A Substituted Hexaosmium Hydrido Cluster with Benzene Ligands in Two Different Bonding Modes; Synthesis and Structural Characterisation of $[Os_6H_2(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$

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Treatment of $[Os_5H_4(CO)_{11}(\eta^6\text{-}C_6H_6)]$ **1** with 1,8-diazabicyclo[5.4.0]undec-7-ene in CH_2Cl_2 gives the dianion $[Os_5H_2(CO)_{11}(\eta^6\text{-}C_6H_6)]^{2-}$ **2**, and subsequent reaction of **2** with $[Os(\eta^6\text{-}C_6H_6)(MeCN)_3][BF_4]_2$ provides the new bis-benzene cluster $[Os_6H_2(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **3** in *ca.* 35% yield, the X-ray analysis of which shows that the six osmium atoms adopt a bicapped tetrahedral geometry with one benzene ligand in a terminal η^6 site and the other in a face-capping $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ site.

The chemistry of arene-substituted metal carbonyl clusters has been extensively studied during the last five years,[1] and two modes of co-ordination of the arene to the metal cluster, involving interaction between all six aromatic carbon atoms and the metals, have been observed.[2–8] These are the conventional η^6 bonding mode and $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ face-capping mode, where the arene ring interacts with three metal atoms and takes on some of the characteristics of a cyclohexatriene ligand. This latter mode is of interest because of the relationship to arenes chemisorbed onto metal surfaces,[9] and clusters containing arenes in the $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ bonding mode may be used as models for the chemisorbed systems.[10] A number of examples of clusters containing $\mu_3\text{-}\eta^2:\eta^2:\eta^2$-arene ligands are now known, but only one complex $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$,[11] has been structurally characterised which contains two arene ligands, one adopting the η^6 bonding mode and the other the $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ face-capping mode. With recent synthetic developments[2–8] it should be possible to prepare a range of complexes containing two or more arene rings displaying both bonding modes, and to study the chemical and spectroscopic properties of these systems.

We have demonstrated that $[Os(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ is a good starting material for the synthesis of benzene containing clusters.[12] The coupling reactions of this reagent with dianionic carbonyl clusters of ruthenium and osmium give benzene containing clusters in good yield. Recently, we reported the synthesis of $[Os_5H_4(CO)_{11}(\eta^6\text{-}C_6H_6)]$ **1** which was obtained from the reaction of $[Os(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ with $[Os_4H_4(CO)_{11}]^{2-}$.[12] We now report a development of this work to build higher nuclearity clusters containing two benzene ligands, and show that the two ligands display different bonding modes on a hexanuclear cluster.

Treatment of a dichloromethane solution of $[Os_5H_4(CO)_{11}(\eta^6\text{-}C_6H_6)]$ **1** with an excess of 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) affords a dark brown air-sensitive solid which was tentatively formulated† as $[Os_5H_2(CO)_{11}(C_6H_6)]^{2-}$ **2**. Subsequent reaction of the freshly prepared dianion **2** with 1 equivalent of $[Os(\eta^6\text{-}C_6H_6)(MeCN)_3][BF_4]_2$ gives a dark red cluster $[Os_6H_2(CO)_{11}(C_6H_6)_2]$ **3** in 35% yield after chromatographic separation on silica. The new cluster has been characterised spectroscopically† [IR, fast atom bombardment (FAB) MS, ^1H NMR] and by a single-crystal X-ray analysis.‡ The ^1H NMR spectrum of **3**, in CD_2Cl_2, at room temperature, shows two singlets at δ 6.24 (6 H) and 3.98 (6 H) which indicates that the two benzene ligands bond to the cluster in different environments. Preliminary studies show that the mode of co-ordination of the two benzene ligands depends on the polarity of the solvent used and on the temperature of the system.

The molecular structure of **3** is shown in Fig. 1, which includes some important bond parameters. The metal core geometry is a bicapped tetrahedron, and is related to the trigonal-bipyramidal arrangement found in **1**,[12] and presumably in **2**, by the addition of a face-capping '$[Os(C_6H_6)]^{2+}$' fragment to the dianion **2**. Complex **3** is an 84-electron system, and is isoelectronic with the parent binary carbonyl, $[Os_6(CO)_{18}]$,[14] which also exhibits a bicapped tetrahedral metal framework. However, the formal replacement of seven carbonyls in $[Os_6(CO)_{18}]$ by a $\eta^6\text{-}C_6H_6$ ligand, co-ordinated to Os(4), a $\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6$ ligand, capping the Os(2)Os(3)Os(5) face, and the two hydrides, which are presumed, from potential energy calculations,[15] to bridge the Os(1)–Os(5) and Os(1)–Os(6) edges, has a profound influence on the Os–Os distances in **3** compared to $[Os_6(CO)_{18}]$. The two shortest metal–metal distances in **3** are those thought to be bridged by the hydrides, which is in marked contrast to the usual edge lengthening of the hydrides. The three metal–metal edges [Os(2)–Os(3), Os(2)–Os(5) and Os(3)–Os(5)] capped by the $\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6$ ligand are significantly longer than the equivalent uncapped edges [Os(2)–Os(4), Os(2)–Os(6) and Os(4)–Os(6)], a feature that is not evident in the structure of $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$.[11] The metal–metal distances in **3** no longer reflect the differences in co-ordination number and formal oxidation states of the metals as proposed for $[Os_6\text{-}$

