (br m, 1 H), 3.58 (br m, 1 H), 2.36 and 2.12 (app. AB q, 2 H), 1.95 and 1.84 (app. AB, q, 2 H)
7 [$Os_4(\mu-H)_2(CO)_8(\eta^6-C_6H_6)(\eta^4-C_6H_8)$]	^{a} 2068s, 2049m, 2036s, 2021m, 1996vs, 1987s, 1880w ^{b} 2064vs, 2047m, 2022s, 1984vs (br), 1942w, 1845w	1144 (1145)	5.74 (s, 6 H), 5.04 (br m, 2 H), 3.55 (br m, 2 H), 2.16 (br m, 2 H), 1.67 (br m, 2 H), −15.72 (br s, 1 H), −19.44 (br s, 1 H)
8 [$Os_4(CO)_8(\eta^6-C_6H_6)_2$]	^{b} 2059w, 2050m, 2032m, 2017m, 1988vs, 1933m	1140 (1140)	5.75 (s, 12 H)
9 [$Os_4(\mu-H)_2(CO)_{10}(\eta^6-C_6H_5Me)$]	^{a} 2083w, 2062s, 2037s, 2022m, 2004m, 1997s, 1956w ^{b} 2080w, 2058s, 2032s, 1991s, 1955w (br), 1778vw (br)	1134 (1134)	6.36 (t, 1 H), 6.22 (br s, 2 H), 5.62 (d, 2 H), 2.42 (s, 3 H), −19.02 (br s, 1 H), −20.65 (br s, 1 H)
10 [$Os_4(\mu-H)_2(CO)_{10}(\eta^6-C_6H_4Me_2-1,3)$]	^{b} 2078w, 2058s, 2031s, 1991s (br), 1952w (br)	1148 (1148)	
11 [$Os_4(\mu-H)_3(CO)_{11}(C_8H_8Me)$] **a**	^{a} 2099w, 2067vs, 2052s, 2037s, 2023m, 2007m, 1996mw, 1984w	1166 (1166)	
b	^{a} 2098w, 2065s, 2052m, 2038m, 2022ms, 2011s, 1986w, 1935w	1166 (1166)	

^{a} Recorded in hexane solution. ^{b} Recorded in CH_2Cl_2 solution.



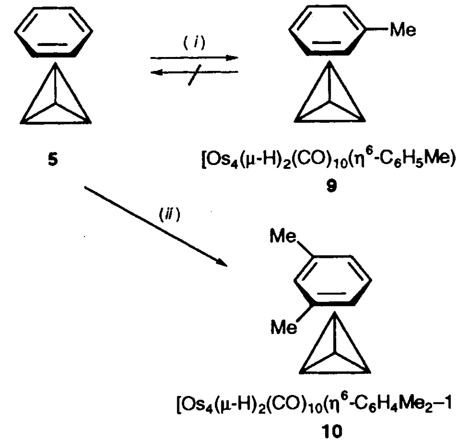
Scheme 2 Products of the photolytic reactions of compounds **1b** and **1c** with cyclohexa-1,3-diene. (*i*) Irradiation in toluene in the presence of 1,3-C_6H_8, 4 h; (*ii*) prolonged irradiation in toluene, 20 h

1c or [$Os_4(\mu-H)_4(CO)_{10}(MeCN)_2$] **1b** with 3-methylcyclohexa-1,4-diene in CH_2Cl_2 under reflux yields two main products: [$Os_4(\mu-H)_2(CO)_{10}(\eta^6-C_6H_5Me)$] **9** and [$Os_4(\mu-H)_3(CO)_{11}(C_6H_8Me)$] **11**. Cluster **11** has been isolated in two distinct isomeric forms **11a** and **11b** (see Scheme 4) which have been characterised on the basis of spectroscopic evidence (see Table 1). These derivatives are clearly analogues of cluster **2**.

The mechanism by which certain of these interconversions occur is of some relevance. Given the formation of compound **2** involves both the hydrogenation and isomerisation of coordinated cyclohexa-1,3-diene and that the formation of **5** involves dehydrogenation of the same diene, we tend to believe that the reaction sequence requires both the presence of a 'sacrificial' and a 'benefactor' molecule of cyclohexa-1,3-diene and suggests the mechanism shown in Scheme 5. This closely resembles a scheme suggested for the reaction of [$Os_3(\mu-H)_2(CO)_{10}$] with C_2H_4 to give derivatives of C_2H_2 and C_2H_6.[14]

Molecular Structures of Compounds **4** *and* **7** *in the Solid State.*—The solid-state molecular structures of [$Os_4(\mu-H)_2(CO)_{11}(\eta^4-C_6H_8)$] **4** and of its benzene derivative [$Os_4(\mu-H)_2(CO)_8(\eta^6-C_6H_6)(\eta^4-C_6H_8)$] **7** are shown in Figs. 1 and 2 respectively. Relevant structural parameters are given in Tables 2 and 3 respectively. Both molecules possess a tetrahedral metal-atom framework. The Os–Os distances range from 2.8069(7) to 2.9354(7) Å in **4** and from 2.7462(10) to 2.9001(10) Å in **7**. The C_6H_8 ligand is terminally bound to one osmium atom of the polyhedron in both clusters. The co-ordination mode is of the η^4 type as observed in the previously reported species [$Os_4(CO)_9(\eta^6-C_6H_6)(\eta^4-C_6H_8)$] **6**.[3] The Os–C($C_6H_8$) bonding distances show large differences between the three structures: in **4** two bonds are 'short' [Os(3)–C(1D) 2.200(13), Os(3)–C(2D)

