

Isolation and structural characterisation of products from the reaction of $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{MeCN})_2]$ with cyclohexa-1,3-diene

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The activated tetraosmium hydrido cluster, $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{MeCN})_2]$ **1**, reacts with cyclohexa-1,3-diene producing a range of tetraosmium derivatives including the known clusters $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{11}(\mu\text{-}\eta^1\text{-}\eta^2\text{-C}_6\text{H}_9)]$ **2**, $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{12}(\eta^2\text{-C}_6\text{H}_8)]$, $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\eta^4\text{-C}_6\text{H}_8)]$, $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{10}(\eta^6\text{-C}_6\text{H}_6)]$ and $[\text{Os}_4(\text{CO})_9(\eta^4\text{-C}_6\text{H}_8)(\eta^6\text{-C}_6\text{H}_6)]$, and the new complexes $[\text{Os}_4(\mu\text{-H})(\text{CO})_{10}(\mu_3\text{-}\eta^1\text{-}\eta^2\text{-}\eta^1\text{-C}_6\text{H}_8)(\eta^3\text{-C}_6\text{H}_9)]$ **3**, $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{10}(\eta^6\text{-C}_6\text{H}_5\text{C}_6\text{H}_9)]$ **4** and $[\text{Os}_5(\mu\text{-H})_2(\text{CO})_{13}(\eta^4\text{-C}_6\text{H}_8)]$ **5**. The molecular structure of clusters **3**, **4** and **5** has been determined by single-crystal X-ray diffraction analysis, and an extensive ¹H NMR study of the cyclohexyne-allyl cluster, **3**, has been described. The conversion of the cyclohexenyl cluster, $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{11}(\mu\text{-}\eta^1\text{-}\eta^2\text{-C}_6\text{H}_9)]$ **2**, into the new cyclohexyne complex, $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\mu_3\text{-}\eta^1\text{-}\eta^2\text{-}\eta^1\text{-C}_6\text{H}_8)]$ **6**, by loss of dihydrogen is also described.

Polynuclear co-ordination is commonly observed to induce a ligand reactivity that is different from that of mononuclear co-ordination.¹ In particular, the activation of C–H bonds in alkanes, alkenes, alkynes and arenes is a feature of a number of cluster systems.² We now wish to report the reaction between cyclohexa-1,3-diene and the activated tetrahedral osmium cluster, $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{MeCN})_2]$, in which C–H bond activation is also predominant. This reaction may be taken to illustrate that upon co-ordination to the cluster unit cyclohexa-1,3-diene undergoes a number of transformations including hydrogenation and C–H bond activation with either isomerisation or dehydrogenation leading ultimately to benzene products.

We have recently described³ how the direct treatment of a solution of the parent tetrahedral osmium cluster, $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}]$, in dichloromethane with Me_3NO in the presence of cyclohexa-1,3-diene, yields four major compounds which have been identified on the basis of their spectroscopic properties and X-ray diffraction analyses as the cyclohexenyl, cyclohexadiene and benzene clusters, $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{11}(\mu\text{-}\eta^1\text{-}\eta^2\text{-C}_6\text{H}_9)]$ **2**, $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{12}(\eta^2\text{-C}_6\text{H}_8)]$, $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\eta^4\text{-C}_6\text{H}_8)]$ and $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{10}(\eta^6\text{-C}_6\text{H}_6)]$, respectively. The cyclohexenyl cluster **2** has also been observed in low yield from the photolytic reaction of a solution of $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}]$ in benzene containing excess cyclohexene.⁴ In a series of separate experiments it was further established that upon heating the η^2 -diene complex undergoes conversion to the η^4 -diene cluster which may then be subsequently converted into the benzene complex $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{10}(\eta^6\text{-C}_6\text{H}_6)]$. It is therefore apparent that these three compounds 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 η^2 - to an η^4 - and then to an η^6 -bonding configuration. The precise mechanism by which these reactions occurred was unclear. However, since the formation of $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{11}(\mu\text{-}\eta^1\text{-}\eta^2\text{-C}_6\text{H}_9)]$ **2** involves both the hydrogenation and isomerisation of co-ordinated cyclohexa-1,3-diene, and the formation of $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{10}(\eta^6\text{-C}_6\text{H}_6)]$ involves dehydrogenation of the same diene, it was considered that the reaction sequence required the presence of both a 'sacrificial' and a 'beneficiary' molecule of cyclohexa-1,3-diene.

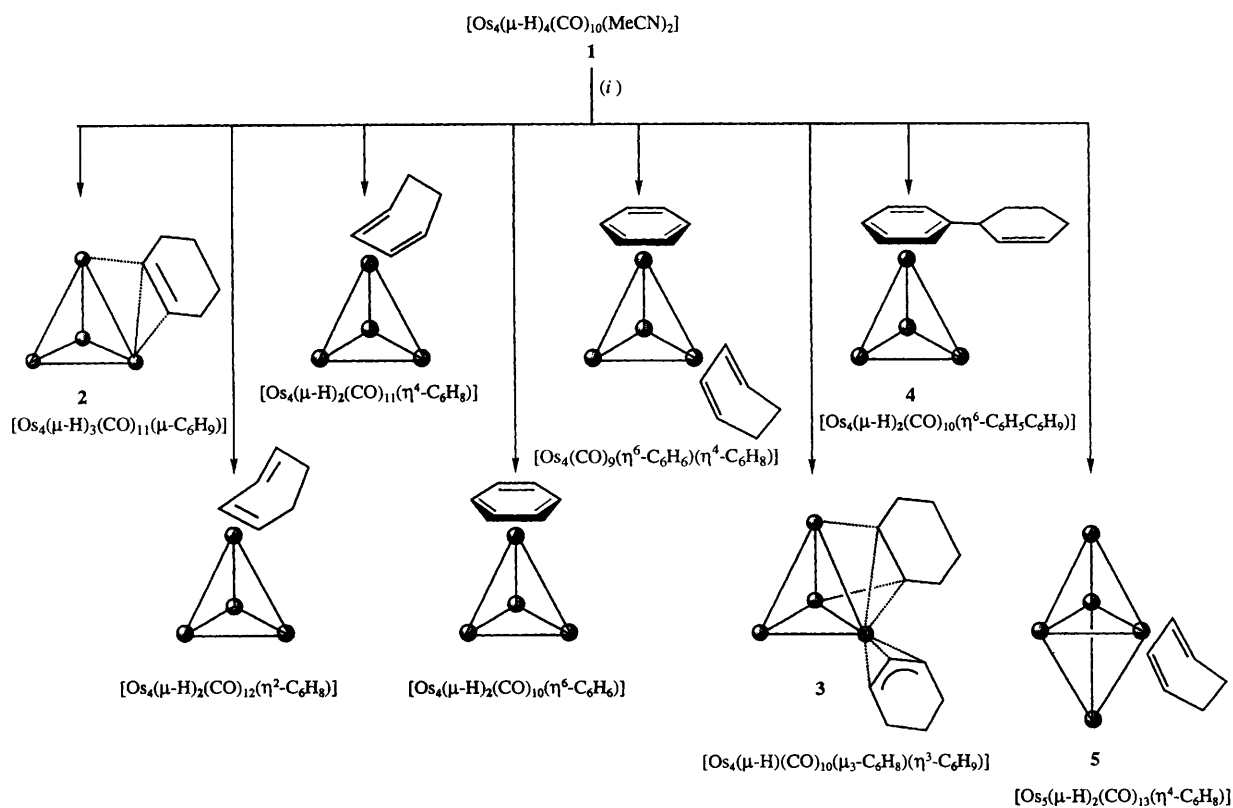
In this paper we present new evidence to suggest that the

