

Sequential Synthesis of Some Tetraosmium–Arene Clusters†

Brian F. G. Johnson,^{*,a} Alexander J. Blake,^a Caroline M. Martin,^a Dario Braga,^{*,b}
Emilio Parisini^b and Hong Chen^c

^a Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK

^b Dipartimento di Chimica G. Ciamician, Università di Bologna, Via Selmi 2, 40126 Bologna, Italy

^c University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

On activation with Me₃NO the tetrahydrido-tetranuclear cluster [Os₄(μ-H)₄(CO)₁₂] **1** underwent reaction with cyclohexa-1,3-diene in CH₂Cl₂ under ambient conditions to give, as the major products, the four organometallic clusters [Os₄(μ-H)₃(CO)₁₁(η³-C₆H₉)] **2**, [Os₄(μ-H)₂(CO)₁₂(η²-C₆H₈)] **3**, [Os₄(μ-H)₂(CO)₁₁(η⁴-C₆H₈)] **4** and [Os₄(μ-H)₂(CO)₁₀(η⁶-C₆H₆)] **5**. On heating in hexane, **3** is converted into **4** and subsequently **4** into **5**. Compound **5** underwent further reaction with Me₃NO in CH₂Cl₂ in the presence of cyclohexa-1,3-diene to produce [Os₄(CO)₉(η⁶-C₆H₆)(η⁴-C₆H₈)] **6** and [Os₄(μ-H)₂(CO)₈(η⁶-C₆H₆)(η⁴-C₆H₈)] **7**. Structural analyses of **4** and **7** by single-crystal X-ray diffraction have shown that the C₆H₈ ligand is bonded through two alkene bonds and that the benzene ligand in **7** is co-ordinated in an η⁶ fashion. In each case the ligands are bonded to single osmium atoms only. Compound **5** was also found to react with Me₃NO in CH₂Cl₂ in the presence of benzene yielding [Os₄(CO)₈(η⁶-C₆H₆)₂] **8**, whilst with either toluene or mesitylene it undergoes arene displacement to produce [Os₄(μ-H)₂(CO)₁₀(η⁶-C₆H₅Me)] **9** or [Os₄(μ-H)₂(CO)₁₀(η⁶-C₆H₄Me₂-1,3)] **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 η⁶-terminal or μ₃-η²:η²:η²-face capping modes. In some clusters, e.g. [Ru₄C(CO)₁₁(η⁶-C₆H₆)(μ₃-η²:η²:η²-C₆H₆)],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 [Ru₅C(CO)₁₂(C₆H₆)].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 η⁶ mode is apparently the only bonding type observed.^{3,4}

In this paper we report a more extended appraisal of the reactions of [Os₄(μ-H)₄(CO)₁₂] **1** with cyclohexa-1,3-diene which lead ultimately to the formation of η⁶-benzene products.

Results and Discussion

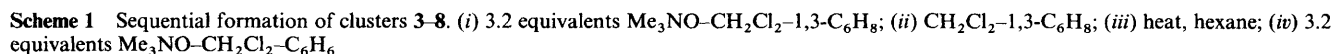
Chemical Synthesis, Characterisation and Mechanistic Proposals.—The tetranuclear cluster [Os₄(μ-H)₄(CO)₁₁(MeCN)] **1a**, together with small amounts of the disubstituted derivative [Os₄(μ-H)₄(CO)₁₀(MeCN)₂] **1b**, were prepared from the reaction of [Os₄(μ-H)₄(CO)₁₂] **1** with Me₃NO in MeCN at room temperature. Reaction of this mixture with cyclohexa-1,3-diene in CH₂Cl₂ at room temperature for 6 h, or the direct reaction of **1** with Me₃NO in CH₂Cl₂ 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 [Os₄(μ-H)₃(CO)₁₁(η³-C₆H₉)] **2**, [Os₄(μ-H)₂(CO)₁₂(η²-C₆H₈)] **3**, [Os₄(μ-H)₂(CO)₁₁(η⁴-C₆H₈)] **4** and [Os₄(μ-H)₂(CO)₁₀(η⁶-C₆H₆)] **5**. Other minor products have not yet been identified, although their IR spectroscopic data appear consistent with their formulation as derivatives