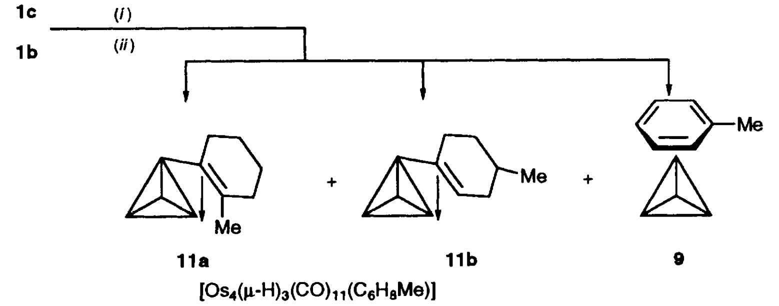
2.191(13) Å] and two 'long' [Os(3)–C(3D) 2.226(13), Os(3)–C(6D) 2.248(13) Å]; in **7** three bonds are instead almost equivalent [Os(1)–C(2D) 2.182(21), Os(1)–C(3D) 2.202(22), Os(1)–C(4D) 2.191(23) Å] and one is 'long' [Os(1)–C(1D) 2.278(20) Å]; while they range between 2.20(2) and 2.24(2) and between 2.17(2) and 2.27(2) Å in the two independent molecules of species **6**. Molecule **7** also carries an η^6-bound benzene ligand as in **6**. The Os–C (benzene) distances in **7** are in the range 2.202(24)–2.295(24) Å, while in **6** they range between 2.20(1) and 2.29(1) Å for one independent molecule, whilst in the second all Os–C bond lengths are 2.25(1) Å. All these differences cannot easily be ascribed to differences in bonding between the ligands and the cluster cores. Rather they point to possible effects of intermolecular interactions (*viz.* packing forces) on the geometric features of these 'soft' bonding interactions.



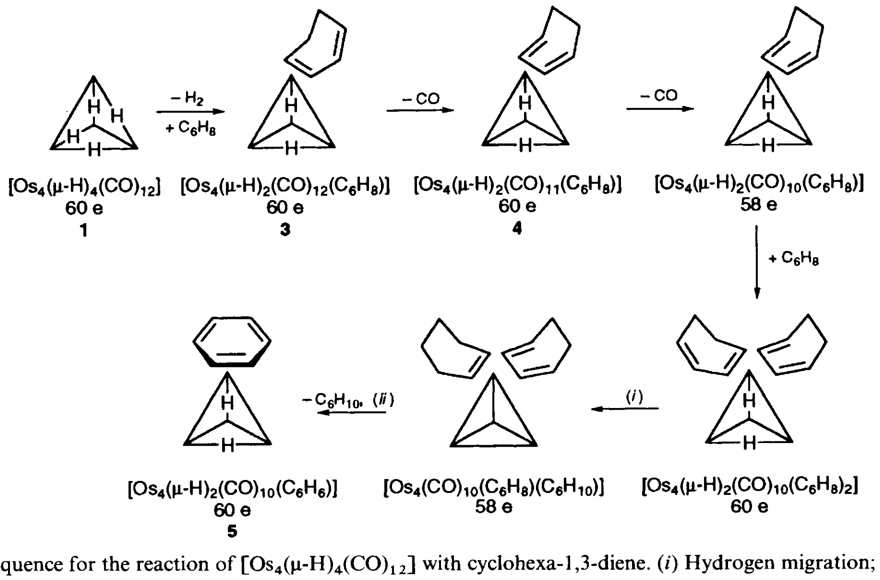
Scheme 3 Arene-exchange reactions of $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ **5**. (*i*) Heating in toluene under reflux; (*ii*) heating in octane at 110 °C in the presence of xylene

The conformation of the two C_6H_8 ligands in the two complexes is of the boat type with the delocalised C_4 system interacting with the osmium atoms while the CH_2CH_2 systems bend away from the cluster core. In **4** there are eleven CO ligands, nine of which are bonded in a terminal mode, three to each of the osmium atoms not involved in the bonding with the C_6H_8 ligand, while the remaining two CO ligands are in asymmetric bridging positions along the Os(1)–Os(3) and Os(3)–Os(4) edges with shorter distances from Os(3) [Os(3)–C(14) 1.933(13), Os(3)–C(31) 1.913(14) Å]. The distribution of the eight CO ligands in **7** can easily be derived from that of **4**: the C_6H_8-bound Os atom is involved in two asymmetric bridging interactions as in **4**, and the benzene ligand is substituted for the three terminally bound CO groups of a neighbouring atom. The relationship with the structure of $[Os_4(CO)_9(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ **6** can be appreciated: the ninth carbonyl [taking the place of the two H(hydride) ligands in the structure of **7**] is in a near triply bridging position over the metal core, generating a far more congested steric situation than in **7**.

The H (hydride) atoms in compounds **4** and **7** could not be located directly from the Fourier maps. However a close analysis of the molecular space-filling diagram of **4** (see Fig. 3) revealed the existence of two large cavities in the ligand envelope along the Os(1)–Os(4) and Os(2)–Os(3) edges. The hydrides were thought to be placed along these bonds on the basis of the least-energetic steric interactions with the surrounding ligands. The Os(1)–Os(4) and Os(2)–Os(3) are



Scheme 4 Formation of clusters **9**, **11a** and **11b**. (*i*) 3-Methylcyclohexa-1,4-diene in toluene at 60 °C; (*ii*) 3-methylcyclohexa-1,4-diene in CH_2Cl_2 under reflux



Scheme 5 A possible sequence for the reaction of $[Os_4(\mu\text{-}H)_4(CO)_{12}]$ with cyclohexa-1,3-diene. (*i*) Hydrogen migration; (*ii*) C–H bond cleavage, hydrogen migration