cyclohexenyl cluster **2** does not appear to be an active intermediate in the formation of the η^2 - and η^4 -diene, and η^6 -benzene clusters, but is now considered to be an intermediate en route to the formation of $\mu_3\text{-}\eta^1\text{-}\eta^2\text{-}\eta^1$ alkyne-type complexes.

Results and Discussion

The thermolysis of $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{MeCN})_2]$ **1** in dichloromethane containing excess cyclohexa-1,3-diene over an 18 h period has previously been shown to yield the benzene and benzene-diene clusters $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{10}(\eta^6\text{-C}_6\text{H}_6)]$ and $[\text{Os}_4(\text{CO})_9(\eta^4\text{-C}_6\text{H}_8)(\eta^6\text{-C}_6\text{H}_6)]$.⁵ A reinvestigation of this reaction has revealed that the range of derivatives, $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{11}(\mu\text{-}\eta^1\text{-}\eta^2\text{-C}_6\text{H}_9)]$ **2**, $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{12}(\eta^2\text{-C}_6\text{H}_8)]$ and $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\eta^4\text{-C}_6\text{H}_8)]$, are also produced in varying yields, together with three previously unobserved compounds $[\text{Os}_4(\mu\text{-H})(\text{CO})_{10}(\mu_3\text{-}\eta^1\text{-}\eta^2\text{-}\eta^1\text{-C}_6\text{H}_8)(\eta^3\text{-C}_6\text{H}_9)]$ **3**, $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{10}(\eta^6\text{-C}_6\text{H}_5\text{C}_6\text{H}_9)]$ **4** and $[\text{Os}_5(\mu\text{-H})_2(\text{CO})_{13}(\eta^4\text{-C}_6\text{H}_8)]$ **5** (see Scheme 1). Compounds **3**, **4** and **5** have been fully characterised by X-ray diffraction analyses and the usual spectroscopic methods (see Table 1).

The infrared spectrum (ν_{CO}) of **3** contains peaks between 2098 and 1966 cm^{-1} which are indicative of terminally bonded carbonyl ligands only. The mass spectrum exhibits a molecular ion at m/z 1202 (calc. 1203), which is followed by the most intense peak at m/z 1121, corresponding to the loss of the C₆H₉ moiety. The sequential loss of several CO groups is then observed. The ¹H NMR spectrum of **3** in CDCl₃ shown in Fig. 1, comprises a complex series of multiplet resonances, labelled A–S, many of which overlap (see Table 1 for the chemical shift values). In addition, a signal assigned to a metal hydride is found at *ca.* δ –22. The C₆H₈ and C₆H₉ rings in **3** are predicted to give rise to a total of 17 resonances which, from the integral trace of the spectrum, appears to be the case. However, a more conclusive assignment was obtained by performing a TOCSY (total correlation spectroscopy) experiment.⁶ This experiment provides a two-dimensional plot in which all the signals from the normal one-dimensional spectrum are displayed by diagonal responses, with all the H signals from a given spin system (*e.g.* one of the six-membered ring systems in this case) being linked by cross peaks. The TOCSY experiment as performed on complex **3** is shown in Fig. 2, and reveals that



Scheme 1 The range of products isolated from the thermolysis of $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{MeCN})_2]$ **1** with cyclohexa-1,3-diene. (i) Heat, CH_2Cl_2 -1,3- C_6H_8 , 18 h

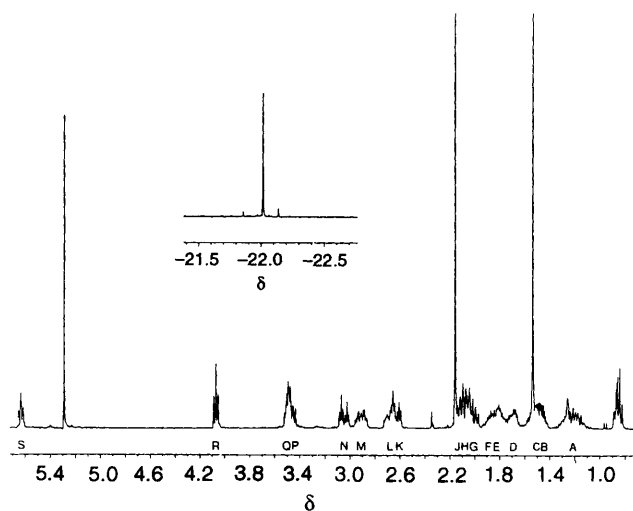


Fig. 1 The 360 MHz ^1H NMR spectrum of compound **3**

signals A, B, G, H, L, M, Q, R and S belong to one spin system, while signals C, D, E, F, J, K, N and P belong to another. Fig. 3 presents the basic ^1H spectrum along with cross sections as indicated on the plot of the TOCSY experiment, and clearly shows nine signals assignable to one ring and eight to the other.

The molecule has also been analysed using a combination of homonuclear ^1H correlation spectroscopy (COSY)-decoupling and nuclear Overhauser enhancement spectroscopy (NOESY) experiments, which suggests that the pairs of signals C/D, E/F, J/K and N/P arise from the geminal protons of the C_6H_8 ring system, with A/B, G/L and H/M being attributed to those of the other ring system. These assumptions were based upon the size of coupling constants and the magnitude of NOE responses, both of which are typically large for geminal protons in six-membered rings. This leaves signals Q, R and S which are associated with the allyl unit [*viz.* C(19)-C(20)-C(21), see Fig.

