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Preliminary communication

Displacement of benzene by an alkyne in a tetraosmium cluster; synthesis and structural characterisation of the novel cluster $[H_2Os_4(CO)_9(\mu_3\text{-}\eta^2\text{-}Ph_2C_2)(\eta^2\text{-}Ph_2C_2)]$

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Abstract

The benzene ligand in $[H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_6)]$ is displaced in the reaction with Ph_2C_2 in the presence of Me_3NO/MeCN. The cluster produced has been characterised as $[H_2Os_4(CO)_9(Ph_2C_2)_2]$ spectroscopically, and an X-ray crystallographic study has shown that one of the diphenylacetylene ligands is coordinated to one metal atom in a η^2-mode and donates four electrons.

We recently reported the synthesis and structural characterisation of a benzene-coordinated tetraosmium cluster, $[H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_6)]$ (**1**) [1], with the benzene in a terminal position. We report here its reaction with Ph_2C_2, and the synthesis and characterisation of $[H_2Os_4(CO)_9(\mu_3\text{-}\eta^2\text{-}Ph_2C_2)(\mu^2\text{-}Ph_2C_2)]$ (**2**).

The tetraosmium cluster $[H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_6)]$ (**1**) can be activated by Me_3NO/MeCN to produce the reactive intermediate, $[H_2Os_4(CO)_9(MeCN)(\eta^6\text{-}C_6H_6)]$ *, which readily reacts with Ph_2C_2 in dichloromethane at room temperature to produce an orange complex **2** in ca. 75% yield. The ^{1}H NMR spectrum of **2** ** shows that the characteristic resonance of the benzene molecule in the parent cluster $[H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_6)]$ at δ 5.95 has disappeared, and has been replaced by multiplets corresponding to the diphenylacetylene ligands. Two sharp singlets in the hydride region are also observed (δ −11.99 and δ −13.35, respectively). As also

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* IR spectral data for $[H_2Os_4(CO)_9(MeCN)(\eta^6\text{-}C_6H_6)]$: ν(CO) (MeCN) 2062m, 2038m, 2022s, 1997s, 1975s, 1942m,sh.

** Spectroscopic data for **2**: IR [ν(CO) (hexane)] 2084s, 2058vs, 2023vs, 2016vs, 2005s, 1989w; MS (^{192}Os) *m/e* 1378; ^{1}H NMR (δ, $CDCl_3$, 298 K) 7.63 (m, 10H), 6.37 (m, 10H), −11.99 (s, 1H), −13.35 (s, 1H).