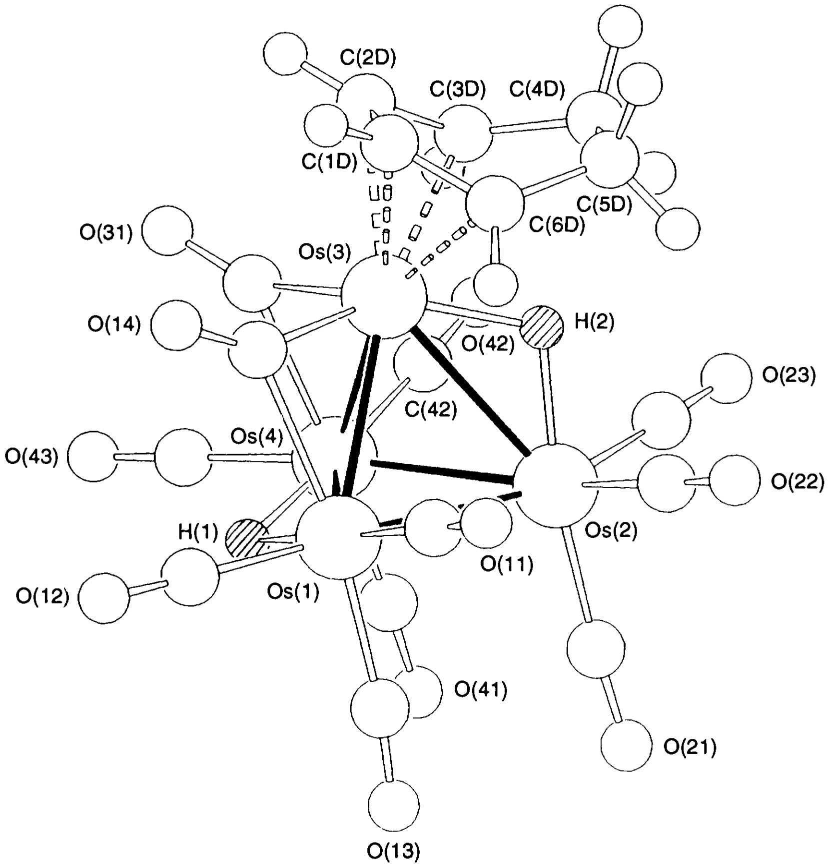


Fig. 1 Molecular structure of $[Os_4(\mu\text{-}H)_2(CO)_{11}(\eta^4\text{-}C_6H_8)]$ **4** in the solid state showing the atom labelling; the C atoms of the carbonyl ligands bear the same numbers as those of the corresponding O atoms. The H (hydride) positions are those afforded by XHYDEX,[8] and correspond to niches in the ligand coverage

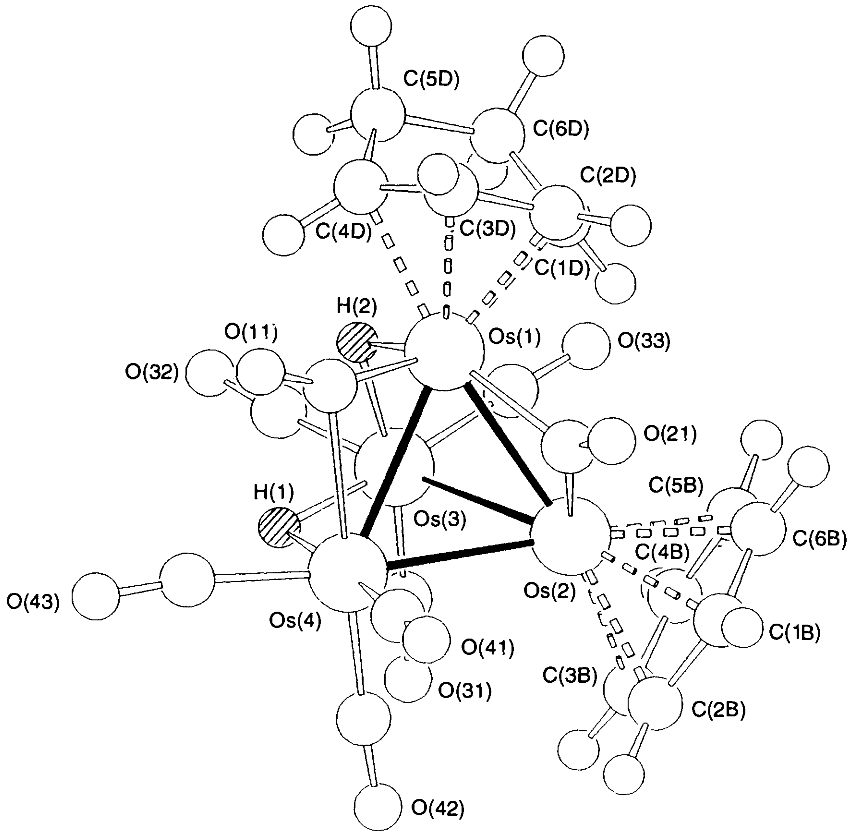


Fig. 2 Molecular structure of $[Os_4(\mu\text{-}H)_2(CO)_8(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ **7** in the solid state showing the atom labelling. Details as in Fig. 1

