Synthesis and Structural Characterisation of $[Os_6(CO)_{12}(\eta^6\text{-}C_6H_6)_2]$

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Reaction of $[Os_4H_2(CO)_{12}]^{2-}$ with $[Os(\eta^6\text{-}C_6H_6)(MeCN)_3][BF_4]_2$ in CH_2Cl_2 affords the pentanuclear cluster $[Os_5H_2(CO)_{12}(\eta^6\text{-}C_6H_6)]$ which upon treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene in CH_2Cl_2 gives the dianion $[Os_5(CO)_{12}(\eta^6\text{-}C_6H_6)]^{2-}$, whose subsequent reaction with $[Os(\eta^6\text{-}C_6H_6)(MeCN)_3][BF_4]_2$ provides the new bis(benzene) cluster $[Os_6(CO)_{12}(\eta^6\text{-}C_6H_6)_2]$ in *ca.* 40% yield; the crystal structure of $[Os_6(CO)_{12}(\eta^6\text{-}C_6H_6)_2]$ shows that the six osmium atoms adopt a bicapped tetrahedral geometry with both benzene ligands in terminal η^6 sites but co-ordinated to two osmium atoms with different metal connectivities.

The chemistry of arene-substituted metal-carbonyl clusters has been extensively studied,[1] and the arene groups have been found to co-ordinate in either the terminal η^6-bonding mode or in the face-capping $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ mode.[2] The latter mode is interesting because of the potential relevance to the chemisorption of benzene on metal surfaces. Recent work within our group has focused on the synthesis and characterisation of high-nuclearity arene-containing ruthenium and osmium clusters.[3–13] Among these clusters the bis(arene) complexes $[Ru_6C(CO)_{11}(arene)_2]$ have been characterised, and X-ray crystal-structure analyses show that these molecules exist in several crystalline forms with the arene ligands in η^6-terminal and/or face-capping $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ modes.[10] The results suggest that both steric and electronic effects may influence the interaction of arene with the cluster.

Previously, using the dication $[Os(C_6H_6)(MeCN)_3]^{2+}$ as the arene-containing fragment, we have reported the synthesis and molecular structure of $[Os_6H_2(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$[12] in which the benzene ligands displayed different bonding modes on a hexaosmium cluster. As part of our continuing studies of arene interactions with metal clusters, we report here a two-step addition of the cation $[Os(C_6H_6)(MeCN)_3]^{2+}$ to the tetrahedral Os_4 dianion $[Os_4H_2(CO)_{12}]^{2-}$ which leads to the formation of the complex $[Os_6(CO)_{12}(\eta^6\text{-}C_6H_6)_2]$. In contrast to the previously reported hexaosmium cluster,[12] both benzene ligands exhibit the conventional η^6-co-ordination mode.

The synthetic methodology is analogous to that used in the synthesis of $[Os_6H_2(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$.[12] Reaction of the anionic species $[Os_4H_2(CO)_{12}]^{2-}$ with $[Os(\eta^6\text{-}C_6H_6)(MeCN)_3][BF_4]_2$, in dichloromethane, yields the purple pentanuclear arene-containing cluster $[Os_5H_2(CO)_{12}(\eta^6\text{-}C_6H_6)]$ **1** † in 60% yield. Treatment of a dichloromethane solution of **1** with an excess of 1,8-diazabicyclo[5.4.0]undec-7-ene affords a dark brown air-sensitive solid which was tentatively formulated † as $[Os_5(CO)_{12}(C_6H_6)]^{2-}$ **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 the dark brown cluster $[Os_6(CO)_{12}(C_6H_6)_2]$ **3** in 40% yield after chromatographic separation on silica. The new cluster has been characterised spectroscopically † (IR, FAB MS, ^1H NMR) and by a single-crystal X-ray analysis.‡ The ^1H NMR spectrum of **3** in $CDCl_3$, at room temperature, shows two singlets at δ 6.08 (6 H) and 6.00 (6 H) which indicates that the two benzene ligands bond to the cluster in a η^6 mode but that they occupy inequivalent co-ordination sites. The spectrum shows no change in the chemical shift of the benzene in the temperature range 215–320 K and there appears to be no evidence for benzene migration over the cluster surface on the NMR time-scale.