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† Spectroscopic data. **2**: IR (CH_2Cl_2) ν(CO) 2017vs, 1986m, 1963w; **3**: IR (CH_2Cl_2) ν(CO) 2058w, 2017vs, 1995s, 1983s, 1943m cm^{-1}; FAB mass spectrum 1607 (obs.), 1607 (calc.); ^1H NMR (CD_2Cl_2) δ 6.24 (s, 6 H), 3.98 (s, 6 H), −10.24 (s, 2 H).

‡ Crystal data for **3**: $[Os_6H_2(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$, $C_{23}H_{14}O_{11}Os_6$, $M = 1607.5$, monoclinic, space group $P2_1/c$ (no. 14), $a = 14.405(6)$, $b = 18.877(4)$, $c = 17.746(7)$ Å, $\beta = 103.63(3)°$, $U = 2702(2)$ Å^3, $Z = 4$, $D_c = 3.951$ g cm^{-3}, $F(000) = 2784$, Mo-Kα radiation, $\lambda = 0.710\,73$ Å, μ(Mo-Kα) = 281.59 cm^{-1}, crystal dimensions 0.22 × 0.25 × 0.41 mm, 2392 observed diffractometer data [$F > 4\sigma(F)$]. Structure solved by direct methods and Fourier difference techniques, refined by full-matrix least-squares analysis (Os and O atoms anisotropic) to $R = 0.060$, $R' = 0.073$, $w^{-1} = \sigma^2F + 0.0025F^2$, program used SHELXTL PLUS.[13] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

