Isolation and *X*-Ray Structure Determination of $[Os_4(CO)_{12}(C_9H_6)]$, an Indyne 'Butterfly' Cluster

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The cluster $[Os_4(CO)_{12}(C_9H_6)]$ (**1**) has been isolated from the reaction of $[Os_3(CO)_{12}]$ with indene in nonane under reflux; *X*-ray analysis has shown that (**1**) has a 'butterfly' metal framework while the indyne group interacts with the metal atoms *via* two σ-bonds and two π-bonds.

We have recently established a new face-capping bonding mode for benzene in the trimetallic clusters $[M_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)]$ (M = Ru[1] or Os[2]). Molecular structure determinations on these species have shown that this bonding mode bears a striking resemblance to the Kekulé type of distortion forms for benzene adsorbed on Rh (111)[3] and Os (001)[4] single crystal surfaces. It has also been reported[5] that when $[Ru_3(CO)_{11}(PPh_3)]$ is heated in toluene, one of the products is the pentanuclear cluster $[Ru_5(CO)_{13}(\mu_4\text{-PPh})(\mu_5\text{-}\eta^6\text{-}C_6H_4)]$ which contains a μ_5-benzyne and which may be considered to serve as a model for the dissociative chemisorption at a step site on a metal (111) surface. The generation of benzyne by pyrolysis of a tertiaryphenylphosphine complex *via ortho*-metallation followed by P–C bond cleavage is not without precedent and has been observed on several other occasions.[6] There are relatively few examples of direct 'benzyne' formation from the appropriate arene precursor, the best characterised have been those derived from $[Os_3(CO)_{12}]$.[7] In this communication we wish to report the synthesis and full characterisation of the cluster $[Os_4(CO)_{12}(C_9H_6)]$ (**1**) in which the arene unit, C_9H_6, has been shown to bond to a 'butterfly' arrangement of four osmium atoms in an indyne bonding mode.

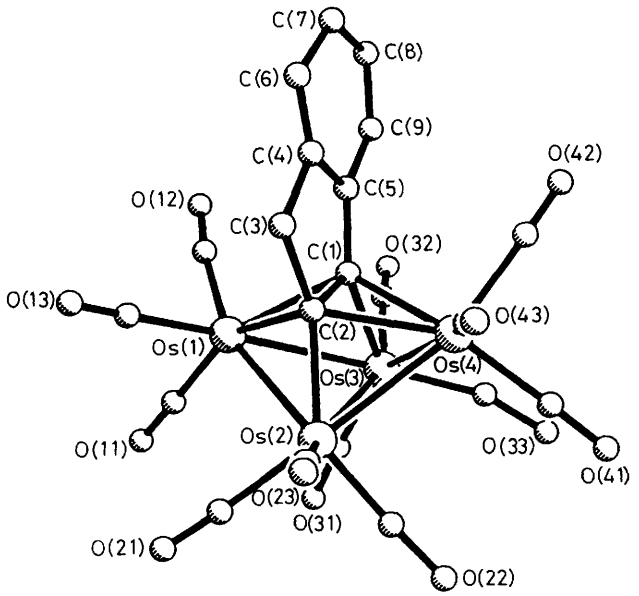

Figure 1. The molecular structure of $[Os_4(CO)_{12}(C_9H_6)]$ (**1**) showing the atom numbering scheme; hydrogen atoms have been omitted for clarity. Bond lengths: Os(1)–Os(2) 2.747(3), Os(1)–Os(3) 2.737(2), Os(2)–Os(3) 2.883(3), Os(2)–Os(4) 2.735(3), Os(3)–Os(4) 2.760(3), Os(1)–C(1) 2.28(3), Os(1)–C(2) 2.25(3), Os(2)–C(2) 2.08(3), Os(3)–C(1) 2.19(3), Os(4)–C(1) 2.23(3), Os(4)–C(2) 2.25(3), C(1)–C(2) 1.47(5), C(1)–C(5) 1.40(5), C(2)–C(3) 1.65(4), C(3)–C(4) 1.48(5), C(4)–C(5) 1.41(4), C(4)–C(6) 1.24(5), C(5)–C(9) 1.47(4), C(6)–C(7) 1.37(7), C(7)–C(8) 1.50(7), C(8)–C(9) 1.27(6) Å; bond angles: Os(2)–Os(1)–Os(3) 63.4(1), Os(1)–Os(2)–Os(3) 58.1(1), Os(1)–Os(2)–Os(4) 92.5(1), Os(3)–Os(2)–Os(4) 58.8(1), Os(1)–Os(3)–Os(2) 58.5(1), Os(1)–Os(3)–Os(4) 92.2(1), Os(2)–Os(3)–Os(4) 57.9(1), Os(2)–Os(4)–Os(3) 63.3(1), Os(1)–C(1)–Os(3) 75.7(10), Os(1)–C(1)–Os(4) 123.3(16), Os(3)–C(1)–Os(4) 77.5(11), Os(1)–C(1)–C(2) 70.2(16), Os(3)–C(1)–C(2) 107.2(22), Os(4)–C(1)–C(2) 71.6(17), Os(1)–C(1)–C(5) 116.8(2), Os(3)–C(1)–C(5) 142.2(25), Os(4)–C(1)–C(5) 115.0(21), C(2)–C(1)–C(5) 110.6(27), Os(1)–C(2)–Os(2) 78.6(10), Os(1)–C(2)–Os(4) 123.4(13), Os(3)–C(2)–Os(4) 78.2(9), Os(1)–C(2)–C(1) 71.9(16), Os(2)–C(2)–C(1) 111.5(21), Os(4)–C(2)–C(1) 70.0(15), Os(1)–C(2)–C(3) 112.9(18), Os(2)–C(2)–C(3) 146.2(21), Os(4)–C(2)–C(3) 115.1(18), C(1)–C(2)–C(3) 102.4(25).