The molecular structure of **3** is shown in Fig. 1, together with some important bond parameters. The complex is an 84-electron system, and is isoelectronic with the hexanuclear clusters $[Os_6(CO)_{18}]$,[16] $[Os_6H_2(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$,[12] $[RuOs_5(CO)_{15}(\eta^6\text{-}C_6H_6)]$[11] and $[Os_6(CO)_{15}(arene)]$.[13] The metal framework is the same as in the parent carbonyl cluster $[Os_6(CO)_{18}]$, involving a bicapped tetrahedron of metal atoms, with three different metal environments. The metal connectivities are three for Os(5) and Os(6), four for Os(3) and Os(4), and five for Os(1) and Os(2). It is interesting that the two $\eta^6\text{-}C_6H_6$ ligands are co-ordinated to Os(4) and Os(5) which have four and three metal connectivities, respectively. The Os(5) atom caps the Os(1)Os(2)Os(3) face very asymmetrically with Os(1)–Os(5), Os(3)–Os(5) and Os(2)–Os(5) distances of 2.924(2), 2.880(2) and 2.587(2) Å, respectively. The Os(2)–Os(5) edge is the shortest metal–metal distance in **3**, and is supported by a bridging carbonyl. A similar edge-shortening effect has been observed in $[RuOs_5(CO)_{15}(\eta^6\text{-}C_6H_6)]$[11] and $[Os_6(CO)_{15}(\eta^6\text{-}C_6H_5Me)]$.[13] The substitution

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† Spectroscopic data for **1**: IR (CH_2Cl_2): ν(CO) 2082m, 2038vs, 2028s(sh), 1995w, 1981w cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.16 (s, 6 H); FAB mass spectrum: *m/z* 1375(obs.), 1376(calc.); **2**: IR (CH_2Cl_2): ν(CO) 2046w, 2017vs, 2003m, 1961s, 1933vs, 1855w cm^{-1}; **3**: IR (CH_2Cl_2): ν(CO) 2055w, 2017s, 1994vs, 1973w, 1942w cm^{-1}; FAB mass spectrum: *m/z* 1644(obs.), 1644(calc.); ^1H NMR ($CDCl_3$): δ 6.08 (s, 6 H), 6.00 (s, 6 H).

‡ Crystal data for **3**. $C_{24}H_{12}O_{12}Os_6$, $M = 1633.5$, orthorhombic, space group *Pbca*, $a = 15.397(3)$, $b = 17.800(5)$, $c = 20.660(4)$ Å, $U = 5662(2)$ Å^3, $Z = 8$, $D_c = 3.832$ g cm^{-3}, $F(000) = 5664$, Mo-Kα radiation, $\lambda = 0.710\,73$ Å, μ(Mo-Kα) = 268.83 cm^{-1}, crystal dimensions 0.53 × 0.11 × 0.08 mm, 3722 unique diffractometer data. Structure solved by direct methods (SHELXTL PLUS[14]) and Fourier difference techniques, refined by full-matrix least-squares analysis (Os atoms anisotropic, arene H-atoms in geometrically idealised positions, arene rings restrained to be planar) (SHELX 92[15]) to $R_1 = 0.054$, $wR_2 = 0.112$, for 2545 reflections with $F > 4\sigma(F)$, $w^{-1} = [\sigma^2F^2 + 0.0690P]$ where $P = [0 \text{ or } F_o^2 + 2F_c^2]/3$. 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.