containing a basic Os₄ 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 η²-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 Os₄ tetrahedron and contains a C₆H₈ ligand bonded to a single osmium atom in the η⁴ mode. The compounds **3–5** emerge as a closely related series. As a CO ligand is lost, additional electron-pair donation from the C₆ organic fragment is observed, paralleling the change from an η²- to an η⁴- and then to an η⁶-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 H₂. We have no evidence to suggest that hydrogenation of the η⁶-C₆H₆ 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, [Os₄(μ-H)₄(CO)₁₁(NMe₃)] **1c**, reacts similarly. Again, in a separate experiment, we have established that on

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

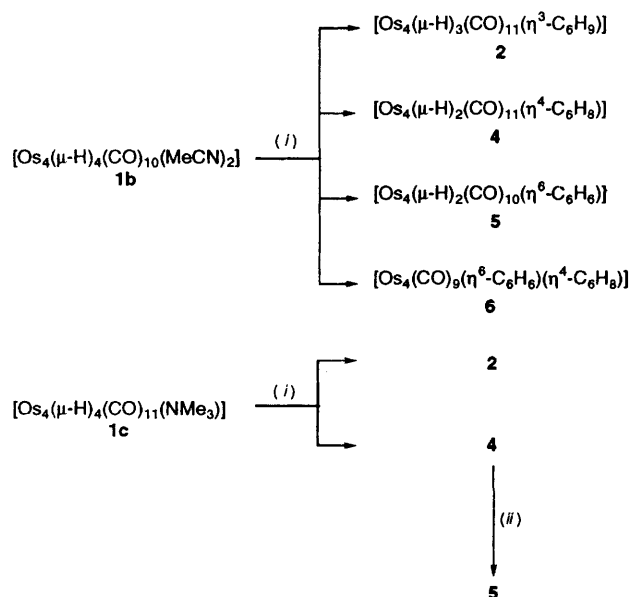


The η^6 -benzene product, **5**, undergoes further reaction with Me_3NO in CH_2Cl_2 in the presence of cyclohexa-1,3-diene to produce the compounds $[\text{Os}_4(\text{CO})_9(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-C}_6\text{H}_8)]$ **6** and $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_8(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-C}_6\text{H}_8)]$ **7**. If benzene is used in the place of cyclohexa-1,3-diene a new product, tentatively characterised as $[\text{Os}_4(\text{CO})_8(\eta^6\text{-C}_6\text{H}_6)_2]$ **8**, results in low yield (Scheme 1). Compound **6** has previously been reported as one of the products of the reaction of $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{10}(\text{MeCN})_2]$ 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 tetrahedral osmium core 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 $\delta -15.72$ 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

Complex **9** has also been prepared by an alternative route. Treatment of the activated clusters $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{11}(\text{NMe}_3)]$

Table 1 Spectroscopic data for complexes 2–11

Compound	IR($\tilde{\nu}_{\text{CO}}$ /cm ⁻¹)	Mass spectrum, obs. (calc.) m/z	¹ H NMR (CDCl ₃)
2 [Os ₄ (μ-H) ₃ (CO) ₁₁ (η ³ -C ₆ H 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 (μ-H) ₂ (CO) ₁₂ (η ² -C ₆ H 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 (μ-H) ₂ (CO) ₁₁ (η ⁴ -C ₆ H 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 (μ-H) ₂ (CO) ₁₀ (η ⁶ -C ₆ H 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 (η ⁶ -C ₆ H ₆)(η ⁴ -C ₆ H 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 (μ-H) ₂ (CO) ₈ (η ⁶ -C ₆ H ₆)(η ⁴ -C ₆ H 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 (η ⁶ -C ₆ H ₆) ₂]	^b 2059w, 2050m, 2032m, 2017m, 1988vs, 1933m	1140 (1140)	5.75 (s, 12 H)
9 [Os ₄ (μ-H) ₂ (CO) ₁₀ (η ⁶ -C ₆ H ₅ Me)]	^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 (μ-H) ₂ (CO) ₁₀ (η ⁶ -C ₆ H ₄ Me ₂ -1,3)]	^b 2078w, 2058s, 2031s, 1991s (br), 1952w (br)	1148 (1148)	
11 [Os ₄ (μ-H) ₃ (CO) ₁₁ (C ₆ H ₈ Me)] 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 CH₂Cl₂ 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-C₆H₈, 4 h; (ii) prolonged irradiation in toluene, 20 h

