Reaction of $[Os_4(\mu\text{-}H)_4(CO)_{12}]$ with Cyclohexa-1,3-diene *via* Chemical Activation: Synthesis and Structural Characterisation of $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ and $[Os_4(CO)_9(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ and Their Interconversion†

Hong Chen,[a] Brian F. G. Johnson,[a] Jack Lewis,*[,a] Dario Braga,*[,a] Fabrizia Grepioni[b] and Emilio Parisini[b]

[a] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK*

[b] *Dipartimento di Chimica 'G. Ciamician, Universita degli Studi di Bologna, Via Selmi 2, 40126 Bologna, Italy*

The tetranuclear hydrido cluster $[Os_4(\mu\text{-}H)_4(CO)_{12}]$ **1** has been activated by Me_3NO–MeCN to give a reactive intermediate $[Os_4(\mu\text{-}H)_4(CO)_{10}(MeCN)_2]$ **2** which reacts further with cyclohexa-1,3-diene in CH_2Cl_2 under refluxing to produce new clusters including the benzene-co-ordinated compounds $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ **5** and $[Os_4(CO)_9(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ **6**. Structural analyses of **5** and **6** by X-ray diffraction have shown that the benzene ligand is co-ordinated to one metal atom in an η^6 fashion, and the C_6H_8 ligand in **6** is also terminally bonded to one metal atom. Crystal data: **5**, a = 8.209(1), b = 15.029(2), c = 16.453(2) Å, β = 89.90(1)° and Z = 4; **6**, a = 15.614(2), b = 16.465(2), c = 18.010(2) Å, β = 89.42(2)° and Z = 8. Interconversion between compounds **5** and **6** has been observed. Reaction of **5** with cyclohexa-1,3-diene *via* Me_3NO–MeCN activation leads to the formation of **6**, while thermal decomposition of **6** affords **5**.

The interactions between arenes and metal atoms, metal surfaces and metal clusters is an important aspect of organometallic chemistry.[1,2] Recent studies have shown that benzene adopts a variety of bonding modes in cluster systems.[3–6] In the trinuclear cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)]$[4] the benzene ligand sits on the metal triangular face and is symmetrically bonded to three metal atoms, while in the hexanuclear complex $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)]$[4] one of the benzene ligands adopts a terminal bonding mode. Benzene migration from the face-capping position to a terminal position has also been observed.[5] In terms of the synthetic approach to arenemetal cluster species, cyclohexa-1,3-diene has been a good source of the benzene ligand.[4,7,8] We report here the reaction of the reactive intermediate $[Os_4(\mu\text{-}H)_4(CO)_{10}(MeCN)_2]$, with cyclohexa-1,3-diene, leading to the formation of two benzene-co-ordinated tetraosmium clusters $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ and $[Os_4(CO)_9(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ both of which have been characterised by single-crystal X-ray analyses.

Experimental

Materials and Methods.—All reactions were performed under nitrogen atmospheres using standard Schlenk techniques. Dichloromethane was dried over CaH_2 and acetonitrile over P_2O_5. The compound $[Os_4(\mu\text{-}H)_4(CO)_{12}]$ was prepared by a refinement of a published method.[9,10] Infrared spectra were recorded on a Perkin-Elmer 983 or 1710 spectrometer using solution cells (0.1 mm), NMR spectra in $CDCl_3$ solutions on a Bruker AM-400 or WM-250 spectrometer, chemical shifts being reported relative to $SiMe_4$. Mass spectra were recorded on an AEI MS12 or a FAB MS902 instrument. Neutral products were purified by thin-layer chromatography (TLC) on 20 cm × 20 cm × 0.25 mm silica plates (Merck Kieselgel $60F_{254}$).