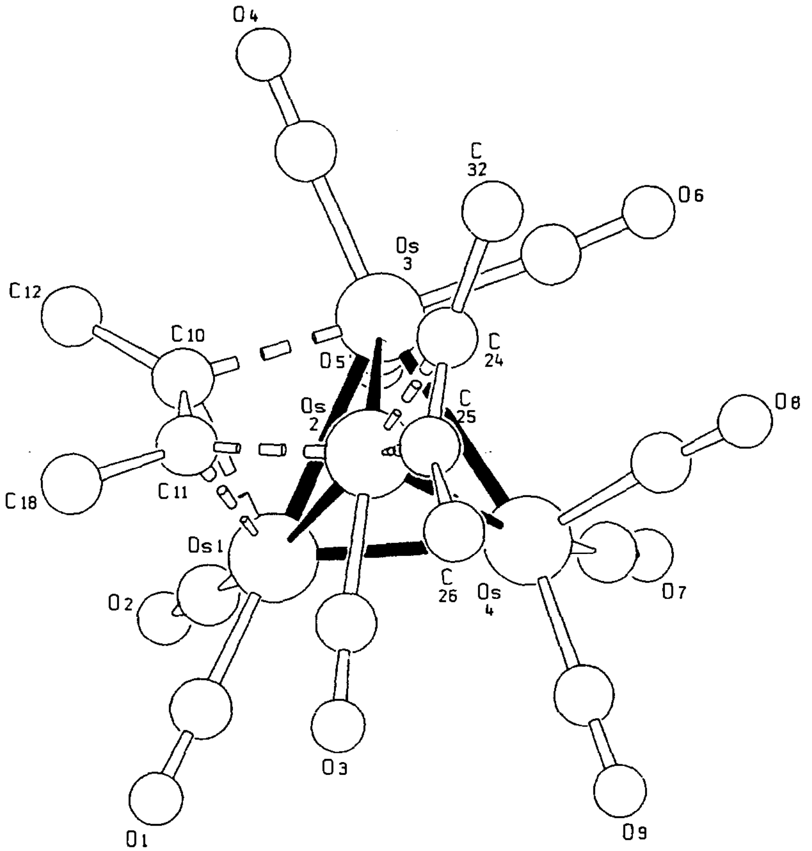

Fig. 1. Crystal structure of $[H_2Os_4(CO)_9(\mu_3\text{-}\eta^2\text{-}Ph_2C_2)(\eta^2\text{-}Ph_2C_2)]$ (2) with selected bond distances (Å) and angles (°). For clarity, only the first atoms of the phenyl groups have been included. Os(1)–Os(2) 2.791(1), Os(1)–Os(3) 2.791(1), Os(1)–Os(4) 2.727(1), Os(2)–Os(3) 2.900(1), Os(2)–Os(4) 2.720(1), Os(3)–Os(4) 2.894(1), Os(1)–C(10) 2.148(5), Os(1)–C(11) 2.155(5), Os(2)–C(11) 2.065(5), Os(3)–C(10) 2.215(5), Os(2)–C(24) 2.057(6), Os(2)–C(25) 2.031(5), C(10)–C(11) 1.44(1), C(24)–C(25) 1.29(1), C(18)–C(11)–C(10) 123.8(4), C(11)–C(10)–C(12) 127.9(4), C(24)–C(25)–C(26) 147.3(6), C(25)–C(24)–C(32) 139.6(5).

indicated by the mass spectrum, there are two diphenylacetylene ligands in this new cluster and so, on the basis of its spectroscopic data, 2 was formulated as $[H_2Os_4(CO)_9(Ph_2C_2)_2]$. In the formation of 2 from 1, the benzene molecule and the MeCN ligand have been displaced by two diphenylacetylene ligands, revealing the lability of the benzene coordination to the tetraosmium metal core in 1. In order to establish the molecular structure of 2, a single-crystal X-ray analysis was undertaken ***.

*** Crystal data for 2: $C_{37}H_{22}O_9Os_4$, $M = 1371.3$, monoclinic, space group $P2_1/a$, a 21.521(2), b 8.581(2), c 21.757(2) Å, β 116.74(1)°, U 3587.9 Å^3, $Z = 4$, $F(000) = 2479$, D_c 2.55 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ 150.7 cm^{-1}, θ-range 2.5–25°, 6936 reflections collected, final R value 0.019 ($R_w = 0.020$) for 4963 out of 5905 independent reflections [$I_0 > 2\sigma(I_0)$] collected by the $\omega/2\theta$ scan method. Absorption correction was by the Walker and Stuart method (correction range 0.68–1.0) [8]. The structure was solved by direct methods and refined anisotropically by full-matrix least squares (phenyl rings treated as rigid groups with C–H 1.08 Å). A complete table of bond lengths and angles and a list of observed and calculated structure factors are available from D.B.

Red plates of $[H_2Os_4(CO)_9(Ph_2C_2)_2]$ (**2**) were obtained from a CH_2Cl_2/hexane solution at −5°C. The structure of $[H_2Os_4(CO)_9(Ph_2C_2)_2]$ (**2**) is shown in Fig. 1, and some important bonding parameters are shown in the caption.

The four osmium atoms of **2** adopt a tetrahedral geometry, with the Os–Os distances ranging from 2.720(1) to 2.900(1) Å. One of the diphenylacetylene ligands is coordinated to a metal cluster triangular face in a conventional μ_3-η^2-mode, forming two σ-bonds with Os(2) and Os(3), and one π-bond with Os(1). The second diphenylacetylene molecule, however, interacts in only the η^2-mode with Os(2), and lies coplanar with the μ_3-η^2-bridged triangular face of the cluster. This latter ligand is required to supply four electrons to the cluster orbitals in order to attain the number of 60 valence electrons required by the E.A.N. rule for tetrahedral clusters. η^2-Coordination of both two-electron and four-electron donor alkynes has been observed in a number of mononuclear species [2–7]. Complex **2** represents an interesting case where both kinds of interactions are present on the metal frame. The values of the C–C distances and of the C(Ph)–C–C angles clearly indicate that the C atoms of the η^2-coordinated ligand retain a substantial *sp* character with respect to the μ_3-η^2-ligand [C–C 1.29(1) Å versus 1.44(1) Å, C(Ph)–C–C 147.3(6)° and 139.6(5)° versus 123.8(4)° and 127.9(4)°]. What is more, the Os–C (η^2-alkyne) distances [average 2.044(5) Å] are shorter not only than the Os–C distances involved in the π-interaction of the μ_3-η^2-alkyne ligand [average 2.152(5) Å] but also than the two σ-interactions [average 2.140(5) Å]. On the basis of the final difference Fourier map and of space-filling diagrams the most likely positions for the two bridging hydride atoms are judged to be along the Os(1)–Os(4) and Os(2)–Os(3) edges.

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