1c or [Os₄(μ-H)₄(CO)₁₀(MeCN)₂] **1b** with 3-methylcyclohexa-1,4-diene in CH₂Cl₂ under reflux yields two main products: [Os₄(μ-H)₂(CO)₁₀(η⁶-C₆H₅Me)] **9** and [Os₄(μ-H)₃(CO)₁₁-

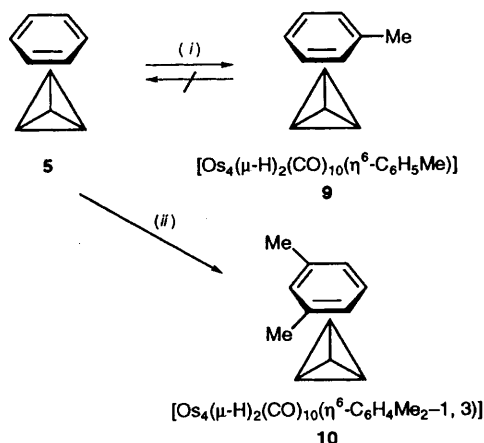
(C₆H₈Me)] **11**. Cluster **11** has been isolated in two distinct isomeric forms **11a** and **11b** (see Scheme 4) which have been characterised on the basis of spectroscopic evidence (see Table 1). These derivatives are clearly analogues of cluster **2**.

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 co-ordinated 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 [Os₃(μ-H)₂(CO)₁₀] with C₂H₄ to give derivatives of C₂H₂ and C₂H₆.¹⁴

Molecular Structures of Compounds **4** and **7** in the Solid State.

—The solid-state molecular structures of [Os₄(μ-H)₂(CO)₁₁(η⁴-C₆H₈)] **4** and of its benzene derivative [Os₄(μ-H)₂(CO)₈(η⁶-C₆H₆)(η⁴-C₆H₈)] **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 C₆H₈ ligand is terminally bound to one osmium atom of the polyhedron in both clusters. The co-ordination mode is of the η⁴ type as observed in the previously reported species [Os₄(CO)₉(η⁶-C₆H₆)(η⁴-C₆H₈)] **6**.³ The Os–C(C₆H₈) 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

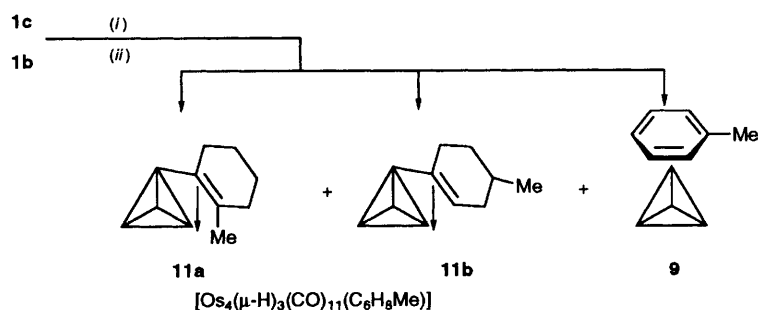


Scheme 3 Arene-exchange reactions of $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{10}(\eta^6\text{-C}_6\text{H}_6)]$ 5. (i) Heating in toluene under reflux; (ii) heating in octane at 110 °C in the presence of xylene