Synthesis of Clusters **3**–**6**. The compound $[Os_4(\mu\text{-}H)_4(CO)_{12}]$ **1** (50 mg) was suspended in MeCN (10 cm^3). Two equivalents of Me_3NO in MeCN were added dropwise at room temperature, which gradually produced a clear yellow-orange solution. The reaction was completed in 1 h as indicated by the IR spectrum. The solution was then filtered through silica gel to remove the excess of Me_3NO and some decomposition material. The solvent was removed *in vacuo* and the orange solid of $[Os_4(\mu\text{-}H)_4(CO)_{10}(MeCN)_2]$ **2** was dissolved in CH_2Cl_2 (10 cm^3), to which was added an excess of cyclohexa-1,3-diene. The mixture was heated to reflux for 24 h, and the colour of the resultant mixture was red. The solvent was removed on a rotary evaporator, and the residue was worked up by TLC with 50% CH_2Cl_2 in hexane as eluent. A range of bands were afforded, amongst which only four were separated as clear bands. The first orange band was characterised as $[Os_4(\mu\text{-}H)_3(CO)_{11}(C_6H_9)]$ **3** (10%). The second orange compound was identified as $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^4\text{-}C_6H_8)]$ **4** (6%), whereas the third orange complex and the fourth red-brown band were characterised as $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ **5** (23%) and $[Os_4(CO)_9(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ **6** (15%), respectively.

Crystal-structure Determination of Compounds **5** *and* **6**.—For both structures intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer by the ω-scan method. The structure was solved by direct methods, followed by Fourier difference syntheses and least-square refinements. For all calculations the SHELX 76 program was used.[11] All non-H atoms were allowed to vibrate anisotropically. The H atoms were added in calculated positions (C–H 1.08 Å) and refined 'riding' on their respective C atoms; a single isotropic thermal parameter was also refined for the H atoms [0.25(1) and 0.08(1) $Å^2$ for compounds **5** and **6**, respectively]. Absorption correction was applied by the Walker and Stuart

---

† 4(η^6)-Benzene-μ-carbonyl-1:4κC-nonacarbonyl-1κ^3C,2κ^3C,3κ^3C-di-μ-hydrido-1:2κ^2H;2:3κ^2H-*tetrahedro*-tetraosmium and 4(η^6)-benzene-μ_3-carbonyl-2:3:4κ^3C-di-μ-carbonyl-1:3κ^2C;2:3κ^2C-hexacarbonyl-1κ^3C-2κ^3C-3(η^4)-cyclohexa-3-diene-*tetrahedro*-tetraosmium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Spectroscopic data for complexes **3–6**

Compound	IR (ν_{CO}/cm^{-1})	MS(^{192}Os) obs. (calc.)	^{1}H NMR
3 [$Os_4(\mu$-$H)_3(CO)_{11}(C_6H_9)$]	[a] 2098w, 2066vs, 2051s, 2037s, 2022s, 2010vs, 1995ms, 1985m, 1954mw	1160 (1160)	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)
4 [$Os_4(\mu$-$H)_2(CO)_{11}(\eta^4$-$C_6H_8)$]	[a] 2092w, 2069s, 2049s, 2012s, 1998m, 1850vw [b] 2091w, 2066s, 2044s, 2009s	1158 (1158)	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), 1958w, 1774(br)vw [c] 2082m, 2058s, 2021vs, 1996s, 1972vs, 1929s, 1799w	1128 (1128)	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] 2083vw, 2061w, 2052w, 2026vs, 2021vs, 2014s, 2003w, 1983ms, 1969w, 1965w, 1949w, 1865w, 1798vw [c] 2080vw, 2054m, 2019s, 2000m(sh), 1977m, 1948w(sh), 1847vw(br), 1774vw(br)	1172 (1172)	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)

[a] Recorded in hexane solution. [b] Recorded in CH_2Cl_2 solution. [c] Recorded in KBr disc.