Table 2 Selected bond distances (Å) and angles (°) for compound **4**

Os(1)–Os(2)	2.8277(8)	Os(3)–C(14)	1.933(13)
Os(1)–Os(3)	2.8295(8)	Os(1) ··· C(14)	2.326(13)
Os(1)–Os(4)	2.9354(7)	C(14)–O(14)	1.172(16)
Os(2)–Os(3)	2.9009(8)	Os(3)–C(31)	1.913(14)
Os(2)–Os(4)	2.8113(7)	Os(4) ··· C(31)	2.311(14)
Os(3)–Os(4)	2.8069(7)	C(31)–O(31)	1.179(17)
Os(3)–C(1D)	2.200(13)	C(1D)–C(2D)	1.442(18)
Os(3)–C(2D)	2.191(13)	C(2D)–C(3D)	1.449(18)
Os(3)–C(3D)	2.226(13)	C(3D)–C(4D)	1.525(19)
Os(3)–C(6D)	2.248(13)	C(4D)–C(5D)	1.502(19)
mean Os–C (terminal)	1.912(14)	C(5D)–C(6D)	1.477(18)
mean C–O (terminal)	1.137(18)	C(6D)–C(1D)	1.357(18)
Os(3)–C(14)–O(14)	148.4(11)	C(3D)–C(4D)–C(5D)	110.5(11)
Os(3)–C(31)–O(31)	150.0(12)	C(4D)–C(5D)–C(6D)	112.7(11)
C(1D)–C(2D)–C(3D)	112.5(11)	C(5D)–C(6D)–C(1D)	119.9(12)
C(2D)–C(3D)–C(4D)	119.0(11)	C(6D)–C(1D)–C(2D)	116.6(12)

Table 3 Selected bond distances (Å) and angles (°) for compound **7**

Os(1)–Os(2)	2.7462(10)	Os(2)–C(21)	2.03(2)
Os(1)–Os(3)	2.8628(10)	Os(1) ··· C(21)	2.11(2)
Os(1)–Os(4)	2.8815(10)	C(21)–O(21)	1.150(25)
Os(2)–Os(3)	2.8191(10)	Os(1)–C(11)	1.889(21)
Os(2)–Os(4)	2.7754(10)	Os(4) ··· C(11)	2.515(21)
Os(3)–Os(4)	2.9001(10)	C(11)–O(11)	1.16(3)
Os(1)–C(1D)	2.278(20)	Os(2)–C(1B)	2.202(24)
Os(1)–C(2D)	2.182(21)	Os(2)–C(2B)	2.250(20)
Os(1)–C(3D)	2.202(22)	Os(2)–C(3B)	2.258(24)
Os(1)–C(4D)	2.191(23)	Os(2)–C(4B)	2.295(24)
mean Os–C (terminal)	1.886(23)	Os(2)–C(5B)	2.248(21)
mean C–O (terminal)	1.15(3)	Os(2)–C(6B)	2.206(22)
C(1D)–C(2D)	1.43(3)	C(1B)–C(2B)	1.40(4)
C(2D)–C(3D)	1.37(3)	C(2B)–C(3B)	1.44(3)
C(3D)–C(4D)	1.42(3)	C(3B)–C(4B)	1.42(3)
C(4D)–C(5D)	1.47(3)	C(4B)–C(5B)	1.37(3)
C(5D)–C(6D)	1.56(3)	C(5B)–C(6B)	1.35(3)
C(6D)–C(1D)	1.49(3)	C(6B)–C(1B)	1.37(3)
C(1D)–C(2D)–C(3D)	116.2(19)	C(1B)–C(2B)–C(3B)	116.4(22)
C(2D)–C(3D)–C(4D)	115.3(20)	C(2B)–C(3B)–C(4B)	119.4(22)
C(3D)–C(4D)–C(5D)	116.3(20)	C(3B)–C(4B)–C(5B)	120.7(22)
C(4D)–C(5D)–C(6D)	111.5(19)	C(4B)–C(5B)–C(6B)	119.3(21)
C(5D)–C(6D)–C(1D)	110.2(18)	C(5B)–C(6B)–C(1B)	122.5(21)
C(6D)–C(1D)–C(2D)	118.8(18)	C(6B)–C(1B)–C(2B)	121.6(22)

the longest M–M bonds of the molecule [2.9354(7) and 2.9009(8) Å, respectively]. The molecular space-filling diagram of **7** (see Fig. 4) was also analysed in order to establish the correct positions of the two hydrides. Again, the presence of two large niches within the ligand envelope was a first indication of the likely positions of the two missing H atoms. By analogy with **4**, one hydride was thought to be spanning the Os(3)–Os(4) edge, occupying a cavity formed by four carbonyl ligands [C(31)O(31), C(32)O(32), C(42)O(42) and C(43)–O(43)], whilst the second one bridges the Os(1)–Os(3) bond and is accommodated in the hollow of the diene and two carbonyls [C(32)O(32) and C(33)–O(33)]. The Os(3)–Os(4) bond is the longest [2.9001(10) Å] of the whole M–M set, while the edge-bridging location of the second hydride, Os(1)–Os(3), does not result in an equally noticeable lengthening of this bond with respect to the others in the molecule.

The program XHYDEX[8] was used to calculate the site of minimum potential energy corresponding to the hydride locations. The Os–H distance was chosen to be 1.83 Å. The results of the calculations run on all the edges of the tetrahedra were in total agreement with the supposedly preferred location of the hydrides within the largest cavities in the ligand envelope. The H (hydride) coordinates calculated *via* XHYDEX are reported in Tables 4 and 5 for the corresponding compounds.

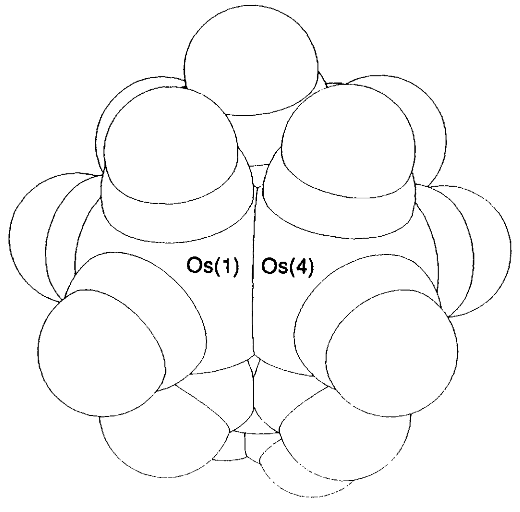


Fig. 3 Space-filling representation of the structure of compound **4** showing a large niche in the ligand envelope corresponding to the XHYDEX location of H(1) (compare with Fig. 1)