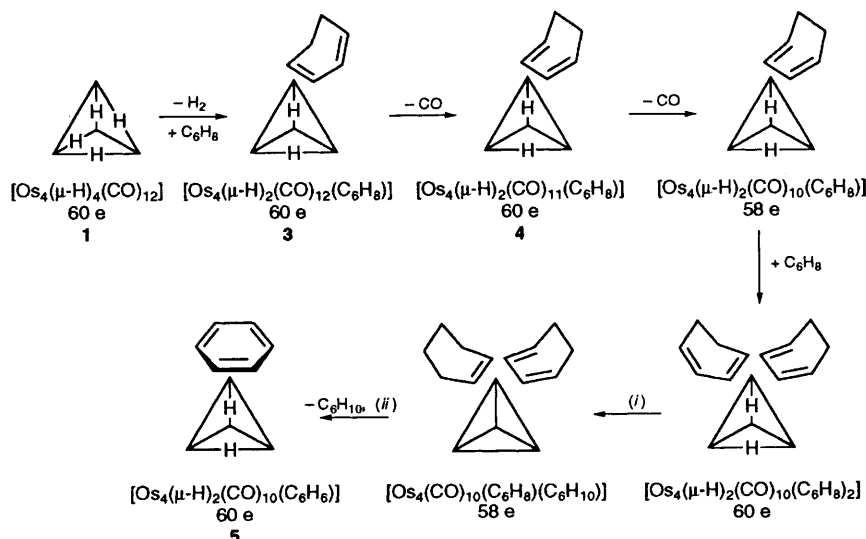
cannot easily be ascribed to differences in bonding between the ligands and the cluster cores. Rather they point to possible effects of intermolecular interactions (*viz.* packing forces) on the geometric features of these 'soft' bonding interactions.

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 $[\text{Os}_4(\text{CO})_9(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-C}_6\text{H}_8)]$ 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 $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}]$ with cyclohexa-1,3-diene. (i) Hydrogen migration; (ii) C–H bond cleavage, hydrogen migration