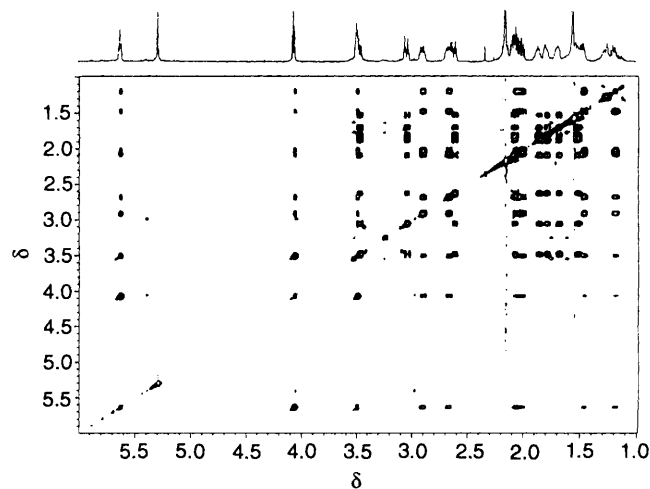


Fig. 2 The 600 MHz ^1H TOCSY results for compound **3**, using a spin-lock mixing time of 65 ms

4] of the C_6H_9 ring. Signal R appears to couple to both S and Q, and is hence assigned to H(20). The assignments of S and Q to either H(19) or H(21) is open to speculation. The ^1H spectrum indicates they are in markedly different environments but it is unclear from the crystallographically obtained structure why this should be so (see below). Since signals Q and L couple together, as do signals S and M, it would appear that the G/L protons derive from the same side of the ring as the Q proton, and the H/M protons are on the same side as the S proton. This places the A/B protons on C(17). The data are not sufficiently conclusive to permit a full characterisation, however, Table 2 summarises the probable assignments of the protons on the two rings.

Compound **4** has been fully characterised as $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{10}(\eta^6\text{-C}_6\text{H}_5\text{C}_6\text{H}_9)]$ by spectroscopic techniques and by a single-crystal X-ray diffraction analysis. The profile of the

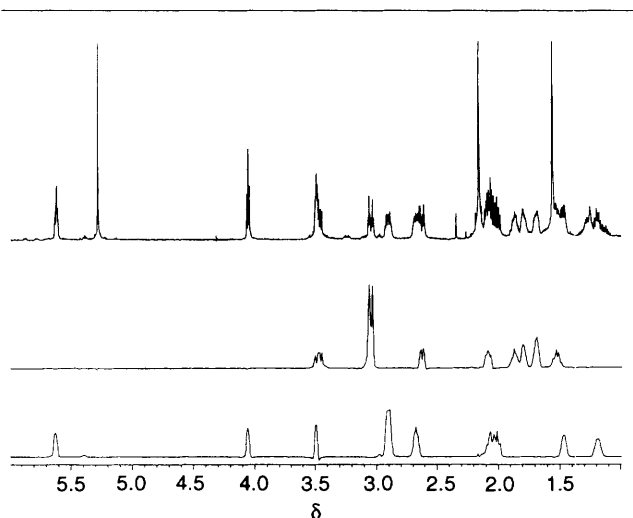
Table 1 Spectroscopic data for compounds 2–6

Compound	IR ($\tilde{\nu}_{\text{CO}}/\text{cm}^{-1}$)	^1H NMR (CDCl_3)	Mass spectrum, obs. (calc.) m/z
2	^a 2098m, 2084w, 2066vs, 2049s, 2034s, 2002m (br), 1978w ^b 2098w, 2066vs, 2051s, 2037s, 2022s, 2010vs, 1995m, 1985m, 1954w	4.19 (m, 1 H), 3.33 (m, 2 H), 2.75 (m, 1 H), 2.50 (m, 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)	1154 (1153)
3	^a 2098w, 2085m, 2059s, 2038vs, 2000m, 1966w ^b 2099w, 2086s, 2059vs, 2024vs, 2024m, 2012vs, 1990w, 1973m, 1960w, 1947w	5.62 (m, 1 H), 4.06 (m, 1 H), 3.47 (m, 2 H), 3.06 (m, 1 H), 2.90 (m, 1 H), 2.64 (m, 2 H), 2.05 (m, 3 H), 1.84 (m, 2 H), 1.67 (m, 1 H), 1.50 (m, 2 H), 1.18 (m, 1 H), –22.0 (s, 1 H)	1202 (1203)
4	^a 2082s, 2060vs, 2032vs, 1994s (br), 1958m, 1786w (br) ^b 2083m, 2062s, 2036vs, 2022w, 2004m, 1995s, 1955m, 1797w	5.84 (m, 5 H), 3.58 (m, 2 H), 1.99 (m, 7 H), –19.09 (s, 1 H) and –20.45 (s, 1 H)	1202 (1201)
5	^a 2085w, 2065s, 2050m, 2030m, 2018vs, 1983m, 1940w		1397 (1397)
6	^a 2098m, 2067vs, 2056s, 2017s (br), 2003m, 1979w, 1960w ^b 2099m, 2068vs, 2057s, 2021vs, 2016s, 2005m, 1994w, 1980w, 1960m	3.18 (m, 4 H), 1.76 (m, 4 H), –10.46 (s, 1 H), –21.53 (s, 1 H)	1151 (1151)

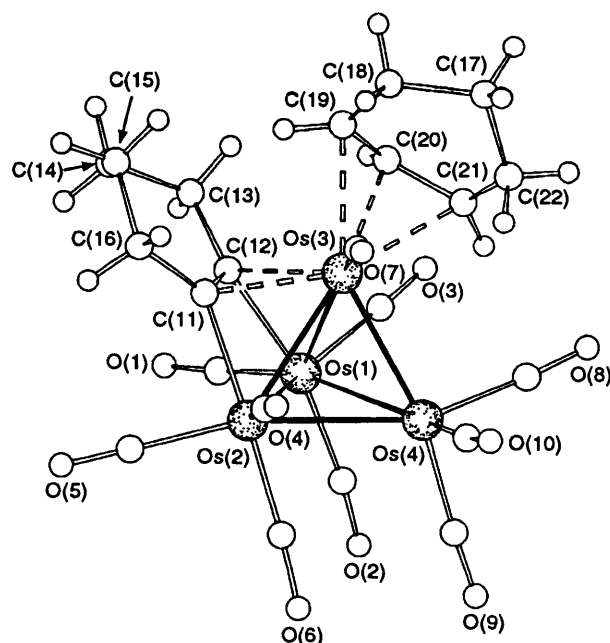
^a Recorded in CH_2Cl_2 solution. ^b Recorded in hexane solution.