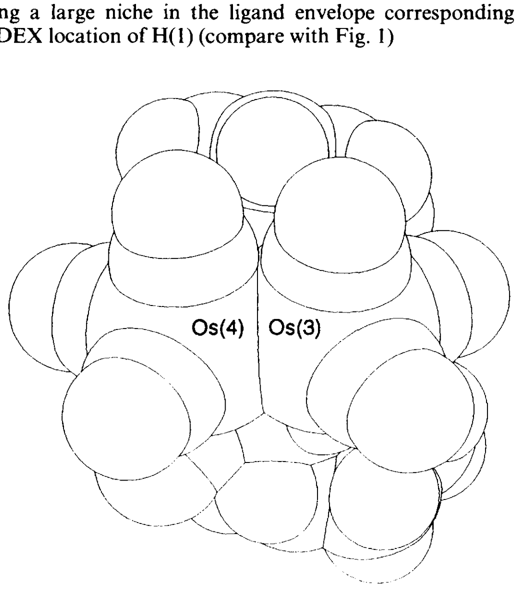


Fig. 4 Space-filling representation of the structure of compound **7** showing a large niche in the ligand envelope corresponding to the XHYDEX location of H(1) (compare with Fig. 2)

Conclusion

In this work we have shown that the ligand cyclohexa-1,3-diene, once bonded to an Os_4 unit, may undergo either hydrogenation and isomerisation or dehydrogenation to yield ultimately benzene derivatives. We believe that these reactions require the interaction of two cyclohexa-1,3-dienes and a mechanistic scheme has been proposed (see Scheme 5). These observations parallel those previously made for the related reactions of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ and are of relevance to the hydrogenation of benzene on a metallic [111] surface.[15] Displacement of η^6-C_6H_6 occurs readily. This behaviour is in contrast to that shown by the $\mu_3:\eta^2:\eta^2:\eta^2$-bonded form and again may be of relevance to surface studies.

Experimental

Synthesis and Characterization.—All experiments were carried out with the exclusion of air using freshly distilled solvents. Product separation was achieved by thin-layer chromatography using plates supplied by Merck pre-coated with a 0.25 mm layer of Kieselgel $60F_{254}$. Eluents were mixed from standard laboratory-grade solvents. Infrared spectra were recorded in dichloromethane and/or hexane using NaCl cells

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

Atom	*x*	*y*	*z*
Os(1)	0.087 23(6)	0.820 03(4)	0.788 19(3)
Os(2)	0.307 35(6)	0.674 13(4)	0.834 16(3)
Os(3)	0.184 16(6)	0.806 84(4)	0.939 59(3)
Os(4)	0.413 07(5)	0.866 81(4)	0.844 46(3)
C(11)	−0.076 4(15)	0.723 8(9)	0.793 4(7)
O(11)	−0.174 3(12)	0.669 9(8)	0.795 9(6)
C(12)	−0.053 6(15)	0.921 2(10)	0.754 6(7)
O(12)	−0.149 0(11)	0.978 5(7)	0.736 2(6)
C(13)	0.143 6(14)	0.785 9(10)	0.688 0(9)
O(13)	0.171 9(11)	0.773 4(8)	0.631 2(4)
C(14)	0.011 4(15)	0.885 8(9)	0.897 9(7)
O(14)	−0.092 0(11)	0.940 2(7)	0.907 3(6)
C(21)	0.367 4(15)	0.641 0(10)	0.737 6(8)
O(21)	0.401 9(12)	0.616 1(7)	0.682 3(5)
C(22)	0.168 5(16)	0.567 4(9)	0.836 6(7)
O(22)	0.083 7(13)	0.502 5(8)	0.839 0(6)
C(23)	0.488 2(16)	0.613 5(11)	0.882 7(8)
O(23)	0.596 2(12)	0.576 1(8)	0.913 8(6)
C(31)	0.295 4(15)	0.927 5(11)	0.945 6(8)
O(31)	0.323 2(12)	1.001 7(8)	0.975 7(6)
C(41)	0.518 2(14)	0.829 1(9)	0.761 1(7)
O(41)	0.585 9(11)	0.810 3(8)	0.710 5(5)
C(42)	0.582 5(13)	0.820 3(9)	0.910 5(7)
O(42)	0.675 7(10)	0.790 9(8)	0.952 7(5)
C(43)	0.480 8(14)	0.997 2(12)	0.841 4(7)
O(43)	0.524 2(12)	1.075 9(8)	0.839 8(5)
C(1D)	0.026 9(13)	0.790 3(10)	1.030 2(7)
C(2D)	0.177 7(14)	0.829 2(10)	1.058 3(7)
C(3D)	0.309 4(15)	0.765 0(10)	1.046 4(7)
C(4D)	0.290 1(15)	0.656 9(11)	1.059 7(7)
C(5D)	0.127 3(15)	0.623 7(10)	1.031 6(7)
C(6D)	0.030 2(14)	0.702 5(10)	0.997 1(7)
H(1)*	0.242 73	0.912 30	0.786 74
H(2)*	0.270 86	0.688 80	0.929 16

* Hydrogen-atom coordinates calculated by XHYDEX.[8]