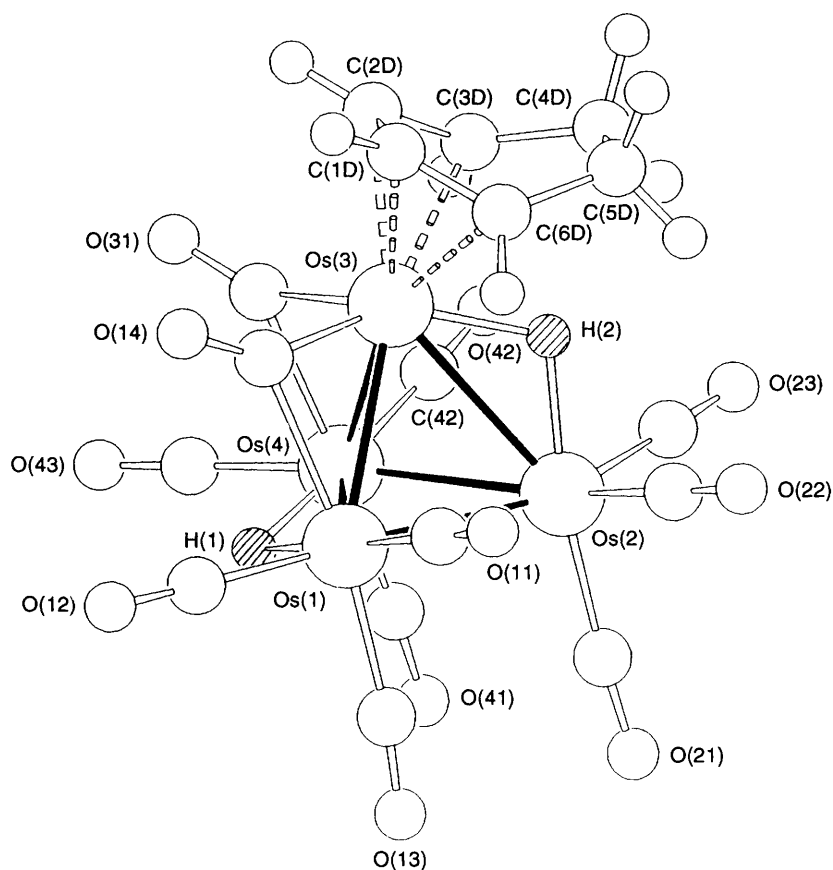


Fig. 1 Molecular structure of $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\eta^4\text{-C}_6\text{H}_8)]$ **4** in the solid state showing the atom labelling; the C atoms of the carbonyl ligands bear the same numbers as those of the corresponding O atoms. The H (hydride) positions are those afforded by XHYDEX,⁸ and correspond to niches in the ligand coverage

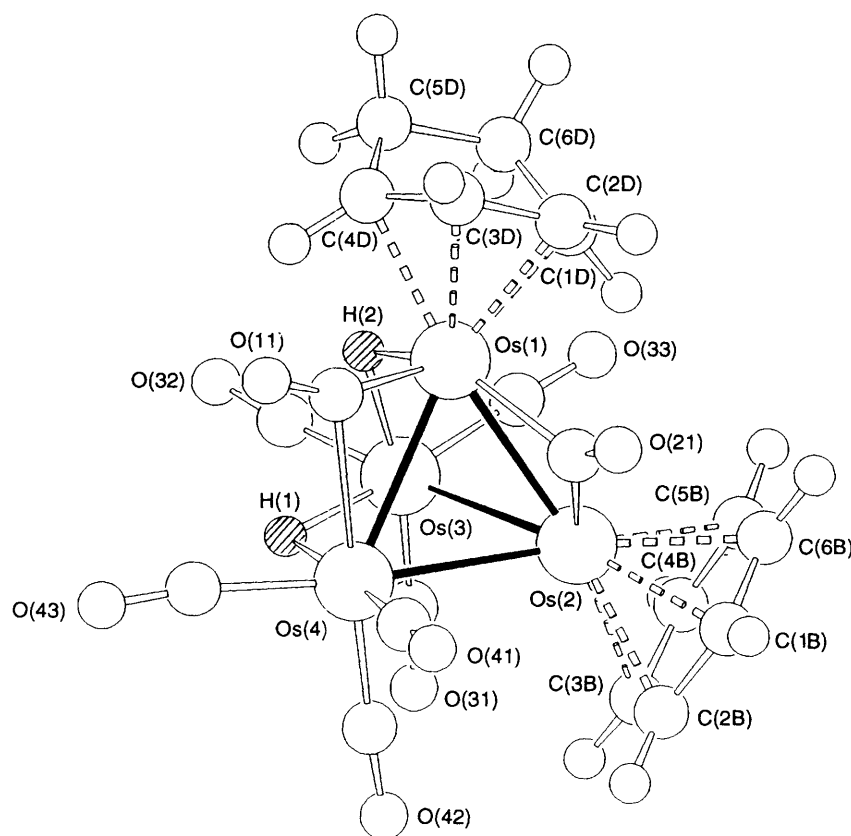


Fig. 2 Molecular structure of $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_8(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-C}_6\text{H}_8)]$ **7** in the solid state showing the atom labelling. Details as in Fig. 1