Table 2 Partial assignment of the ^1H NMR spectrum of compound 3

Proton identity	Assignment
Protons on C(13)	J/K or N/P
Protons on C(14)	C/D or E/F
Protons on C(15)	C/D or E/F
Protons on C(16)	J/K or N/P
Protons on C(17)	A/B
Protons on C(18)	G/L or H/M
H(19)	S or Q
H(20)	R
H(21)	S or Q
Protons on C(22)	G/L or H/M

**Fig. 3** The 600 MHz ^1H NMR spectrum of compound 3 (top) together with cross-sections of the TOCSY experiment

infrared spectrum of 4 (ν_{CO}) is almost identical in both symmetry and wavenumber to that of the closely related benzene cluster, $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{10}(\eta^6\text{-C}_6\text{H}_6)]$, with peaks suggesting the presence of both terminal and bridging carbonyl ligands (see Table 1). The mass spectrum exhibits a parent peak at m/z 1202 (calc. 1201), together with peaks corresponding to the sequential loss of ten CO groups. The ^1H NMR spectrum in CDCl_3 at room temperature comprises three complex multiplet signals centred at δ 5.84, 3.58 and 1.99 with relative intensities 5:2:7, plus two singlet resonances at δ –19.09 and –20.45. The signal at δ 5.84 may be attributed to the five aromatic ring protons of the arene moiety, with the chemical

**Fig. 4** Molecular structure of $[\text{Os}_4(\mu\text{-H})(\text{CO})_{10}(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-C}_6\text{H}_8)(\eta^3\text{-C}_6\text{H}_9)]$ 3 in the solid state showing the atomic labelling scheme. The C atoms of the CO ligands bear the same numbering as the corresponding O atoms

shift value being typical of η^6 -co-ordination. The resonances at δ 3.58 and 1.99 may be associated with the two olefinic and the seven aliphatic protons of the cyclohexene section of the ligand, respectively. The two signals at very low frequency may be attributed to two inequivalent hydride ligands.

The final product to be isolated from the reaction between 1 and cyclohexa-1,3-diene was characterised as $[\text{Os}_5(\mu\text{-H})_2(\text{CO})_{13}(\eta^4\text{-C}_6\text{H}_8)]$ 5. The mass spectrum of 5 contains a strong parent peak at m/z 1397 (calc. 1397), together with peaks corresponding to the loss of several carbonyl groups in succession. A single-crystal X-ray structural analysis has been carried out and confirms the formulation proposed from mass spectroscopy (see below).

The formation of 5 from 1 involves an increase in cluster nuclearity. It is well established that the thermal loss of CO from $[\text{Os}_3(\text{CO})_{12}]$, for example, may result in a range of higher nuclearity clusters with between four and twenty metal atoms,⁷ however, it is unusual for osmium clusters to build up under

such ambient reaction conditions as those employed during this reaction. Nonetheless, this reaction does involve the reactive bis(acetonitrile) complex **2**, which is unstable and prone to break down forming highly reactive fragments. Thus, the formation of **5** is feasible if these fragments undergo recombination to form clusters with nuclearities differing from that of the starting material. A number of higher nuclearity benzene clusters of osmium have recently been reported in the literature,^{8–11} one of which is a related pentanuclear trigonal-bipyramidal benzene cluster, $[\text{Os}_5(\mu\text{-H})_2(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)]$.¹⁰ This complex was prepared from the ionic condensation reaction between the dianionic cluster species, $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{12}]^{2-}$, and the dicationic osmium–benzene fragment, $[\text{Os}(\eta^6\text{-C}_6\text{H}_6)(\text{MeCN})_3]^{2+}$.

An investigation into the reactivity of the cyclohexenyl cluster, $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{11}(\mu\text{-}\eta^1:\eta^2\text{-C}_6\text{H}_9)]$ **2**, has revealed that it is likely to be an intermediate product on route to the formation of a $\mu_3\text{-}\eta^1:\eta^2:\eta^1$ alkyne-type complex, similar to that observed in the cyclohexyne–allyl complex **3**. The thermolysis of an octane solution of **2** over a period of 2 h resulted in dehydrogenation of the cyclohexenyl moiety and the formation, in low yield, of a compound which has been tentatively formulated as the cyclohexyne complex, $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-C}_6\text{H}_8)]$ **6**. The reaction mixture consists mainly of decomposition products and unreacted starting material as well as the new product **6**, which can be isolated by TLC using a dichloromethane–hexane solution (1 : 3, v/v) as eluent.

The infrared spectrum (ν_{CO}) of **6** is comparable to that observed for the related acyclic alkyne complex $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-RC=CR}')] (R = \text{H}, R' = \text{H}, \text{Ph}$ or $\text{CMe}_3; R = R' = \text{Ph})$.⁴ Its mass spectrum exhibits a parent peak at m/z 1151 (calc. 1151), after which peaks corresponding to the successive loss of several CO groups are observed. Since compound **6** is only produced in low yield, the ¹H NMR spectrum, recorded in CDCl_3 , is not particularly clear owing to a low signal-to-noise ratio. Nonetheless, four signals are observed at δ 3.18, 1.76, –10.46 and –21.53 with relative intensities of 4:4:1:1; the first two signals are multiplet resonances which may be attributed to the four sets of geminal protons of the cyclohexyne ring, with the signal at higher frequency being associated with the two pairs furthest from the cluster and that centred at δ 1.76 representing those protons nearest the metal core. The two signals at low frequency are singlet resonances which can be attributed to two hydride ligands. Even though the spectrum is of poor quality, it is clear that the signal derived from the vinylic proton in compound **2** (δ 4.19, see Table 1) is no longer present. Also, only two resonances are exhibited at negative frequencies, suggesting the presence of two hydride ligands as opposed to the three found in complex **2**. This spectroscopic evidence is consistent with the dehydrogenation of compound **2** to give compound **6** which is believed to contain the C_6H_8 fragment bound as cyclohexyne *via* two σ and one π bond to a triangular face of the Os_4 cluster unit.