Table 5 Fractional atomic coordinates for compound **7**

Atom	*x*	*y*	*z*
Os(1)	0.236 82(8)	0.574 33(8)	0.184 48(5)
Os(2)	0.192 43(8)	0.724 91(8)	0.335 43(5)
Os(3)	0.434 79(8)	0.792 34(8)	0.194 21(5)
Os(4)	0.485 12(8)	0.492 92(8)	0.291 01(5)
C(11)	0.373 1(23)	0.367 2(24)	0.187 1(13)
O(11)	0.434 5(17)	0.237 8(16)	0.167 5(11)
C(21)	0.097 5(22)	0.546 6(22)	0.310 1(13)
O(21)	0.008 6(16)	0.467 8(18)	0.341 6(9)
C(31)	0.521 5(24)	0.899 0(30)	0.262 6(14)
O(31)	0.579 4(19)	0.964 2(20)	0.303 1(11)
C(32)	0.585 7(22)	0.828 4(23)	0.095 9(13)
O(32)	0.676 0(19)	0.867 1(23)	0.031 4(10)
C(33)	0.262 7(23)	0.966 4(25)	0.171 7(14)
O(33)	0.154 0(16)	1.072 9(16)	0.160 7(10)
C(41)	0.394 6(22)	0.343 1(23)	0.369 6(13)
O(41)	0.341 2(18)	0.252 1(17)	0.415 0(9)
C(42)	0.564 0(30)	0.569 0(30)	0.377 2(16)
O(42)	0.603 6(19)	0.618 3(20)	0.431 5(11)
C(43)	0.686 1(22)	0.338 1(23)	0.245 5(13)
O(43)	0.808 0(17)	0.248 4(19)	0.227 0(11)
C(1B)	0.016(3)	0.729(3)	0.460 1(16)
C(2B)	0.166(3)	0.747(3)	0.477 9(17)
C(3B)	0.229(3)	0.877(3)	0.434 0(16)
C(4B)	0.137(3)	0.980(3)	0.377 9(16)
C(5B)	−0.005 1(23)	0.951 0(25)	0.360 9(14)
C(6B)	−0.064(3)	0.830(3)	0.403 2(14)
C(1D)	0.030 5(22)	0.746 9(23)	0.128 8(13)
C(2D)	−0.003 8(24)	0.594 1(24)	0.148 8(14)
C(3D)	0.108 9(24)	0.471(3)	0.105 0(14)
C(4D)	0.254(3)	0.509(3)	0.052 1(15)
C(5D)	0.224(3)	0.646(3)	−0.008 2(16)
C(6D)	0.094(3)	0.791(3)	0.037 4(15)
H(1)*	0.593 27	0.611 54	0.208 14
H(2)*	0.388 84	0.674 01	0.118 04

* Hydrogen-atom coordinates calculated by XHYDEX.[8]

(path length 0.1 mm) on a Perkin-Elmer 1710 Fourier-transform spectrometer using carbon monoxide gas as calibrant, mass spectra by fast atom bombardment on a Kratos MS50TC instrument using CsI as calibrant and ^1H NMR spectra in $CDCl_3$ using a Bruker AM360 spectrometer, chemical shifts being reported relative to $SiMe_4$. The $[Os_4(\mu\text{-}H)_4(CO)_{12}]$ cluster was prepared by the literature procedure.[16] Trimethylamine *N*-oxide was sublimed prior to use and cyclohexa-1,3-diene was used as received from Aldrich Chemicals.

Preparation of $[Os_4(\mu\text{-}H)_4(CO)_{11}(MeCN)]$ **1a** *and* $[Os_4(\mu\text{-}H)_4(CO)_{10}(MeCN)_2]$ **1b**.—In a similar manner to that reported earlier,[3] the compound $[Os_4(\mu\text{-}H)_4(CO)_{12}]$ **1** (100 mg) was suspended in MeCN (50 cm^3). Two equivalents of Me_3NO (14 mg) in MeCN (20 cm^3) were added dropwise at room temperature, which gradually produced a clear yellow-orange solution. The reaction was complete in 1 h as indicated by IR spectroscopy. The solution was then filtered through silica gel to remove any excess of Me_3NO and some decomposition material. The solvent was removed *in vacuo* and an orange solid obtained, this being a mixture of $[Os_4(\mu\text{-}H)_4(CO)_{11}(MeCN)]$ **1a** and $[Os_4(\mu\text{-}H)_4(CO)_{10}(MeCN)_2]$ **1b** (90%). Owing to the sensitivity of this material, it was used *in situ* in subsequent reactions without further purification.

Preparation of $[Os_4(\mu\text{-}H)_4(CO)_{11}(NMe_3)]$ **1c**.—The compound $[Os_4(\mu\text{-}H)_4(CO)_{12}]$ **1** (100 mg) was suspended in CH_2Cl_2 (40 cm^3) and 2 equivalents of Me_3NO (14 mg) in CH_2Cl_2 (20 cm^3) were added dropwise, at room temperature, gradually producing a bright yellow solution. The reaction was monitored by IR spectroscopy which indicated the complete consumption of starting material after 1 h. The solution was filtered through silica gel to remove any excess of Me_3NO and some decomposition material. The yellow solid, $[Os_4(\mu\text{-}H)_4(CO)_{11}(NMe_3)]$ **1c** (88%), obtained after removal of solvent *in vacuo* was sufficiently pure to be used in further reactions.

Synthesis of Clusters **2**–**5**.—*Method* 1. An excess of cyclohexa-1,3-diene (2 cm^3) was added to a solution of compound **1a** and **1b** (92 mg) in CH_2Cl_2 (50 cm^3). The mixture was stirred at room temperature for 6 h and the reaction monitored by IR spectroscopy. The solvent was removed under reduced pressure and the residue separated by TLC using 30% CH_2Cl_2 in hexane as eluent. A range of bands was produced, amongst which four were isolated. In order of elution the bands were characterised as $[Os_4(\mu\text{-}H)_3(CO)_{11}(\eta^3\text{-}C_6H_9)]$ **2** (orange, 10), $[Os_4(\mu\text{-}H)_2(CO)_{11}(\eta^4\text{-}C_6H_8)]$ **4** (orange, 12) [Found (Calc.): C, 17.80 (17.75); H, 0.95 (0.85%)], $[Os_4(\mu\text{-}H)_2(CO)_{12}(\eta^2\text{-}C_6H_8)]$ **3** (green, 8) and $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ **5** (orange, 28%), respectively.