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

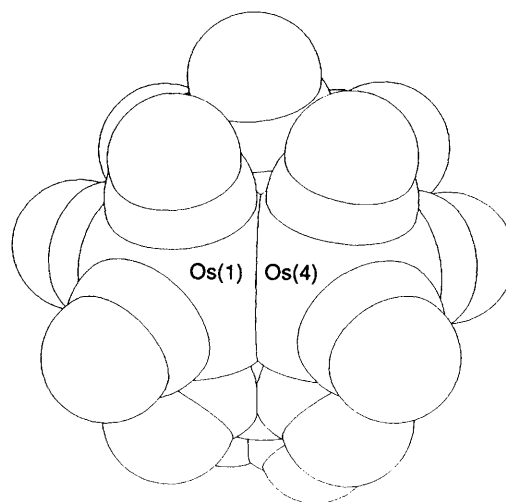
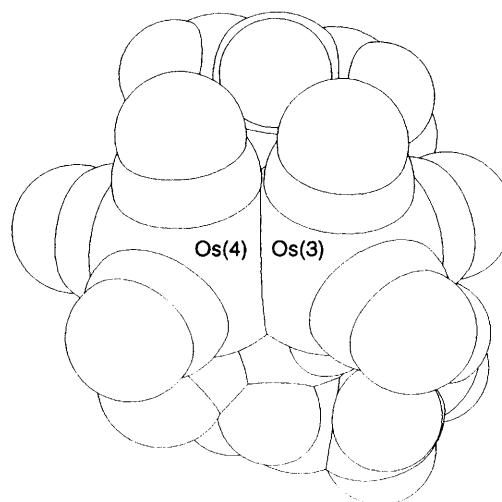
Os(1)–Os(2)	2.8277(8)	Os(3)–C(14)	1.933(13)
Os(1)–Os(3)	2.8295(8)	Os(1)···C(14)	2.326(13)
Os(1)–Os(4)	2.9354(7)	C(14)–O(14)	1.172(16)
Os(2)–Os(3)	2.9009(8)	Os(3)–C(31)	1.913(14)
Os(2)–Os(4)	2.8113(7)	Os(4)···C(31)	2.311(14)
Os(3)–Os(4)	2.8069(7)	C(31)–O(31)	1.179(17)
Os(3)–C(1D)	2.200(13)	C(1D)–C(2D)	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 XHYDEX⁸ 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 Os₄ 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 [Os₃(μ-H)₂(CO)₁₀] and are of relevance to the hydrogenation of benzene on a metallic [111] surface.¹⁵ Displacement of η⁶-C₆H₆ occurs readily. This behaviour is in contrast to that shown by the μ₃:η²:η²:η²-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 60F₂₅₄. 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 CDCl₃ using a Bruker AM360 spectrometer, chemical shifts being reported relative to SiMe₄. The [Os₄(μ-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 [Os₄(μ-H)₄(CO)₁₁(MeCN)] 1a and [Os₄(μ-H)₄(CO)₁₀(MeCN)₂] 1b.—In a similar manner to that reported earlier,³ the compound [Os₄(μ-H)₄(CO)₁₂] **1** (100 mg) was suspended in MeCN (50 cm³). Two equivalents of Me₃NO (14 mg) in MeCN (20 cm³) 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 Me₃NO and some decomposition material. The solvent was removed *in vacuo* and an orange solid obtained, this being a mixture of [Os₄(μ-H)₄(CO)₁₁(MeCN)] **1a** and [Os₄(μ-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 [Os₄(μ-H)₄(CO)₁₁(NMe₃)] 1c.—The compound [Os₄(μ-H)₄(CO)₁₂] **1** (100 mg) was suspended in CH₂Cl₂ (40 cm³) and 2 equivalents of Me₃NO (14 mg) in CH₂Cl₂ (20 cm³) 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 Me₃NO and some decomposition material. The yellow solid, [Os₄(μ-H)₄(CO)₁₁(NMe₃)] **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 cm³) was added to a solution of compound **1a** and **1b** (92 mg) in CH₂Cl₂ (50 cm³). 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% CH₂Cl₂ in hexane as eluent. A range of bands was produced, amongst which four were isolated. In order of elution the bands were characterised as [Os₄(μ-H)₃(CO)₁₁(η³-C₆H₉)] **2** (orange, 10), [Os₄(μ-H)₂(CO)₁₁(η⁴-C₆H₈)] **4** (orange, 12) [Found (Calc.): C, 17.80 (17.75); H, 0.95 (0.85%)], [Os₄(μ-H)₂(CO)₁₂(η²-C₆H₈)] **3** (green, 8) and [Os₄(μ-H)₂(CO)₁₀(η⁶-C₆H₆)] **5** (orange, 28%), respectively.