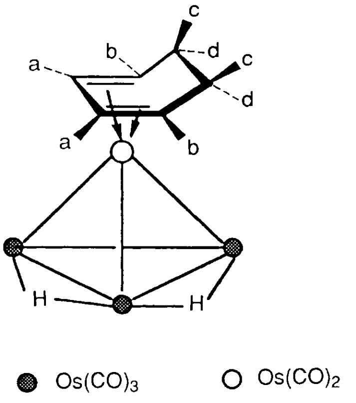

Fig. 1 Proposed structure of [$Os_4(\mu$-$H)_2(CO)_{11}(C_6H_8)$] **4**

method[12] (correction range, 0.37–1.00 and 0.46–1.00 for **5** and **6** respectively).

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

Interconversion between compounds **5** *and* **6**.—To an acetonitrile solution (10 cm^3) of [$Os_4(\mu$-$H)_2$ $(CO)_{10}(\eta^6$-$C_6H_6)$] **5** (15 mg), was added dropwise 1 equivalent of Me_3NO in MeCN. The mixture was stirred at room temperature (r.t.) for 45 min. The IR spectrum showed that the starting material **5** was consumed, and a new species, tentatively formulated as [$Os_4(\mu$-$H)_2(CO)_9(MeCN)(\eta^6$-$C_6H_6)$] **7** was formed [IR: ν_{CO}(MeCN) 2062m, 2038m, 2022s, 1997s, 1975s and 1942m(sh) cm^{-1}]. After removal of solvent *in vacuo*, the orange-red solid **7** was dissolved in CH_2Cl_2 (10 cm^3), and an excess of cyclohexa-1,3-diene was added. The mixture was stirred at r.t. for 2 h, and the colour turned from orange to deep red. The IR spectrum of the reaction mixture showed bands due to [$Os_4(CO)_9(\eta^6$-$C_6H_6)(\eta^4$-$C_6H_8)$] **6**. Work-up of the resultant mixture by TLC with 50% CH_2Cl_2 in hexane afforded **6** in *ca.* 40% yield, together with some unidentified minor products.

When a benzene solution (5 cm^3) of compound **6** (10 mg) was heated to reflux for 4 h the colour of the solution turned from red to orange, and the IR spectrum showed the bands for complex **5**. Work-up of the resultant mixture by TLC after removal of solvent, eluting with 50% CH_2Cl_2 in hexane, gave one orange band as the major product which was identified as **5**.

Results and Discussion

The tetranuclear cluster [$Os_4(\mu$-$H)_4(CO)_{12}$] **1** was treated with 2 mole equivalents of Me_3NO in MeCN at room temperature to give a highly reactive species [$Os_4(\mu$-$H)_4$-$(CO)_{10}(MeCN)_2$] **2** which was not isolated but was characterised on the basis of its IR spectrum [ν_{CO}(MeCN) 2080vw, 2051m, 2020s, 1998vs, 1983s and 1944w cm^{-1}]. Further reaction of **2** with an excess of cyclohexa-1,3-diene in refluxing dichloromethane for 24 h produced a variety of products, amongst which four major compounds have been characterised, on the basis of their spectroscopic data (Table 1), as [$Os_4(\mu$-$H)_3(CO)_{11}(C_6H_9)$] **3**, [$Os_4(\mu$-$H)_2(CO)_{11}(\eta^4$-$C_6H_8)$] **4**, [$Os_4(\mu$-$H)_2(CO)_{10}(\eta^6$-$C_6H_6)$] **5** and [$Os_4(CO)_9$-$(\eta^6$-$C_6H_6)(\eta^4$-$C_6H_8)$], **6**.

Cluster **3** has been previously reported from the direct reaction of **1** with cyclohexene under UV irradiation and has been structurally characterised.[13] The cyclohexenyl ligand is σ bonded to one osmium atom and π bonded to another. In respect of the formation of the cyclohexenyl ligand from cyclohexa-1,3-diene, hydrogen transfer from the metal framework to the organic ligand and from one C atom to another might have occurred.