Method 2. The compound $[Os_4(\mu\text{-}H)_4(CO)_{12}]$ **1** (100 mg) was dissolved in CH_2Cl_2 (100 cm^3), an excess of cyclohexa-1,3-diene (2 cm^3) was added and the solution cooled to −78 °C. A solution of Me_3NO (22 mg, 3.2 mol equivalents) in CH_2Cl_2 (20 cm^3) was added dropwise over 30 min. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The solvent was removed *in vacuo* and the products separated by TLC using 30% CH_2Cl_2 in hexane as eluent, resulting in the isolation of the same four products: **2** (6), **4** (10), **3** (4) and **5** (20%). An additional band was also observed and characterised as $[Os_4(CO)_9(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ **6** (red, 10%).

Conversion of $[Os_4(\mu\text{-}H)_2(CO)_{12}(\eta^2\text{-}C_6H_8)]$ **3** *into* $[Os_4(\mu\text{-}H)_2(CO)_{11}(\eta^4\text{-}C_6H_8)]$ **4**.—The complex $[Os_4(\mu\text{-}H)_2\text{-}$

$(CO)_{12}(\eta^2\text{-}C_6H_8)]$ **3** (15 mg) was suspended in hexane (20 cm^3) and heated to reflux for 3 h. The solvent was removed *in vacuo* and purification by TLC using 40% CH_2Cl_2 in hexane afforded one product characterised by IR spectroscopy as $[Os_4(\mu\text{-}H)_2(CO)_{11}(\eta^4\text{-}C_6H_8)]$ **4** (orange, 10%).

Conversion of $[Os_4(\mu\text{-}H)_2(CO)_{11}(\eta^4\text{-}C_8H_8)]$ **4** *into* $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ **5**.—*Thermally*. The complex $[Os_4(\mu\text{-}H)_2(CO)_{11}(\eta^4\text{-}C_8H_8)]$ **4** (20 mg) was suspended in hexane (30 cm^3) and heated to reflux for 3 h. The solvent was removed *in vacuo* and purification by TLC using 30% CH_2Cl_2 in hexane as eluent resulted in two products, the first of which was starting material and the second was characterised as $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ **5** (12%). Decomposition was also observed.

Photolytically. The complex $[Os_4(\mu\text{-}H)_2(CO)_{11}(\eta^4\text{-}C_6H_8)]$ **4** (20 mg) was dissolved in toluene (10 cm^3) in a quartz Schlenk tube, and was irradiated with an HPK 125 W lamp for 15 h. The reaction was monitored by IR spectroscopy which showed little change over this period of time. The solvent was removed under reduced pressure and the products separated by TLC using 30% CH_2Cl_2 in hexane as eluent. Apart from recovering the starting material **4**, $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ **5** (< 10%) was isolated and identified by IR and mass spectroscopy.

Photolysis of $[Os_4(\mu\text{-}H)_4(CO)_{10}(MeCN)_2]$ **1b** *and* $[Os_4(\mu\text{-}H)_4(CO)_{11}(NMe_3)]$ **1c** *with Cyclohexa*-1,3-*diene*.—The complex $[Os_4(\mu\text{-}H)_4(CO)_{10}(MeCN)_2]$ **1b** (40 mg) was dissolved in toluene (10 cm^3) in a quartz Schlenk tube, and an excess of cyclohexa-1,3-diene (2 cm^3) was added. The mixture was photolysed with a high-pressure mercury-vapour lamp (HPK 125 W) for 4 h at room temperature and the solution turned orange. The solvent was removed under reduced pressure and the residue subjected to TLC eluting with 40% CH_2Cl_2 in hexane. Four bands were obtained and characterised as **2** (20), **4** (16), **5** (23) and $[Os_4(CO)_9(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ **6** (5%). The complex $[Os_4(\mu\text{-}H)_4(CO)_{11}(NMe_3)]$ **1c** was found to react in a similar manner, but only **2** (22) and **4** (20%) were produced after 4 h. However, if photolysis was prolonged for 20 h **5** (15%) was also observed.

Reactions of $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ **5**.—*With* Me_3NO *and cyclohexa*-1,3-*diene*. The compound Me_3NO (3.2 equivalents, 4.3 mg) in CH_2Cl_2 (10 cm^3) was added dropwise to a CH_2Cl_2 solution (30 cm^3) of $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ **5** (20 mg) at −78 °C, containing an excess of cyclohexa-1,3-diene (2 cm^3). The solution was allowed to warm to room temperature (1 h), then stirred for 30 min during which it turned from orange to deep red. The solvent was removed *in vacuo*, and the residue chromatographed using 40% CH_2Cl_2 in hexane as eluent, affording three main products. In order of elution, they were characterised as starting material (25), **6** (red, 20) and $[Os_4(\mu\text{-}H)_2(CO)_8(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ **7** (orange, 25%) [Found (Calc.): C, 21.25 (20.95); H, 1.50 (1.40%)].

With Me_3NO *and benzene*. The complex $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ **5** (30 mg) was dissolved in CH_2Cl_2–acetone–benzene (30:5:5 cm^3) and cooled to −78 °C. A solution of Me_3NO (6.4 mg, 3.2 equivalents) in CH_2Cl_2 (10 cm^3) was added dropwise over 10 min, and the mixture then allowed to warm to room temperature (1 h) during which it darkened. The solvent was removed under reduced pressure and the residue subjected to TLC, eluting with 30% CH_2Cl_2 in hexane. Two orange bands were obtained and characterised as the starting material **5** (22) and $[Os_4(CO)_8(\eta^6\text{-}C_6H_6)_2]$ **8** (14%). Decomposition was also observed.