Method 2. The compound [Os₄(μ-H)₄(CO)₁₂] **1** (100 mg) was dissolved in CH₂Cl₂ (100 cm³), an excess of cyclohexa-1,3-diene (2 cm³) was added and the solution cooled to -78 °C. A solution of Me₃NO (22 mg, 3.2 mol equivalents) in CH₂Cl₂ (20 cm³) 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% CH₂Cl₂ 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 [Os₄(CO)₉(η⁶-C₆H₆)(η⁴-C₆H₈)] **6** (red, 10%).

Conversion of [Os₄(μ-H)₂(CO)₁₂(η²-C₆H₈)] 3 into [Os₄(μ-H)₂(CO)₁₁(η⁴-C₆H₈)] 4.—The complex [Os₄(μ-H)₂-

(CO)₁₂(η²-C₆H₈)] **3** (15 mg) was suspended in hexane (20 cm³) and heated to reflux for 3 h. The solvent was removed *in vacuo* and purification by TLC using 40% CH₂Cl₂ in hexane afforded one product characterised by IR spectroscopy as [Os₄(μ-H)₂(CO)₁₁(η⁴-C₆H₈)] **4** (orange, 10%).

Conversion of [Os₄(μ-H)₂(CO)₁₁(η⁴-C₆H₈)] **4 into [Os₄(μ-H)₂(CO)₁₀(η⁶-C₆H₆)] **5**.—*Thermally*. The complex [Os₄(μ-H)₂(CO)₁₁(η⁴-C₆H₈)] **4** (20 mg) was suspended in hexane (30 cm³) and heated to reflux for 3 h. The solvent was removed *in vacuo* and purification by TLC using 30% CH₂Cl₂ in hexane as eluent resulted in two products, the first of which was starting material and the second was characterised as [Os₄(μ-H)₂(CO)₁₀(η⁶-C₆H₆)] **5** (12%). Decomposition was also observed.**

Photolytically. The complex [Os₄(μ-H)₂(CO)₁₁(η⁴-C₆H₈)] **4** (20 mg) was dissolved in toluene (10 cm³) 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% CH₂Cl₂ in hexane as eluent. Apart from recovering the starting material **4**, [Os₄(μ-H)₂(CO)₁₀(η⁶-C₆H₆)] **5** (<10%) was isolated and identified by IR and mass spectroscopy.

Photolysis of [Os₄(μ-H)₄(CO)₁₀(MeCN)₂] **1b and [Os₄(μ-H)₄(CO)₁₁(NMe₃)] **1c** with Cyclohexa-1,3-diene**.—The complex [Os₄(μ-H)₄(CO)₁₀(MeCN)₂] **1b** (40 mg) was dissolved in toluene (10 cm³) in a quartz Schlenk tube, and an excess of cyclohexa-1,3-diene (2 cm³) 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% CH₂Cl₂ in hexane. Four bands were obtained and characterised as **2** (20), **4** (16), **5** (23) and [Os₄(CO)₉(η⁶-C₆H₆)(η⁴-C₆H₈)] **6** (5%). The complex [Os₄(μ-H)₄(CO)₁₁(NMe₃)] **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 [Os₄(μ-H)₂(CO)₁₀(η⁶-C₆H₆)] **5.—*With Me₃NO and cyclohexa-1,3-diene*. The compound Me₃NO (3.2 equivalents, 4.3 mg) in CH₂Cl₂ (10 cm³) was added dropwise to a CH₂Cl₂ solution (30 cm³) of [Os₄(μ-H)₂(CO)₁₀(η⁶-C₆H₆)] **5** (20 mg) at −78 °C, containing an excess of cyclohexa-1,3-diene (2 cm³). 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% CH₂Cl₂ in hexane as eluent, affording three main products. In order of elution, they were characterised as starting material (**25**), **6** (red, 20) and [Os₄(μ-H)₂(CO)₈(η⁶-C₆H₆)(η⁴-C₆H₈)] **7** (orange, 25%) [Found (Calc.): C, 21.25 (20.95); H, 1.50 (1.40%)].**

With Me₃NO and benzene. The complex [Os₄(μ-H)₂(CO)₁₀(η⁶-C₆H₆)] **5** (30 mg) was dissolved in CH₂Cl₂-acetone-benzene (30:5:5 cm³) and cooled to −78 °C. A solution of Me₃NO (6.4 mg, 3.2 equivalents) in CH₂Cl₂ (10 cm³) 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% CH₂Cl₂ in hexane. Two orange bands were obtained and characterised as the starting material **5** (**22**) and [Os₄(CO)₈(η⁶-C₆H₆)₂] **8** (14%). Decomposition was also observed.