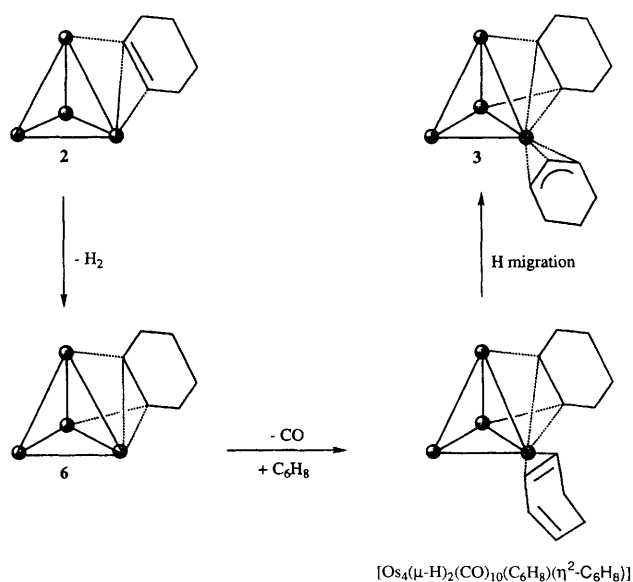
The elimination of dihydrogen from σ,π -vinyl complexes of this type to yield the corresponding dihydrido alkyne products has previously been observed in a related cluster system. The tetraosmium cluster $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}]$ has been found to undergo reaction with the acyclic alkenes (R) $\text{H}_2\text{C}=\text{CH}_2$, $\text{CH}_2=\text{CHPh}$, $\text{H}_2\text{C}=\text{CHCMe}_3$ and *cis*- $\text{HPhC}=\text{CHPh}$ to give a range of complexes of formula $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{11}(\text{R}-\text{H})]$, which contain the alkene ligand bonded to the cluster in the same manner as that observed in complex **2**.⁴ These clusters lose H_2 upon heating, resulting in the formation of the dihydrido complexes, $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\text{RC}=\text{CR}')]$, which contain the $\text{RC}=\text{CR}'$ unit co-ordinated to a triangular face of the Os_4 cluster *via* a similar two σ and one π interaction. The conversion of an edge-bridging σ,π -vinyl complex into a face-capping alkyne-type complex has also been observed in a similar

triosmium cluster system, although in this example CO is lost rather than dihydrogen; $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ reacts with terminal or cyclic alkenes under mild conditions to produce complexes of the type $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-}\eta^1:\eta^2\text{-RH})]$.¹² On heating, this complex is transformed into the $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-}\eta^1:\eta^1:\eta^2\text{-C}=\text{CR}_2)]$ derivative, however, a competing sequence of 1,2-diactions may also lead to complexes of the type $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-RCCR})]$.¹³

We may speculate that the formation of the cyclohexenyl derivative **2** may occur *via* a sequence involving olefin complexation of the ligand in an η^2 -manner at one metal atom, followed by C–H activation at an adjacent metal site. On heating, this product appears to undergo a second C–H bond cleavage to form the ‘yne’ derivative, $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-C}_6\text{H}_8)]$ **6**, in which the C_6H_8 moiety spans the tetrahedral Os_4 face. It is also possible that this dehydrogenation process may occur first by H-transfer from the vinylic group to the Os_4 core, and then by H_2 ejection from the resulting Os_4H_4 unit. It is possible that $[\text{Os}_4(\mu\text{-H})(\text{CO})_{10}(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-C}_6\text{H}_8)(\eta^3\text{-C}_6\text{H}_9)]$ **3** may be derived from **6** by the loss of CO and co-ordination of a second C_6H_8 unit to the metal cluster, again *via* an η^2 -interaction. Hydrogen migration from the cluster framework is then considered to follow, with C–H bond formation at an olefinic C atom of the unco-ordinated diene double bond resulting in the η^3 -allyl moiety. This sequence of reactions is illustrated in Scheme 2, but it should be noted that the postulated reaction intermediate, $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{10}(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-C}_6\text{H}_8)(\eta^2\text{-C}_6\text{H}_8)]$, has not been observed as yet.

Molecular structures of compounds 3, 4 and 5. Crystallisation of **3** and **4** was achieved from toluene solutions at -25°C , and crystals of **5** were grown by the diffusion of pentane vapour into a dichloromethane solution at room temperature.

The molecular structure of **3** is illustrated in Fig. 4 together with the atomic labelling scheme and relevant structural parameters are in Table 3. The metal atom framework of compound **3** constitutes a distorted Os_4 tetrahedron, with Os–Os distances ranging from 2.653(1) to 2.891(1) Å, the longest edge [$\text{Os}(1)\text{--}\text{Os}(2)$] being that thought to be bridged by the hydride ligand. The molecule contains two C_6 ring systems, one of which is a C_6H_9 ring that co-ordinates to a tetrahedron apex [$\text{Os}(3)$] in an η^3 allylic manner, and the other is a C_6H_8 cyclohexyne-type ligand which bridges a triangular face of the cluster *via* two σ and one π interaction. The C_6H_9 moiety



Scheme 2 A possible sequence of reactions for the formation of compound **3** from **2**

Table 3 Selected bond distances (Å) for compound 3

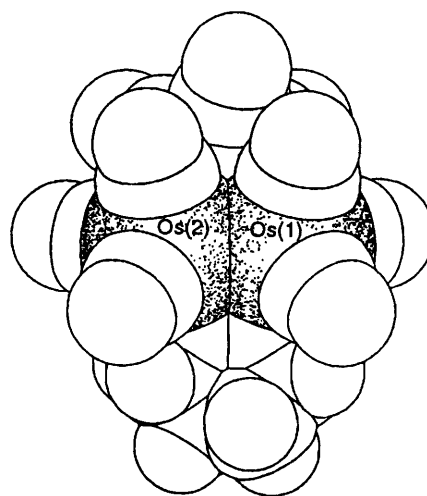
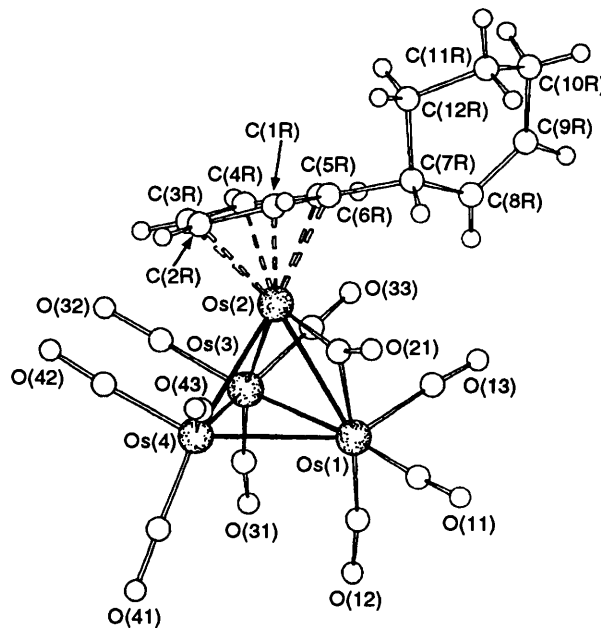
Os(1)–Os(2)	2.891(1)	C(12)–C(13)	1.55(4)
Os(1)–Os(3)	2.794(1)	C(13)–C(14)	1.51(1)
Os(1)–Os(4)	2.868(1)	C(14)–C(15)	1.51(1)
Os(2)–Os(3)	2.796(1)	C(15)–C(16)	1.51(1)
Os(2)–Os(4)	2.852(1)	Os(3)–C(19)	2.34(4)
Os(3)–Os(4)	2.653(1)	Os(3)–C(20)	2.12(4)
mean Os–C(CO)	1.90(3)	Os(3)–C(21)	2.29(4)
mean C–O(CO)	1.15(4)	C(17)–C(18)	1.52(1)
Os(1)–C(12)	2.18(3)	C(17)–C(22)	1.52(1)
Os(2)–C(11)	2.17(2)	C(18)–C(19)	1.43(1)
Os(3)–C(11)	2.19(2)	C(19)–C(20)	1.42(1)
Os(3)–C(12)	2.23(3)	C(20)–C(21)	1.41(1)
C(11)–C(12)	1.40(4)	C(21)–C(22)	1.44(1)
C(11)–C(16)	1.50(3)		