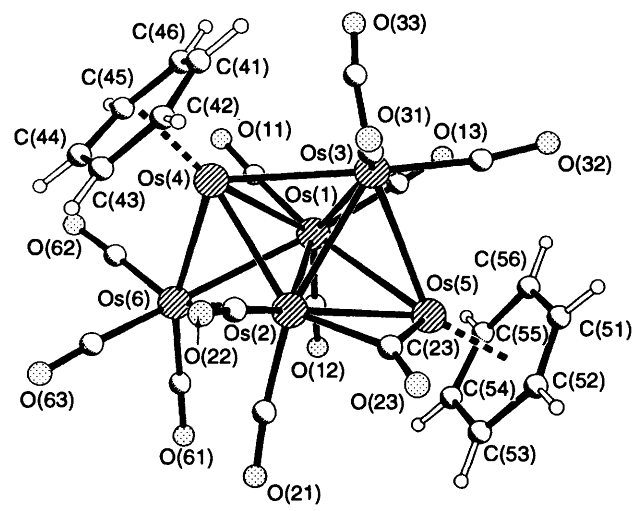

Fig. 1 Molecular structure of $[Os_6(CO)_{12}(\eta^6\text{-}C_6H_6)_2]$ **3** showing the atomic numbering scheme. Selected bond lengths (Å) and angles (°): Os(1)–Os(2) 2.770(1), Os(1)–Os(3) 2.741(2), Os(1)–Os(4) 2.859(2), Os(1)–Os(5), 2.924(2), Os(1)–Os(6) 2.860(2), Os(2)–Os(3) 2.791(2), Os(2)–Os(4) 2.672(2), Os(2)–Os(5) 2.587(2), Os(2)–Os(6) 2.722(2), Os(3)–Os(4) 2.757(2), Os(3)–Os(5) 2.880(2), Os(4)–Os(6) 2.712(2), Os(2)–C(23) 2.02(3), Os(5)–C(23) 2.10(3), C(41)–C(42) 1.43(4), C(41)–C(46) 1.39(4), C(42)–C(43) 1.44(5), C(43)–C(44) 1.41(4), C(44)–C(45) 1.42(4), C(45)–C(46) 1.43(4), C(51)–C(52) 1.34(4), C(51)–C(56) 1.44(4), C(52)–C(53) 1.44(5), C(53)–C(54) 1.51(5), C(54)–C(55) 1.39(5), C(55)–C(56) 1.41(4), Os(2)–C(23)–O(23) 144(2), Os(5)–C(23)–O(23) 137(3), Os(2)–C(23)–Os(5) 78(1)

of carbonyls by benzene at the metal centre Os(5) leads to the formation of a bridging carbonyl group between Os(2) and Os(5) whilst no bridging carbonyl occurs on substitution at the Os(4) metal centre. This reflects the difference in charge distribution within the molecule. The bonding in the parent carbonyl, $[Os_6(CO)_{18}]$, may be viewed as involving a donor-metal bond from Os(1) and Os(2) to the acceptor metal centres Os(5) and Os(6). The replacement of the carbonyls at the electron deficient metal Os(5) by the weaker π-acidic arene ligand leads to the formation of the bridging carbonyl between Os(2) and Os(5) and the loss of the donor-metal bond which is consistent with lower electron demands of the arene groupings.

It is interesting to compare the two related hexaosmium clusters $[Os_6H_2(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$[12] and $[Os_6(CO)_{12}(\eta^6\text{-}C_6H_6)_2]$ **3**. The replacement of the two hydrides in the former by a carbonyl ligand in **3** may influence whether the second benzene ligand adopts a terminal η^6-bonding mode or a face-capping $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ mode. The carbonyl ligand can only formally donate electron density to a single metal or two adjacent metal centres in a relatively localised bonding scheme whereas the two hydrides can donate electron density to metal centres at opposite ends of the molecule. The availability of electron density from the bridging carbonyl co-ordinated to Os(5) in **3** may reduce the requirement for the second arene ligand to donate electron density to three metals as would occur if it adopted the face-capping $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ mode.

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