

Preliminary communication

Indene in a novel bonding mode in a carbonyl cluster: isolation, characterisation, and crystal and molecular structure of $[\text{HOs}_4(\text{CO})_9(\text{C}_9\text{H}_6)(\text{C}_9\text{H}_7)]$

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Abstract

The reaction of $[\text{Os}_3(\text{CO})_{12}]$ with indene at 150°C under reflux affords the known compounds $[\text{H}_2\text{Os}_3(\text{CO})_9(\text{C}_9\text{H}_6)]$ (**2**) and $[\text{Os}_4(\text{CO})_{12}(\text{C}_9\text{H}_6)]$ (**3**). When the reaction temperature is increased to 170°C , the yield of **2** is greatly reduced, and a new tetraosmium cluster $[\text{HOs}_4(\text{CO})_9(\text{C}_9\text{H}_6)(\text{C}_9\text{H}_7)]$ (**1**) is isolated. An X-ray diffraction study of **1** has shown that one face of the Os_4 tetrahedron is capped by an indyne ligand coordinated in a $\mu_3\text{-}\eta^2\text{-||}$ bonding mode, while the indenyl ligand (C_9H_7) is coordinated to a single Os atom in a η^5 bonding mode through the five-membered ring.

Recently we have reinvestigated the reaction between indene and $[\text{Os}_3(\text{CO})_{12}]$, and we now report the isolation and characterisation of a new cluster species, $[\text{HOs}_4(\text{CO})_9(\text{C}_9\text{H}_6)(\text{C}_9\text{H}_7)]$ (**1**). It has been reported that the reaction of $[\text{Os}_3(\text{CO})_{12}]$ with indene in nonane under reflux (150°C) for 24 h affords as the major product, $[\text{H}_2\text{Os}_3(\text{CO})_9(\text{C}_9\text{H}_6)]$ (**2**) [1]. We recently isolated a tetraosmium complex from this reaction, $[\text{Os}_4(\text{CO})_{12}(\text{C}_9\text{H}_6)]$ (**3**), a “butterfly” cluster, which was characterized by both spectroscopic and crystallographic studies [2]. When the reaction is carried out at higher temperature (170°C) for the same period of time, the yield of **2** is greatly reduced, whereas that of **3** increases, and a new tetraosmium species $[\text{HOs}_4(\text{CO})_9(\text{C}_9\text{H}_6)(\text{C}_9\text{H}_7)]$ (**1**) can be isolated. In complexes **2** and **3**, the indene ligand adopts the $\mu_3\text{-}\eta^2$ and $\mu_4\text{-}\eta^2$ bonding mode, respectively, similar to that often adopted by alkyne ligands [3], and can plausibly be regarded as a four-electron donor. The new species **1** has been shown spectroscopically to have two indene ligands coordinated to the tetraosmium core (MS: $m/e = 1250(^{192}\text{Os})$; IR ($\nu(\text{CO})$, cm^{-1} , hexane): 2081m, 2059s, 2038vs, 2002vs, 1972m; ^1H NMR: δ (CD_2Cl_2): -22.45 (s, 1H), 3.77 (AB quartet, 2H), 4.77 (m, 1H), 4.86 (m, 1H), 5.74 (obscured by the solvent peak), 5.98 (m, 1H), 6.77 (m, 2H), 6.99 (m, 2H), 7.32 (m, 2H), 7.50 (m, 1H). $\delta(\text{CD}_3\text{COCD}_3)$: -22.44 (s, 1H), 3.93 (AB quartet, 2H), 4.99 (m, 1H), 5.17

(m, 1H), 5.50 (m, 1H), 5.88 (m, 1H), 6.86 (m, 2H), 7.04 (m, 2H), 7.36 (m, 2H), 7.53 (m, 1H)). The ^1H NMR spectrum of **1** shows one AB quartet in the normal region for a geminal CH_2 group, and three signals in the vinyl region. A COSY NMR experiment shows two sets of interactions of the protons belonging to two separate groups in phenyl region, and another set of interactions among the three proton signals in the vinyl region. This information implies that these two indene ligands adopt completely different bonding modes. However, the ^1H NMR spectral data cannot indicate the precise bonding modes of these two indene ligands, and so a single-crystal X-ray analysis was carried out, and a novel bonding mode of one of the indene ligands in a cluster species revealed.