The C_6H_8 ligand in complex **4** is probably terminally bonded to one metal centre (Fig. 1), since to date there has been no report of a cyclohexadiene ligand co-ordinating to a metal triangular face. The band at 1850 cm^{-1} in the IR spectrum implies the presence of a bridging carbonyl ligand, possibly due to the steric repulsion of the C_6H_8 ligand. The ^{1}H NMR spectrum shows one broad resonance in the hydride region, and three resonances in the organic region. The apparent AB quartet at δ 2.02 is assigned to protons H_c and H_d, while the broad signal at δ 3.96 and the multiplet at δ 5.58 correspond to H_b and H_a, respectively. This requires a plane of symmetry in the molecule or some fluxional behaviour to generate such a plane, which might be similar to that observed in [$Os_3(CO)_{10}$-(C_6H_8)][14] since they possess similar ^{1}H NMR spectra.

The complex [$Os_4(\mu$-$H)_2(CO)_{10}(\eta^6$-$C_6H_6)$] **5** is easily identified from its ^{1}H NMR spectrum. A singlet at δ 5.95 is consistant with a benzene bonded in a terminal position and is comparable to the chemical shifts of δ 5.94 for [$Os_3(CO)_7$-$(\eta^6$-$C_6H_6)(Me_2C_2)$][5] and δ 5.54 for [$Ru_6C(CO)_{11}(\eta^6$- $C_6H_6)$-

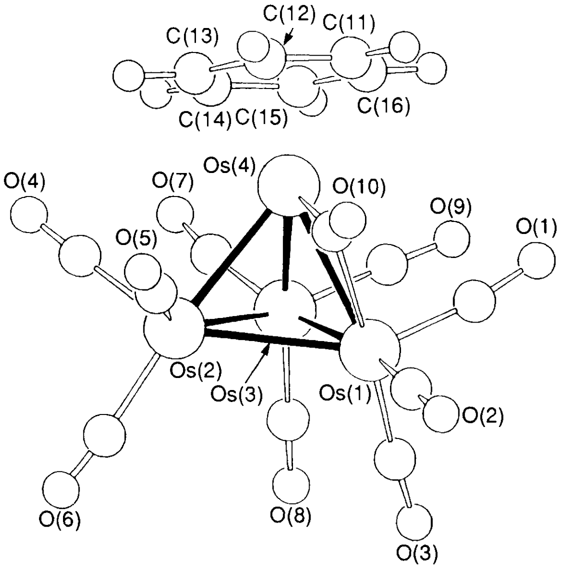

Fig. 2 Crystal structure of [$Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)$] **5** showing the atom labelling; the O atoms of the carbonyl ligands bear the same number as the relevant carbon atoms

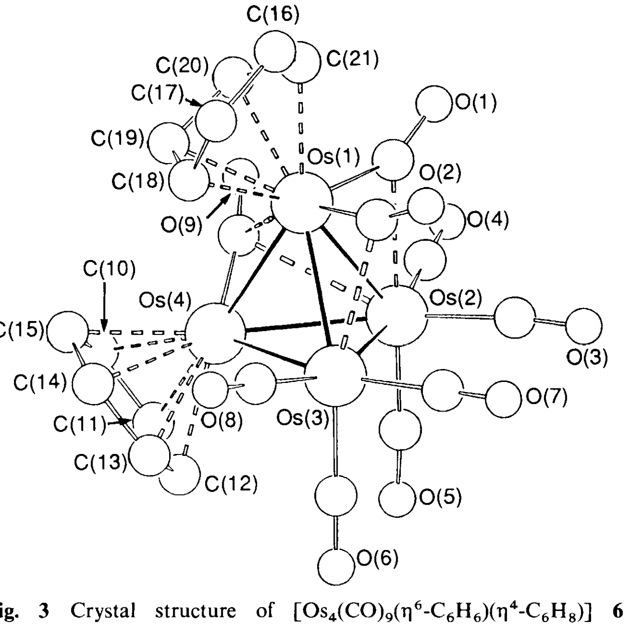

Fig. 3 Crystal structure of [$Os_4(CO)_9(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$] **6** showing the atom labelling; the O atoms of the carbonyl ligands bear the same number as the relevant carbon atoms