Arene exchange. The complex $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ **5** (15 mg) was dissolved in toluene (6 cm^3) and the solution heated under reflux for 72 h. It remained orange. The solvent was removed under reduced pressure and the residue worked up by TLC, eluting with 40% CH_2Cl_2 in hexane. Two main orange bands were collected and identified as $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_5Me)]$ **9** (15) and the starting material **5** (52%) respectively.

Complex **5** (10 mg) was suspended in octane (10 cm^3) and xylene (0.5 cm^3) was added. The solution was heated to 110 °C for 4 d, after which the solvent was removed *in vacuo* and the residue subjected to TLC, eluting with 40% CH_2Cl_2 in hexane. Two orange bands were produced, the first being characterised as $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_4Me_2\text{-}1,3)]$ **10** (low yield) and the second as the starting material **5**.

Reactions of $[Os_4(\mu\text{-}H)_4(CO)_{11}(NMe_3)]$ **1c** *and* $[Os_4(\mu\text{-}H)_4(CO)_{10}(MeCN)_2]$ **1b** *with* 3-*Methylcyclohexa*-1,4-*diene*.—A toluene solution (10 cm^3) of $[Os_4(\mu\text{-}H)_4(CO)_{11}(NMe_3)]$ **1c** (20 mg) or a CH_2Cl_2 solution (20 cm^3) of $[Os_4(\mu\text{-}H)_4(CO)_{10}(MeCN)_2]$ **1b** (40 mg) containing an excess of 3-methylcyclohexa-1,4-diene (2 cm^3) was heated to 60 °C for 43 h or under reflux for 42 h, respectively. The resultant orange-brown mixture was subjected to TLC after the removal of solvent, eluting with 40% CH_2Cl_2 in hexane. In both cases, complexes $[Os_4(\mu\text{-}H)_3(CO)_{11}(C_6H_8Me)]$ **11** and **9** were isolated in low yields and characterised by direct analogy with **2** and **5**, derived from the reaction with cyclohexa-1,3-diene.

Crystal Structure Determination for Compounds **4** *and* **7**.—*Crystal data*. $C_{17}H_{10}O_{11}Os_4$ **4**, $M = 1151.0$, monoclinic, space group $P2_1/n$, $a = 8.4465(22)$, $b = 13.852(3)$, $c = 18.259(6)$ Å, $\beta = 93.837(24)°$, $U = 2131$ Å^3, $\lambda = 0.710\,73$ Å, $Z = 4$, $D_c = 3.586$ g cm^{-3}, $T = 150 \pm 0.1$ K, orange column, 0.54 × 0.35 × 0.31 mm, $\mu = 23.863$ mm^{-1}, $F(000) = 2016$.

$C_{20}H_{16}O_8Os_4$ **7**, $M = 1145.10$, triclinic, space group $P\bar{1}$, $a = 8.4267(14)$, $b = 8.7464(17)$, $c = 15.871(6)$ Å, $\alpha = 84.924(18)$, $\beta = 77.617(12)$, $\gamma = 75.525(10)°$, $U = 1105.5$ Å^3, $\lambda = 0.710\,73$ Å, $Z = 2$, $D_c = 3.440$ g cm^{-3}, $T = 298$ K, red plate, 0.198 × 0.185 × 0.060 mm, $\mu = 22.995$ mm^{-1}, $F(000) = 1008$.

Data collection and processing. All X-ray measurements were made on a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device,[17] and graphite-monochromated Mo-Kα X-radiation. For complex **4**, ω–2θ scans were employed, 3657 unique data collected ($2\theta_{max}$ 45, h −9 to 9, k 0–14, l 0–19), semiempirical absorption correction[18] applied (minimum and maximum transmission factors 0.003 and 0.013 respectively), giving 2585 reflections with $F \geqslant 4\sigma(F)$ for use in all calculations. For **7**, as for **4** except 4369 unique data collected (h −8 to 9, k −9 to 9, l 0–17), minimum and maximum transmission factors 0.017 and 0.109, giving 2622 observed reflections. A correction for linear isotropic crystal decay (3%) was incorporated in the data reduction.

Structure solution and refinement. The osmium atoms were located by automatic direct methods[19] and subsequent iterative cycles of least-squares refinement and Fourier-difference synthesis located all non-H atoms.[20] At isotropic convergence, final corrections (minimum 0.826, 0.630, maximum 1.150, 1.276 for **4** and **7** respectively) for absorption were applied using DIFABS.[21] For complex **4** all non-H atoms were then refined (by least squares on F)[20] with anisotropic thermal parameters, whereas for **7** only the Os and O atoms were refined anisotropically, with the C atoms allowed isotropic thermal motion. The benzene and diene H atoms were included at fixed, calculated positions and the hydrides were located using XHYDEX.[8]

For complex **4** at final convergence R, $R' = 0.0350$, 0.0490 respectively, $S = 1.066$ for 290 refined parameters and the final ΔF synthesis showed no $\Delta\rho$ above 1.29 or below −1.02 e Å^{-3}, the major features lying near the Os atoms. A secondary extinction parameter refined to $1.8(2) \times 10^{-8}$; the weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,227F^2$ gave satisfactory agreement analyses and in the final cycle $(\Delta/\sigma)_{max}$ was 0.260. For **7** R, $R' = 0.0493$, 0.0609 respectively, $S = 0.938$ for 189 refined parameters and the final ΔF synthesis showed no $\Delta\rho$ above 2.15 or below −2.45 e Å^{-3}, the major features lying near the Os atoms. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,130F^2$ gave satisfactory agreement analyses and in the final cycle $(\Delta/\sigma)_{max}$ was 0.002. Atomic scattering factors were inlaid,[20] or taken from ref. 22. Molecular geometry calculations utilised CALC[23] and Figs. 1–4 were produced using SCHAKAL 93.[24] Fractional atomic coordinates for compounds **4** and **7** are given in Tables 4 and 5 respectively.

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

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