The molecular structure of **1** is shown in Fig. 1 together with some important bond parameters*. The four osmium atoms form a tetrahedral framework, in which the long Os(2)–Os(3) edge is bridged by a hydride atom. This Os–Os distance is similar to the average length of 2.964(2) Å of the bridged Os–Os edges in $\text{H}_4\text{Os}_4(\text{CO})_{12}$ [4]. By contrast, the Os(1)–Os(4) separation is very short, being ca. 0.04 Å shorter than the dihydride bridged edge in $\text{H}_2\text{Os}_3(\text{CO})_{10}$ [5], in which the metal–metal interaction may be regarded as having double bond character. This cannot be the case for the Os(1)–Os(4) edge, since Os(1) is an 18 electron atom and Os(4) a 17 electron atom, and it would be conventional to regard the bonding between them as a two-centre two-electron bond. This short distance may be a reflection of the formal electron deficiency of Os(4), or may be a result of the coordination of the indenyl ligand to Os(1). The remaining Os–Os distances are similar to the average value (2.817(2) Å) for the unbridged Os–Os bonds in $\text{H}_4\text{Os}_4(\text{CO})_{12}$ [4]. The two indene ligands are bonded differently to the metal framework. One of them, the C_9H_6 indyne unit, has a normal $\mu_3\text{-}\eta^2$ bonding mode with σ -bonding to Os(2) and Os(3) and π -bonding to Os(1), as previously observed in complex (2). The other, the C_9H_7 indenyl unit, adopts a completely different bonding mode. One proton of the former methylene group on the five-membered ring has migrated to the metal framework, so that the five-membered ring has become a five-electron donor ligand, and is π -bonded to a single osmium atom, Os(1), acting like a cyclopentadienyl ligand. The indenyl ligand, C_9H_7 , has been reported to show a η^3 or η^5 bonding mode in many mononuclear organometallic species, and the slip-fold distortion in these species has been thoroughly investigated [6], but to our knowledge, there have been no reports of indenyl coordination in

* *Crystal data.* $\text{C}_{27}\text{H}_{14}\text{O}_9\text{Os}_4$, $M = 1153.18$, monoclinic, space group $P2_1/c$ (no. 14), a 16.843(5), b 9.341(2), c 17.056(7) Å, β 95.63(6)°, V 2670.5 Å³, D_c 2.867 g cm⁻³, $Z = 4$, $F(000) = 2208$, $\lambda(\text{Mo-K}\alpha)$ 0.71069 Å, $\mu(\text{Mo-K}\alpha)$ 190.16 cm⁻¹. Dark red platelet, crystal dimensions: 0.076 × 0.228 × 0.508 mm, $\mu R = 2.2$. 3872 data measured on a Stoe-Siemens four-circle diffractometer ($5.0 \leq 2\theta \leq 45.0^\circ$, $+h$, $+k$, $\pm l$), corrected for absorption, 3012 unique observed reflections with $|F| > 4\sigma(F)$. Structure solved by a combination of direct methods and Fourier difference techniques, and refined by blocked full-matrix least-squares techniques, with all non-hydrogen atoms assigned anisotropic displacement parameters; the organic H-atoms were placed in idealised positions (C–H, 1.08 Å) and allowed to ride on the relevant C-atom; these H-atoms were assigned a common isotropic displacement parameter. The hydride atom was located in the Fourier difference map, but was fixed in position for refinement. The weighting scheme employed was $w = 1.520/[\sigma^2 F + 0.0005 F^2]$. The final residuals were $R = 0.043$ and $R_w = 0.042$. The atomic coordinates for this work are available on request from The Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Great Britain).