Arene exchange. The complex [Os₄(μ-H)₂(CO)₁₀(η⁶-C₆H₆)] **5** (15 mg) was dissolved in toluene (6 cm³) 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% CH₂Cl₂ in hexane. Two main orange bands were collected and identified as [Os₄(μ-H)₂(CO)₁₀(η⁶-

C₆H₅Me)] **9** (**15**) and the starting material **5** (52%) respectively.

Complex **5** (10 mg) was suspended in octane (10 cm³) and xylene (0.5 cm³) 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% CH₂Cl₂ in hexane. Two orange bands were produced, the first being characterised as [Os₄(μ-H)₂(CO)₁₀(η⁶-C₆H₄Me₂-1,3)] **10** (low yield) and the second as the starting material **5**.

Reactions of [Os₄(μ-H)₄(CO)₁₁(NMe₃)] **1c and [Os₄(μ-H)₄(CO)₁₀(MeCN)₂] **1b** with 3-Methylcyclohexa-1,4-diene**.—A toluene solution (10 cm³) of [Os₄(μ-H)₄(CO)₁₁(NMe₃)] **1c** (20 mg) or a CH₂Cl₂ solution (20 cm³) of [Os₄(μ-H)₄(CO)₁₀(MeCN)₂] **1b** (40 mg) containing an excess of 3-methylcyclohexa-1,4-diene (2 cm³) 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% CH₂Cl₂ in hexane. In both cases, complexes [Os₄(μ-H)₃(CO)₁₁(C₆H₈Me)] **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*. C₁₇H₁₀O₁₁Os₄ **4**, *M* = 1151.0, monoclinic, space group P2₁/n, *a* = 8.4465(22), *b* = 13.852(3), *c* = 18.259(6) Å, β = 93.837(24)°, *U* = 2131 Å³, λ = 0.710 73 Å, *Z* = 4, *D*_c = 3.586 g cm^{−3}, *T* = 150 ± 0.1 K, orange column, 0.54 × 0.35 × 0.31 mm, μ = 23.863 mm^{−1}, *F*(000) = 2016.

C₂₀H₁₆O₈Os₄ **7**, *M* = 1145.10, triclinic, space group P $\bar{1}$, *a* = 8.4267(14), *b* = 8.7464(17), *c* = 15.871(6) Å, α = 84.924(18), β = 77.617(12), γ = 75.525(10)°, *U* = 1105.5 Å³, λ = 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, μ = 22.995 mm^{−1}, *F*(000) = 1008.

Data collection and processing. All X-ray measurements were made on a Stoe 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 (2θ_{max} 45, *h* −9 to 9, *k* 0–14, *l* 0–19), semiempirical absorption correction¹⁸ applied (minimum and maximum transmission factors 0.003 and 0.013 respectively), giving 2585 reflections with *F* ≥ 4σ(*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 methods¹⁹ 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 Δ*F* synthesis showed no Δρ 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) × 10^{−8}; the weighting scheme *w*^{−1} = σ²(*F*) + 0.000 227*F*² gave satisfactory agreement analyses and in the final cycle (Δ/σ)_{max} was 0.260. For **7** *R*, *R'* = 0.0493, 0.0609 respectively, *S* = 0.938 for 189 refined parameters and the final Δ*F* synthesis showed no Δρ 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 CALC²³ 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.

Acknowledgements

We thank ICI Wilton (C. M. M.) and the SERC for financial support, and NATO for a travel grant (to D. B. and B. F. G. J.).

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Received 22nd February 1994; Paper 4/01064G