Table 2 Selected bond lengths (Å) and angles (°) for compound **5**

Os(1)–Os(2)	2.979(1)	Os(1)–Os(3)	2.758(1)
Os(1)–Os(4)	2.811(1)	Os(2)–Os(3)	2.892(1)
Os(2)–Os(4)	2.787(1)	Os(3)–Os(4)	2.808(1)
Os(4)–C(12)	2.21(2)	Os(4)–C(13)	2.22(2)
Os(4)–C(14)	2.27(1)	Os(4)–C(15)	2.26(2)
Os(4)–C(16)	2.25(2)	Os(4)–C(11)	2.21(1)
C(11)–C(12)	1.39(2)	C(12)–C(13)	1.38(2)
C(13)–C(14)	1.38(2)	C(14)–C(15)	1.39(2)
C(15)–C(16)	1.38(2)	C(11)–C(16)	1.38(2)
Os(4)–C(10)	1.91(1)	Os(1)–C(10)	2.35(2)
mean Os–C (terminal)	1.81(2)	C(10)–O(10)	1.21(2)
Os(4)–C(10)–O(10)	150(1)	meanC–O(terminal)	1.13(2)

($\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6$)].[4] The IR spectra of a CH_2Cl_2 solution and a KBr pellet show a band at 1774 and 1799 cm^{-1}, respectively, implying the existence of a bridging carbonyl ligand. This has been confirmed by X-ray analysis. A red, plate crystal of **5** was grown from a CH_2Cl_2–hexane solution at −5 °C, and subjected to single-crystal X-ray analysis, as discussed later.

The NMR studies of [$Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)$] **5** show that the molecule undergoes some fluxional processes in solution. Thus, the ^1H NMR spectrum displays two broad singlets in the hydride region implying possible exchange between these two hydrides. The $^{13}C\text{-}\{^1H\}$ NMR spectrum of **5** in CD_2Cl_2 at room temperature shows a sharp singlet at δ 81.90 for the benzene ligand, but the carbonyl resonances are broadened to baseline indicating fluxional behaviour of the molecule. A low-temperature (200 K) $^{13}C\text{-}\{^1H\}$ NMR spectrum displays, apart from the sharp benzene resonance, ten resonances in the carbonyl region as expected: δ(CD_2Cl_2) 200.4, 182.4, 180.3, 176.6, 175.0, 171.0, 169.1, 168.9, 166.8 and 166.5, with the downfield resonance (δ 200.4) being assigned to the bridging carbonyl ligand. However, it is difficult to obtain a more detailed ^{13}C NMR study on **5** due to its low solubility, and therefore we cannot propose a mechanism for this fluxional behaviour.

The complex [$Os_4(CO)_9(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$] **6** cannot be isolated in pure form by TLC, but can be purified by crystallisation from CH_2Cl_2–hexane. Its IR spectrum shows the existence of bridging carbonyl ligands (1847 and 1774 cm^{-1}), which has also been confirmed by X-ray crystal analysis. More information is provided by the ^1H NMR spectrum. No hydride resonance is observed. There is a strong singlet at δ 5.75, implying a terminal-bonded benzene as in the case of **5**. There are, however, another eight resonances with relative intensity of one proton each between δ 1.5 and 5.5, which is consistent with a cyclohexadiene system. The two apparent AB quartets at higher field correspond to the two sets of geminal protons, and the two second-order multiplets at lowest field in this region are recognisable as the two protons non-adjacent to those geminal protons. The observation of eight resonances for the C_6H_8 ligand might imply asymmetry of the molecule and rigidity of the ligand.