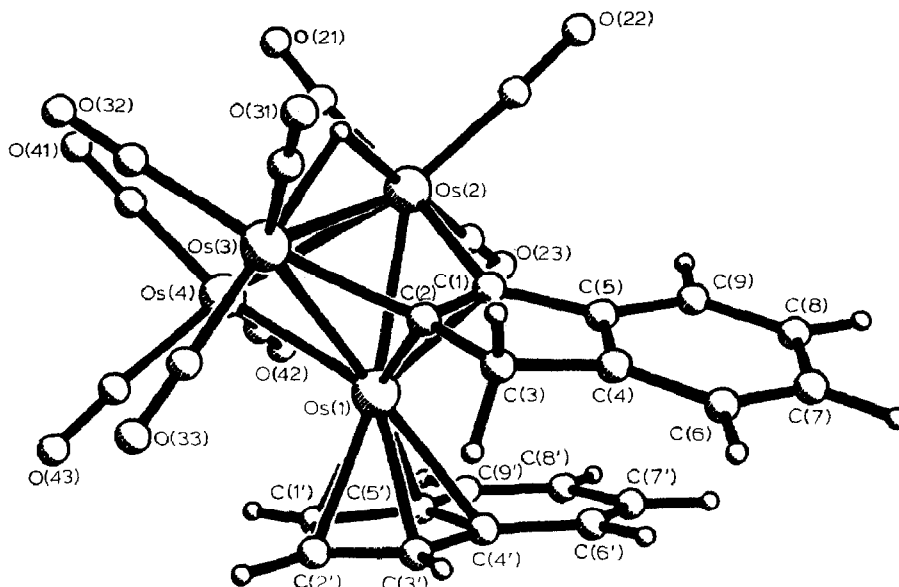


Fig. 1. The molecular structure of $[\text{HOs}_4(\text{CO})_9(\text{C}_9\text{H}_6)(\text{C}_9\text{H}_7)]$ (**1**) showing the atom numbering scheme. Bond lengths (Å): Os(1)–Os(2), 2.803(1); Os(1)–Os(3), 2.778(1); Os(1)–Os(4), 2.640(1); Os(1)–C(1), 2.10(1); Os(1)–C(2), 2.08(1); Os(1)–C(1'), 2.26(2); Os(1)–C(2'), 2.02(2); Os(1)–C(3'), 2.20(2); Os(1)–C(4'), 2.30(1); Os(1)–C(5'), 2.32(2); Os(2)–Os(3), 2.936(1); Os(2)–Os(4), 2.849(1); Os(2)–C(1), 2.13(1); Os(3)–Os(4), 2.845(1); Os(3)–C(2), 2.12(1); C(1)–C(2), 1.42(2); C(1')–C(2'), 1.42(3); C(1')–C(5'), 1.45(2); C(2')–C(3'), 1.39(3); C(3')–C(4'), 1.44(2); C(4')–C(5'), 1.44(2). Bond angles ($^\circ$): Os(2)–Os(1)–Os(3), 63.5(1); Os(2)–Os(1)–Os(4), 63.0(1); Os(3)–Os(1)–Os(4), 63.3(1); Os(3)–Os(2)–Os(1), 57.8(1); Os(1)–Os(2)–Os(4), 55.7(1); Os(3)–Os(2)–Os(4), 58.9(1); Os(1)–Os(3)–Os(2), 58.7(1); Os(1)–Os(3)–Os(4), 56.0(1); Os(2)–Os(3)–Os(4), 59.0(1); Os(2)–Os(4)–Os(1), 61.3(1); Os(1)–Os(4)–Os(3), 60.7(1); Os(3)–Os(4)–Os(2), 62.1(1).

cluster species. Therefore, complex **1** is an interesting example of η^5 -indenyl coordination in a cluster. The nine carbonyl ligands are all essentially linear, and are equally distributed between Os(2), Os(3) and Os(4), while Os(1) bears no carbonyl ligand.

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