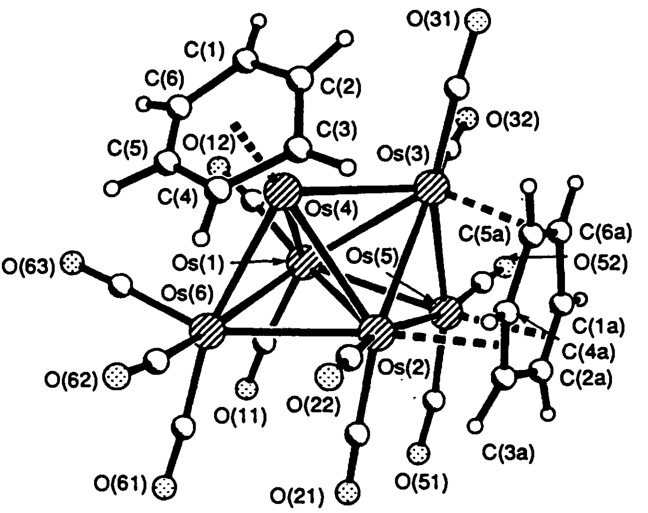

Fig. 1 The molecular structure of $[Os_6H_2(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **3** showing the atomic numbering scheme. Selected bond lengths (Å): Os(1)–Os(2) 2.779(2), Os(1)–Os(3) 2.841(2), Os(1)–Os(4) 2.785(2), Os(1)–Os(5) 2.712(3), Os(1)–Os(6) 2.693(3), Os(2)–Os(3) 2.809(3), Os(2)–Os(4) 2.810(3), Os(2)–Os(5) 2.929(3), Os(2)–Os(6) 2.830(3), Os(3)–Os(4) 2.778(3), Os(3)–Os(5) 2.789(3), Os(4)–Os(6) 2.753(3), Os(4)–C(1) 2.23(6), Os(4)–C(2) 2.23(5), Os(4)–C(3) 2.26(5), Os(4)–C(4) 2.26(5), Os(4)–C(5) 2.17(5), Os(4)–C(6) 2.19(5), Os(5)–C(1a) 2.23(5), Os(5)–C(2a) 2.34(4), Os(2)–C(3a) 2.23(4), Os(2)–C(4a) 2.29(4), Os(3)–C(5a) 2.29(4), Os(3)–C(6a) 2.28(4), C(1)–C(2) 1.46(6), C(2)–C(3) 1.39(7), C(3)–C(4) 1.37(7), C(4)–C(5) 1.33(5), C(5)–C(6) 1.37(7), C(6)–C(1) 1.34(8), C(1a)–C(2a) 1.29(7), C(2a)–C(3a) 1.41(6), C(3a)–C(4a) 1.42(6), C(4a)–C(5a) 1.40(7), C(5a)–C(6a) 1.36(7), C(6a)–C(1a) 1.53(7). Selected bond angles (°): C(2)–C(1)–C(6) 114(5), C(1)–C(2)–C(3) 130(5), C(2)–C(3)–C(4) 110(4), C(3)–C(4)–C(5) 118(5), C(4)–C(5)–C(6) 133(5), C(1)–C(6)–C(5) 114(4), C(2a)–C(1a)–C(6a) 122(5), C(1a)–C(2a)–C(3a) 117(4), C(2a)–C(3a)–C(4a) 122(4), C(3a)–C(4a)–C(5a) 120(4), C(4a)–C(5a)–C(6a) 118(4) and C(1a)–C(6a)–C(5a) 120(4)

$(CO)_{18}]$,[14] nor is there any indication of the presence of incipient bridging carbonyls found in other bicapped tetrahedral Os_6 derivatives.[16]

It is interesting that in **3** the $\eta^6\text{-}C_6H_6$ ligand is co-ordinated to an Os atom with four metal connectivities, similar to that observed in the starting material $[Os_5H_4(CO)_{11}(\eta^6\text{-}C_6H_6)]$ **1**. This is in contrast to the site occupied by the $\eta^6\text{-}C_6H_6$ ligand in $[RuOs_5(CO)_{15}(\eta^6\text{-}C_6H_6)]$ where the arene is co-ordinated to the capping Ru atom which has three metal connectivities.[17] This might suggest that the $\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6$ ligand is the one added by the addition of the '$[Os(C_6H_6)]^{2+}$' unit to **2**, however, it is known that arenes may migrate over cluster surfaces.[7]

The Os–C(arene) distances in **3** for both the $\eta^6\text{-}C_6H_6$ and the $\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6$ ligands are similar to those in $[Os_5H_4(CO)_{11}(\eta^6\text{-}C_6H_6)]$[12] and $[Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$,[11] respectively. The high estimated standard deviations on the C–C distances within the arene rings prevent an analysis of the delocalisation within these rings. However, the orientation of the $\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6$ ring in **3** is similar to that found in $[Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ and $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$,[11] with the mid-points of the alternate C–C bonds lying over the three Os atoms of the capped face.

An analysis of the crystal packing for **3** shows that as in $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$[7] the η^6- and the $\mu_3\text{-}\eta^2:\eta^2:\eta^2$-fragments establish graphitic-like interactions in the lattice. In **3** the angle between the $\eta^6\text{-}C_6H_6$ and the $\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6$ planes is 102.4° compared to 127° in $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$, but in both cases the molecules are placed with their benzene ligands almost face to face across crystallographic centres of symmetry. The arene–arene sequence, which is shown in Fig. 2, is $\eta^6\eta^6\text{-}\mu_3\mu_3\text{-}\eta^6\eta^6\text{-}\mu_3\mu_3$, *etc.* The centroid-to-centroid ring separation for the $\eta^6\eta^6$-pairs, at 4.01 Å, is greater than that for the $\mu_3\mu_3$-pairs, at 3.59 Å. This pattern of molecular coupling leads to the formation of infinite 'saw-tooth' chains of arene-linked molecules which extend in the 111 direction in the monoclinic cell.

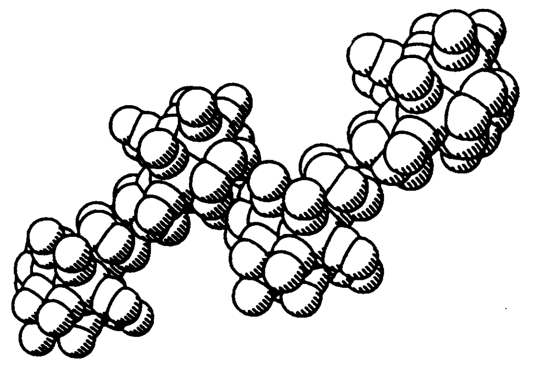

Fig. 2 A van der Waals packing diagram for **3** showing the interaction between pairs of $\eta^6\eta^6$ and $\mu_3\mu_3$ benzene rings

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