Dark red crystals of compound **6** were obtained by slow evaporation of a CH_2Cl_2–hexane solution at −5 °C, and a single-crystal analysis has been carried out.

The molecular structures of **5** and **6** are closely related and will be discussed together. They are shown in Figs. 2 and 3, respectively, together with the labelling schemes. Because of the presence of two independent molecules in the unit cell of **6**, the average parameters discussed in the following are calculated over the equivalent sets of bonds in the two molecules. Relevant bond distances and angles for **5** are listed in Table 2, those for the two molecules (A and B) of **6** are listed separately in Table 3. Crystal data for both compounds are summarized in Table 4.

The metal frameworks of the two species are constituted of distorted Os_4 tetrahedra, with Os–Os distances ranging from 2.758(1) to 2.979(1) Å, and from 2.715(1) to 2.883(1) Å in **5** and **6**, respectively. Both species bear an η^6-benzene ligand co-ordinated to a tetrahedron apex, with average Os–C distances of 2.24(2) and 2.25(1) Å, respectively. These values are strictly comparable to the average Os–C (benzene) distance of 2.25(1) Å observed in [$Os_3(CO)_9(\eta^6\text{-}C_6H_6)(Me_2C_2)$].[5] In **5**, where no geometrical constraints were used during refinement of the C_6 fragment no appreciable deviations from regular D_{6h} symmetry of the ligand can be detected.

As shown in Fig. 3, compound **6** also bears an η^4-co-ordinated C_6H_8 ligand on a second apex of the tetrahedron, with Os–C distances ranging from 2.17(2) to 2.27(2) Å [average 2.22(2) Å], the 'long' bonds being from the C atoms facing the benzene ligand.

In both **5** and **6** the benzene-bound Os atoms also bear a single CO ligand which appears to be forced into a semibridging position in the former species [Os(1) ••• C(10) 2.35(2) Å, see Fig. 1] and in μ_3-semibridging position over a tetrahedron triangular face in the latter one [Os(1) ••• C(9) 2.72(2) and Os(2) ••• C(9) 2.78(2) Å]. These effects must be ascribed to the

Table 3 Relevant bond distances (Å) and angles (°) for compound **6**

	Molecule A	Molecule B		Molecule A	Molecule B
Os(1)–Os(2)	2.883(1)	2.882(1)	mean Os–C (term)	1.88(2)	1.89(2)
Os(1)–Os(3)	2.749(1)	2.736(1)	mean C–O (term)	1.15(2)	1.15(3)
Os(1)–Os(4)	2.844(1)	2.839(1)			
Os(2)–Os(3)	2.715(1)	2.728(1)	Os(1)–C(18)	2.24(2)	2.23(2)
Os(2)–Os(4)	2.782(1)	2.778(1)	Os(1)–C(19)	2.24(2)	2.21(2)
Os(3)–Os(4)	2.862(1)	2.853(1)	Os(1)–C(20)	2.20(2)	2.17(2)
			Os(1)–C(21)	2.20(2)	2.27(2)
Os(1)–C(2)	1.93(2)	1.91(3)	Os(1) ··· C(16)	3.13(2)	3.14(2)
Os(2) ··· C(1)	2.45(2)	2.42(2)	Os(1) ··· C(17)	3.10(2)	3.11(2)
Os(1)–C(2)	1.90(2)	1.87(2)			
Os(3) ··· C(2)	2.63(2)	2.68(2)	Os(4)–C(10)	2.21(1)	2.25(1)
Os(4)–C(9)	1.82(2)	1.85(2)	Os(4)–C(11)	2.20(1)	2.25(1)
Os(1) ··· C(9)	2.72(2)	1.76(2)	Os(4)–C(12)	2.25(1)	2.25(1)
Os(2) ··· C(9)	2.78(2)	2.69(2)	Os(4)–C(13)	2.29(1)	2.25(1)
			Os(4)–C(14)	2.29(1)	2.25(1)
C(1)–O(1)	1.16(2)	1.21(2)	Os(4)–C(15)	2.25(1)	2.25(1)
C(2)–O(2)	1.16(2)	1.16(2)			
C(9)–O(9)	1.20(2)	1.14(2)			
Os(1)–C(1)–O(1)	152(2)	153(2)	C(18)–C(19)–C(20)	114(2)	113(2)
Os(3)–C(2)–O(2)	125(1)	122(2)	C(20)–C(21)–C(16)	120(2)	119(2)
Os(4)–C(9)–O(9)	166(2)	163(2)	C(21)–C(16)–C(17)	111(2)	108(2)
			C(19)–C(20)–C(21)	112(2)	116(2)
C(16)–C(17)–C(18)	112(2)	111(2)			
C(17)–C(18)–C(19)	120(2)	120(2)			