The reaction of $[Os_3CO)_{12}]$ with indene, C_9H_8, was carried out in nonane under reflux at 152 °C for 24 h. In addition to the major compound, $[Os_3H_2(CO)_9(C_9H_6)]$,[8] an orange band was separated on the silica plate, as a mixture. Two compounds, $[Os_4(CO)_{12}(C_9H_6)]$ (**1**)† and $[Os_2(CO)_6(C_9H_6)]$ [MS: *m/z* = 780; IR (hexane): 2079m, 2049vs, 1999s, 1973s, 1943vw, br.] were then isolated as orange and yellow crystals, respectively, by slow evaporation of a CH_2Cl_2/hexane solution of the orange mixture at room temperature. The close similarity between the IR spectra of (**1**) and $[Os_4(CO)_{12}(Ph_2C_2)]$[9] implies that (**1**) adopts the same 'butterfly' metal core structure as the latter species. The ^1H NMR spectrum of (**1**) in CD_2Cl_2 shows a singlet at δ 4.52 for the CH_2 unit, and in the phenyl region, two doublets (δ 7.42 and 7.20) and two apparent triplets (δ 7.32 and 7.05) for the remaining C_6H_4 moiety, implying the asymmetry of the arene unit when bonding to the metal 'butterfly'.

A single crystal *X*-ray diffraction‡ study has confirmed this structure, which is shown in Figure 1, together with some important bond parameters. The four osmium atoms adopt a 'butterfly' configuration, while the arene moiety sits above the

† *Spectroscopic data* for complex (**1**): MS: *m/z* 1218; IR: ν_{CO} (hexane): 2098vw, 2079sh, 2072m, 2048s, 2041m, 2000m, 1973vw cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz, all *J* values in Hz) δ 7.42 (d, *J* 7.5, 1H), 7.32 (t, *J* 7.6, 1H), 7.20 (d, *J* 7.6, 1H), 7.05 (t, *J* 7.6, 1H), 4.52 (s, 2H).

‡ *Crystal data*: $C_{21}H_6O_{12}Os_4$, *M* = 1211.1, triclinic, space group $P\bar{1}$ (No. 2), *a* = 9.633(6), *b* = 10.823(8), *c* = 11.761(8) Å, α = 91.47(5), β = 90.68(5), γ = 99.78(5)°, *U* = 1207.8(14) Å^3, D_c = 3.33 g cm^{-3}, *Z* = 2, *F*(000) = 1064, Mo-K_α radiation, λ = 0.71073 Å, μ = 210.69 cm^{-1}. Nicolet R3mV four-circle diffractometer, 3428 reflections collected, 2θ range 5—45°, semi-empirical absorption correction, 2901 unique reflections with $F > 5\sigma(F)$. Structure solved by direct methods (Os atoms) and Fourier difference syntheses. Refined by full-matrix least-squares with Os, O, and organic ligand C atoms anisotropic, H atoms AFIXed and refined with common isotropic temperature factors, converged $R = 0.073$, $R_w = 0.096$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

hinge of the 'butterfly', forming two σ-bonds with the 'hinge' osmium atoms and two π-bonds with the 'wing-tip' atoms. The dihedral angle between the 'wing-tips' of the metal butterfly is 115.9°. The pseudo-octahedral M_4C_2 core geometry has been observed previously in a number of osmium and ruthenium clusters where the organic ligand is derived from an alkene or an alkyne.[10] In these cases, as in (**1**), the organic group formally acts as a four-electron donor, and the electron count is consistent with there being seven electron pairs available for framework bonding, the characteristic count for a closo-octahedron under Wade's Rules.[11] The only previously structurally characterised cluster in which an organic ring system co-ordinates in this mode is $[Ru_6(CO)_{11}(C_8H_{10})]$,[12] where one unsaturated bond of the octadiene occupies two vertices of the M_4C_2 octahedron while the opposite C–C double bond π-bonds to one of the 'wing-tip' Ru atoms. In the ruthenium cluster,[12] the interaction with the framework may be considered as co-ordination of an alkene C–C double bond to the 'butterfly' metal framework. A related interaction is present in (**1**), here it is the unsaturated C–C bond of a five-membered ring which interacts with the metal framework. The C(1)–C(2) distance in (**1**) is similar to that found in alkene and alkyne substituted clusters,[10] but the high estimated standard deviations on the bond parameters within the five-membered carbon ring precludes a detailed analysis of the bonding.

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