Table 4 Selected bond distances (Å) for compound 4

Os(1)–Os(2)	2.811(2)	Os(2)–C(5R)	2.25(2)
Os(1)–Os(3)	2.766(2)	Os(2)–C(6R)	2.21(3)
Os(1)–Os(4)	2.951(2)	C(1R)–C(2R)	1.43(4)
Os(2)–Os(3)	2.781(1)	C(1R)–C(6R)	1.37(4)
Os(2)–Os(4)	2.788(1)	C(2R)–C(3R)	1.46(5)
Os(3)–Os(4)	2.879(2)	C(3R)–C(4R)	1.37(5)
mean Os–C(CO _{terminal})	1.90(4)	C(4R)–C(5R)	1.41(5)
mean C–O(CO _{terminal})	1.15(4)	C(5R)–C(6R)	1.34(4)
Os(1)···C(21)	2.40(3)	C(6R)–C(7R)	1.62(4)
Os(2)–C(21)	1.95(2)	C(7R)–C(8R)	1.46(5)
C(21)–O(21)	1.11(3)	C(7R)–C(12R)	1.55(5)
Os(2)–C(1R)	2.25(3)	C(8R)–C(9R)	1.36(6)
Os(2)–C(2R)	2.22(3)	C(9R)–C(10R)	1.46(6)
Os(2)–C(3R)	2.22(2)	C(10R)–C(11R)	1.53(7)
Os(2)–C(4R)	2.29(2)	C(11R)–C(12R)	1.54(1)

donates three electrons to the metal framework by co-ordinating to Os(3) through one short and two longer interactions [Os(3)–C(20) 2.12(4) *vs.* Os(3)–C(19) 2.34(4) and Os(3)–C(21) 2.29(4) Å] and the C–C bonds within the ring also vary in length quite considerably. The multiple bond, C(11)–C(12), of the C₆H₈ ligand straddles the Os(1)–Os(2)–Os(3) triangular face in a manner typically adopted by alkynes,¹⁴ and this bond is apparently shorter than the remaining C–C bond lengths of the ring [1.40(4) *vs.* a mean value of 1.52(4) Å for the remaining five distances]. The cyclohexyne moiety donates four electrons to the cluster *via* two σ bonds [Os(1)–C(12) 2.18(3) and Os(2)–C(11) 2.17(2) Å] and a π interaction with the osmium atom bearing the C₆H₉ ring [Os(3)–C(11) 2.19(2) and Os(3)–C(12) 2.23(3) Å]. There are ten carbonyl ligands all of which are bonded in a terminal manner, three are distributed on Os(1), Os(2) and Os(4), and the remaining carbonyl is situated on the osmium atom carrying the allylic ligand, *i.e.* Os(3). The H(hydride) atom in 3 could not be located directly, however, the molecular space-filling diagram reveals the presence of a large niche in the ligand envelope along the Os(1)–Os(2) edge, suggesting its likely position (see Fig. 5). The Os(1)–Os(2) bond is the longest [2.891(1) Å] in the complex, and the results of a series of XHYDEX¹⁵ calculations concur with observations made from the space-filling diagram, suggesting that the hydride atom does in fact bridge this M–M edge.

The solid-state structure of [Os₄(μ -H)₂(CO)₁₀(η^6 -C₆H₅C₆H₉)] 4 is shown in Fig. 6 with relevant structural parameters in Table 4. As anticipated from infrared spectroscopy, in terms of the metal framework and carbonyl distribution the structure is very similar to that of [Os₄(μ -H)₂(CO)₁₀(η^6 -C₆H₆)],⁵ differing only in the nature of the η^6 co-ordinated ligand; the benzene moiety being replaced by a cyclohexenylbenzene group. The metal framework of 4 consists of a tetrahedral arrangement of the four osmium atoms with Os–Os distances ranging from 2.766(2)–2.951(2) Å [*cf.* 2.758(1)–2.979(1) Å in the benzene cluster]. Both cluster species bear an η^6

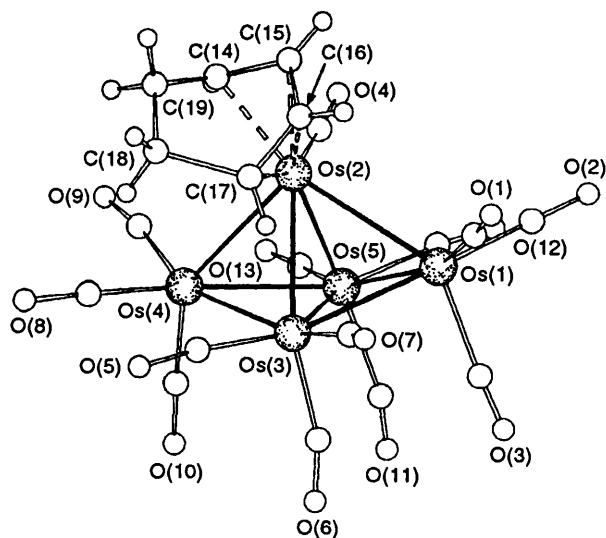
**Fig. 5** Space-filling representation of the structure of compound 3 showing a large niche in the ligand envelope along the Os(1)–Os(2) edge corresponding to the XHYDEX location of the H(hydride) atom**Fig. 6** Molecular structure of [Os₄(μ -H)₂(CO)₁₀(η^6 -C₆H₅C₆H₉)] 4 in the solid state showing the atomic labelling scheme. The C atoms of the CO ligands bear the same numbering as the corresponding O atoms

arene ligand with the same average Os–C bond distance of 2.24(3) Å, and the arene-bound Os atom in each case also bears a single CO ligand which appears to be forced into a semi-bridging position [Os(1)···C(21) 2.40(3), Os(2)–C(21) 1.95(2) Å for 4]. The other three osmium atoms on each cluster also carry three terminal carbonyl groups. From an inspection of the CO ligand displacements in compound 4 the two H(hydride) ligands are believed to bridge the two longest Os–Os edges of the molecule, *i.e.* Os(1)–Os(4) and Os(3)–Os(4), a view supported by XHYDEX calculations.¹⁵ The locations of these hydride atoms also match those in the benzene cluster.