Table 4 Crystal data and details of measurements for compounds **5** and **6**[a]

Formula	**5**	**6**
M_r	$C_{16}H_8O_{10}Os_4$	$C_{21}H_{14}O_9Os_4$
Crystal size/mm	1121	1171
Space group	0.10 × 0.15 × 0.12	0.14 × 0.10 × 0.15
a/Å	$P2_1/n$	$P2_1/c$
b/Å	8.209(1)	15.614(2)
c/Å	15.029(2)	16.465(2)
β/°	16.453(2)	18.010(7)
U/Å^3	89.90(1)	89.42(2)
Z	2029.9	4629.7
F(000)	4	8
D_c/g cm^{-3}	1952	4128
μ(Mo-Kα)/cm^{-1}	3.67	3.36
Range of reflections measured	240.4	210.8
($h_{min}h_{max}$, $k_{min}k_{max}$, $l_{min}l_{max}$)		
Measured reflections	−9 9, 0 17, 0 19	−18 18, 0 19, 0 21
Unique observed reflections used in the refinement	3449	7775
[$F_o > 4\sigma(F_o)$]	2810	6005
No. of refined parameters	273	594
R,R',[b] S	0.043, 0.045, 0.97	0.052, 0.054, 1.11
k,g	1.0, 0.0017	1.2144, 0.0045

[a] Details in common: monoclinic; λ(Mo-Kα) 0.710 69 Å; θ 2.5–25°; ω scan width 0.7°; requested counting $\sigma(I)/I$ 0.01; prescan rate 8° min^{-1}; prescan acceptance $\sigma(I)/I$ 0.5; maximum scan time 100 s. [b] $R' = \Sigma[(F_o - F_c)w^{\frac{1}{2}}]/\Sigma(F_o w^{\frac{1}{2}})$, where $w = k/[\sigma^2(F) + |g|F^2]$.

spatial requirements of the benzene ligands. This observation is substantiated by the comparable effect on the neighbouring CO group, caused by the C_6H_8 ligand in **6**: the two CO co-ordinated to the same Os atom 'bend away' from the ligand towards Os(2) and Os(3) [Os(2) ··· C(1) 2.45(2) and Os(3) ··· C(2) 2.63(2) Å, respectively]. The remaining nine CO ligands in **5** and six CO in **6** are distributed three on each basal Os atom.

In compound **5** the two H(hydride) atoms are believed to bridge the two 'long' Os–Os from the CO ligand displacement around these co-ordination sites.

Altogether, the steric situation in compound **6** appears to be much more congested than in **5**, also because the H(hydride) atoms in this latter species, besides providing two electrons to the cluster by occupying less-demanding edge-bridging positions, help to reduce the ligand crowding over the cluster surface by enlarging the metal framework.

There has been a report on a tetraruthenium cluster with one benzene ligand and one cyclohexadiene ligand, *i.e.* [$Ru_4(CO)_9(C_6H_6)(C_6H_8)$],[8] which is prepared from the reaction between [$Ru_3(CO)_{12}$] and cyclohexa-1,3-diene in refluxing octane. In this case the four ruthenium atoms form a 'butterfly' structure, with the benzene ligand η^6-co-ordinating to one of the hinge ruthenium atoms. The C_6H_8 ligand, however, interacts with the metal frame as cyclohexenylene forming two σ and two π bonds. This is structurally rather different from [$Os_4(CO)_9(\eta^6$-$C_6H_6)(\eta^4$-$C_6H_8)$] **6**.

Finally, it is worth mentioning that, as in the case of [$Os_3(CO)_9(\eta^6$-$C_6H_6)(Me_2C_2)$],[5] potential-energy barrier calculations for **5** based on the atom-atom approach[15] indicate that the benzene fragment can undergo reorientational motion around its co-ordination axis in the solid state [estimated intermolecular barrier *ca.* 5 kcal mol^{-1} (*ca.* 20.92 kJ mol^{-1})].

The conversion of complex **5** into **6** has been observed. The benzene complex $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ **5** can react with Me_3NO–MeCN to give a reactive intermediate $[Os_4(\mu\text{-}H)_2(CO)_9(MeCN)(\eta^6\text{-}C_6H_6)]$ **7** which has not been isolated, and on further reaction with cyclohexa-1,3-diene in CH_2Cl_2 at room temperature produces the cluster $[Os_4(CO)_9(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ **6** in *ca.* 40% yield. On the other hand, when a benzene solution of **6** is heated to reflux, complex **5** is obtained as the major product, with some untractable minor products.

Acknowledgements

We would like to thank the Sino-British Friendship Scholarship Scheme (H. C.) and Ministero Pubblica Istruzione (Italy) for financial support.

References

1 E. L. Muetterties, J. R. Bleake, E. J. Wucherer and T. A. Albright, *Chem. Rev.*, 1982, **82**, 499.
2 E. L. Muetterties, *Pure Appl. Chem.*, 1982, **54**, 83.
3 D. Braga, F. Grepioni, B. F. G. Johnson, J. Lewis, M. Martinelli and A. H. Wright, *J. Chem. Soc., Chem. Commun.*, 1990, 364.
4 M. P. Gomez-Sal, B. F. G. Johnson, J. Lewis, P. R. Raithby and A. H. Wright, *J. Chem. Soc., Chem. Commun.*, 1985, 1682.
5 D. Braga, F. Grepioni, B. F. G. Johnson, J. Lewis, M. Martinelli and M. A. Gallop, *J. Chem. Soc., Chem. Commun.*, 1990, 53.
6 I. U. Khand, G. R. Knox, P. L. Pauson and W. E. Watts, *J. Chem. Soc., Perkin Trans.*, 1973, 975.
7 M. Martinelli, personal communication.
8 S. Aime, L. Milone, D. Osella, G. A. Vaglio, M. Valle, A. Tiripicchio and M. T. Camellini, *Inorg. Chim. Acta*, 1979, **34**, 49.
9 S. A. R. Knox, J. W. Koepke, M. A. Andrews and H. D. Kaesz, *J. Am. Chem. Soc.*, 1975, **97**, 3942.
10 P. H. Darlin, personal communication.
11 G. M. Sheldrick, SHELX 76 Crystal Structure Determination Package, University of Cambridge, 1976.
12 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
13 S. Bhaduri, B. F. G. Johnson, J. Lewis, P. R. Raithby, S. Rehani, G. M. Sheldrick, K. C. Wong and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1979, 562.
14 E. G. Bryan, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1977, 144.
15 D. Braga, F. Grepioni, B. F. G. Johnson, J. Lewis and M. Martinelli, *J. Chem. Soc., Dalton Trans.*, 1990, 1847.

Received 22*nd June* 1990; *Paper* 0/02811H