The cyclohexenylbenzene ligand in complex 4 is rather unusual and deserves further comment. It comprises two ring systems (benzene and cyclohexene) connected *via* a single C–C bond, with the aromatic ring co-ordinating to Os(2) in an η^6 manner. All C–C bonds within the benzene ring are approximately equal [mean 1.40(5) Å] and the ring is essentially planar. The C–C double bond of the cyclohexene ring is represented by C(8R)–C(9R) and these two carbon atoms may be considered as sp² hybridised, and the bond length of 1.36(6) Å is shorter than the remaining C–C bond distances of the C₆H₉

Table 5 Selected bond distances (Å) for compound **5**

Os(1)–Os(2)	3.004(4)	3.037(4)	Os(2)–C(14)	2.16(6)	2.32(8)
Os(1)–Os(3)	2.766(4)	2.797(3)	Os(2)–C(15)	2.18(8)	2.26(6)
Os(1)–Os(5)	2.811(4)	2.770(4)	Os(2)–C(16)	2.20(8)	2.18(7)
Os(2)–Os(3)	2.836(3)	2.827(4)	Os(2)–C(17)	2.35(5)	2.30(9)
Os(2)–Os(4)	2.981(4)	2.987(3)	C(14)–C(15)	1.40(10)	1.51(9)
Os(2)–Os(5)	2.824(4)	2.821(4)	C(14)–C(19)	1.30(10)	1.58(10)
Os(3)–Os(4)	2.763(4)	2.813(4)	C(15)–C(16)	1.42(11)	1.55(9)
Os(3)–Os(5)	2.767(3)	2.789(4)	C(16)–C(17)	1.40(10)	1.34(10)
Os(4)–Os(5)	2.790(4)	2.764(3)	C(17)–C(18)	1.70(20)	1.49(11)
mean Os–C(CO)	1.93(12)	1.87(8)	C(18)–C(19)	1.49(14)	1.58(9)
mean C–O(CO)	1.13(13)	1.18(9)			

**Fig. 7** Molecular structure of $[\text{Os}_5(\mu\text{-H})_2(\text{CO})_{13}(\eta^4\text{-C}_6\text{H}_8)]$ **5** in the solid state showing the atomic labelling scheme. Only one of the two independent molecules is shown. The C atoms of the CO ligands bear the same numbering as the corresponding O atoms

ring [mean 1.51(6) Å]. The two ring systems are connected by the C(6R)–C(7R) single bond, which has a length of 1.62(4) Å.

The molecular structure of **5** is depicted in Fig. 7 with principal bond lengths given in Table 5. Two independent molecules are present in the asymmetric unit of compound **5**. The molecular structure is not of high quality owing to the limited size and quality of crystals obtained even after repeated attempts, and the errors associated with the bond lengths and angles are large. However, the gross features of the structure are worth describing even if caution should be applied when interpreting the actual bond lengths obtained. The metal core of $[\text{Os}_5(\mu\text{-H})_2(\text{CO})_{13}(\eta^4\text{-C}_6\text{H}_8)]$ **5** comprises a trigonal bipyramidal array of the five osmium atoms, with the cyclohexa-1,3-diene moiety co-ordinated in an η^4 fashion to an equatorial osmium atom [Os(2)] having a metal connectivity of four (as opposed to an apical osmium atom which has a connectivity of three), and this osmium atom also carries a terminal carbonyl ligand. The remaining 12 carbonyl groups are all terminal and are divided equally among the four osmium atoms not involved in co-ordination to the diene ligand.

Conclusion

This work has demonstrated that upon co-ordination to a tetraosmium cluster the cyclohexa-1,3-diene moiety may undergo hydrogenation producing both cyclohexenyl and allylic complexes, or isomerisation to yield a cyclohexyne ring. Alternatively, C–H bond activation and dehydrogenation may occur to form benzene derivatives. The ease with which these reactions occur is clearly governed by the ability of the 60-

electron tetrahedral cluster to undergo either H_2 loss (by hydrogenation of the diene) or CO loss to generate highly reactive 58-electron unsaturated intermediates. This behaviour parallels that shown by a number of metal surfaces where hydrogenation and dehydrogenation steps may occur. The cluster therefore has the ability not only to cleave the saturated methylene fragments of the C_6H_8 molecule, but also the olefinic C–H bonds to generate 'yne' complexes. This series of reactions is of importance to the novel activation of these systems.

Experimental

Synthesis and characterisation

All reactions were carried out with the exclusion of air under an atmosphere of dried nitrogen, using freshly distilled solvents. Product separation was achieved by thin layer chromatography (TLC) using glass 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 (0.5 mm path length) on a Perkin-Elmer 1710 Series Fourier-transform spectrometer, calibrated with carbon dioxide. Fast atom bombardment (FAB) mass spectra were obtained on a Kratos MS50TC spectrometer. The instrument was run in positive mode, using CsI as calibrant. Proton NMR spectra were recorded in CDCl_3 on Bruker WH200, AM360 or Varian VXR600S Fourier-transform spectrometers, all chemical shifts being reported relative to internal SiMe_4 . The $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{MeCN})_2]$ cluster was prepared from $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}]$ ¹⁶ by the literature procedure,⁵ whilst cyclohexa-1,3-diene (C_6H_8) was purchased from Aldrich and used without further purification. Percentage yields are given on the basis of Os content.

Thermolysis of $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{MeCN})_2]$ **1 with cyclohexa-1,3-diene.** The compound $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{MeCN})_2]$ **1** (100 mg) in dichloromethane (50 cm^3) containing an excess of cyclohexa-1,3-diene (2 cm^3) was heated to reflux for 18 h. Infrared spectroscopy indicated complete consumption of starting material after this time. The solvent was removed under reduced pressure and the products separated by TLC using a solution of dichloromethane–hexane (1:3, v/v) as eluent. Several bands were obtained, which in order of elution were extracted and characterised spectroscopically as $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{11}(\mu\text{-}\eta^1:\eta^2\text{-C}_6\text{H}_9)]$ **2** (orange, 8%), $[\text{Os}_4(\mu\text{-H})(\text{CO})_{10}(\mu_3\text{-}\eta^1:\eta^1:\eta^2\text{-C}_6\text{H}_8)(\eta^3\text{-C}_6\text{H}_9)]$ **3** (orange, 5%), $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\eta^4\text{-C}_6\text{H}_8)]$ (orange, 8%), $[\text{Os}_5(\mu\text{-H})_2(\text{CO})_{13}(\eta^4\text{-C}_6\text{H}_8)]$ **5** (orange, 6%), $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{10}(\eta^6\text{-C}_6\text{H}_5\text{C}_6\text{H}_9)]$ **4** (orange, 6%), $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{12}(\eta^2\text{-C}_6\text{H}_8)]$ (green, 4%), $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{10}(\eta^6\text{-C}_6\text{H}_6)]$ (orange, 18%) and $[\text{Os}_4(\text{CO})_9(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-C}_6\text{H}_8)]$ (red, 10%), respectively.

Thermolysis of $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{11}(\mu\text{-}\eta^1:\eta^2\text{-C}_6\text{H}_9)]$ **2 in octane.** The complex $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{11}(\mu\text{-}\eta^1:\eta^2\text{-C}_6\text{H}_9)]$ **2** (25 mg) was suspended in octane (30 cm^3) and heated to reflux for 2 h. The solvent was removed *in vacuo* and purification by TLC using dichloromethane–hexane (1:3, v/v) as eluent resulted in two compounds, the first of which was characterised as starting material, $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{11}(\mu\text{-}\eta^1:\eta^2\text{-C}_6\text{H}_9)]$ **2** (orange, 24%), and the second as $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-C}_6\text{H}_8)]$ **6** (orange, 15%).

Crystal structure determination for compounds **3**, **4** and **5**

Crystal data 3. $\text{C}_{22}\text{H}_{18}\text{O}_{10}\text{Os}_4$, $M = 1203.16$, monoclinic, space group $P2_1/n$, $a = 9.442(3)$, $b = 16.900(5)$, $c = 15.555(5)$ Å, $\beta = 97.45(3)^\circ$, $U = 2461.2$ Å³, $\lambda = 0.71073$ Å, $Z = 4$, $D_c = 3.247$ g cm^{-3} , orange crystal 0.15 × 0.12 × 0.20 mm, $\mu(\text{Mo-K}\alpha) = 19.867$ mm^{-1} , $F(000) = 2136$.

4 $C_{22}H_{16}O_{10}Os_4$, $M = 1201.15$, monoclinic, space group $P2_1/n$, $a = 9.018(2)$, $b = 25.198(4)$, $c = 11.336(2)$ Å, $\beta = 95.11(2)^\circ$, $U = 2565.9(8)$ Å³, $\lambda = 0.71073$ Å, $Z = 4$, $D_c = 3.109$ g cm⁻³, dark red needle $0.51 \times 0.12 \times 0.10$ mm, $\mu(\text{Mo-K}\alpha) = 19.797$ mm⁻¹, $F(000) = 2128$.

5 $C_{19}H_{10}O_{13}Os_5$, $M = 1397.27$, triclinic, space group $P\bar{1}$, $a = 9.394(10)$, $b = 16.149(13)$, $c = 17.257(18)$ Å, $\alpha = 105.41(7)^\circ$, $\beta = 97.58(9)^\circ$, $\gamma = 93.30(7)^\circ$, $U = 2490$ Å³, $\lambda = 0.71073$ Å, $Z = 4$, $D_c = 3.727$ g cm⁻³, red plate, $0.15 \times 0.05 \times 0.005$ mm, $\mu(\text{Mo-K}\alpha) = 24.532$ mm⁻¹, $F(000) = 2432$.

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 graphite-monochromated Mo-K α X-radiation. **3**, $T = 150$ K, ω -2 θ scans, 3127 unique data collected ($2\theta_{\text{max}} 45^\circ$, $h - 10$ to 10 , $k 0-18$, $l 0-16$), semi-empirical absorption correction applied,¹⁸ giving 3127 unique reflections with $I > 2\sigma(I)$ for use in all calculations. **4**, $T = 293$ K, ω scans, 3365 unique data collected ($2\theta_{\text{max}} 45^\circ$, $h - 9$ to 9 , $k 0-27$, $l 0-12$), semi-empirical absorption correction applied, giving 3364 reflections with $I > 2\sigma(I)$ for use in all calculations. **5**, $T = 150$ K, ω -2 θ scans, 6433 unique data collected ($2\theta_{\text{max}} 45^\circ$, $h - 10$ to 9 , $k -17$ to 16 , $l 0-18$), semi-empirical absorption correction applied, giving 6419 reflections with $I > 2\sigma(I)$ for use in all calculations.

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 In **4** all non-H atoms were then refined (by least-squares on F^2 using SHELXL 93²⁰) with anisotropic thermal parameters, whereas in **3** only the Os and O atoms, and in **5** only the Os atoms were refined anisotropically, with the remaining non-H atoms allowed isotropic thermal motion. Hydrogen atoms on C were included in the models at fixed, calculated positions, and the hydrides were located using XHYDEX.¹⁵

In **3** at final convergence R , $wR2 = 0.0597$, 0.1731 respectively, $S = 1.028$ for 216 refined parameters and the final ΔF synthesis showed no $\Delta\rho$ above 3.49 or below -4.20 e Å⁻³, the major features lying near the Os atoms. In **4** at final convergence R , $wR2 = 0.0590$, 0.1508 respectively, $S = 1.052$ for 325 refined parameters and the final ΔF synthesis showed no $\Delta\rho$ above 3.66 or below -2.24 e Å⁻³, the major features lying near the Os atoms. In **5** at final convergence R , $wR2 = 0.1033$, 0.2737 respectively, $S = 0.913$ for 347 refined parameters and the final ΔF synthesis showed no $\Delta\rho$ above 7.42 or below -6.24 e Å⁻³, the major features lying near the Os atoms.

Atomic scattering factors were inlaid,²⁰ or taken from ref. 21. Molecular geometry calculations utilised CALC,²² and Figs. 4-7 were produced using SCHAKAL 93.²³

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/8.

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