

## Polynuclear Clusters of Fused-ring Hydrocarbons. The Synthesis and X-Ray Structure of $[\text{Os}_4\text{H}(\text{CO})_9(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^5\text{-C}_{13}\text{H}_{15})]$ ( $\text{C}_{13}\text{H}_{15} = 1,3\text{-diethylindenyl}$ )

Jack Lewis,\* Paul R. Raithby and Gregory N. Ward

University Chemical Laboratory, Lensfield Road, Cambridge, UK CB2 1EW

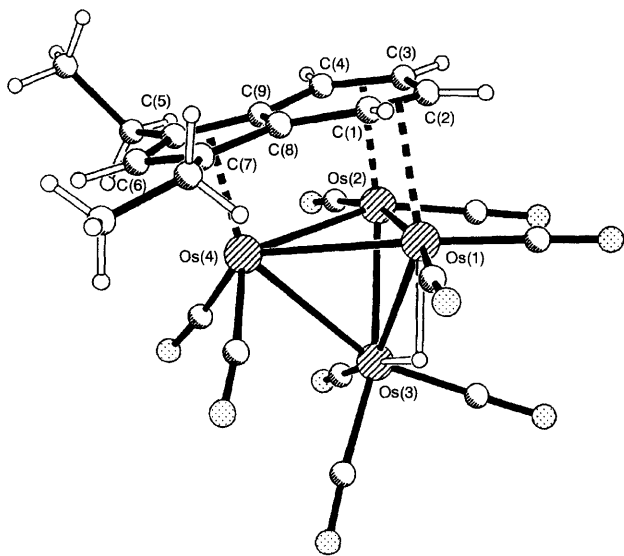
The reaction between  $[\text{Os}_3(\text{CO})_{12}]$  and 1,3-diethylindene yields  $[\text{Os}_4\text{H}(\text{CO})_9(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^5\text{-C}_{13}\text{H}_{15})]$ , the structure of which is shown by X-ray crystallography to consist of a distorted tetrahedral metal framework with one triangular face coordinated by the indenyl such that the six membered ring is in the  $\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2$  face capping mode whilst the five membered ring is  $\eta^5$ -bound to one of the Os atoms.

The chemistry of  $\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2$  arene trinuclear metal carbonyl clusters is well documented.<sup>1-3</sup> However, structurally characterised arene metal carbonyl clusters in which benzene is coordinated in the  $\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2$  face capping mode are rare, existing only for penta- and hexa-nuclear clusters.<sup>4-6</sup> With regard to clusters in which larger arenes exhibit the face capping mode of coordination, there is only one example of a polymetallic indenyl cluster which contains the indenyl coordinated through both rings and has been structurally characterised, this being the spiked tetraruthenium cluster  $[\text{Ru}_4(\text{CO})_9(\text{C}_9\text{H}_7)(\text{C}_9\text{H}_9)]$ .<sup>7</sup> In this compound the indenyl is coordinated through both rings but shows considerable deviation from planarity, with a fold angle of  $8.3^\circ$ . In this communication we report the synthesis and characterisation of a tetraosmium cluster containing the diethylindenyl ( $\text{C}_{13}\text{H}_{15}$ ) group coordinated to the metal framework through both rings. This is the first structurally characterised example of a tetrahedral osmium cluster containing a  $\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2$  face capping arene fragment within the indene in what is essentially an  $\eta^9$ -coordination mode.

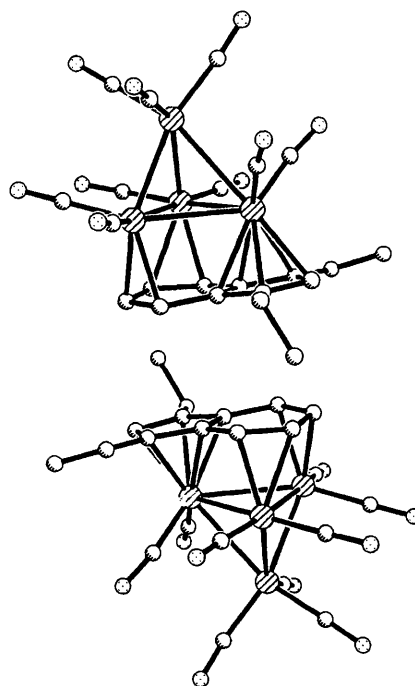
The direct reaction of  $[\text{Os}_3(\text{CO})_{12}]$  with 1,3-diethylindene in nonane, under reflux for 8 h, yields  $[\text{Os}_4\text{H}(\text{CO})_9(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^5\text{-C}_{13}\text{H}_{15})]$  as the only product except for unreacted  $[\text{Os}_3(\text{CO})_{12}]$ . After separation by TLC using  $\text{CH}_2\text{Cl}_2$ -hexane (1 : 1) as eluent, the yellow complex was initially characterised by spectroscopic techniques† and the structure confirmed by a single crystal X-

ray analysis.‡ The molecular structure of  $[\text{Os}_4\text{H}(\text{CO})_9(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^5\text{-C}_{13}\text{H}_{15})]$  is shown in Fig. 1 together with selected bond parameters. The metal framework consists of a tetrahedron with the indenyl group lying over one triangular face in an  $\eta^2\text{-}\eta^2\text{-}\eta^5$ -mode. The nine carbonyls are all terminal and essentially linear. The hydride was not directly located but potential energy calculations<sup>8</sup> suggest that it bridges the Os(1)-Os(3) edge. In this coordination mode the indenyl acts as a nine electron donor, donating four electrons through the two  $\eta^2$ -interactions of the six membered ring and five electrons through the five membered ring. The total electron count for the cluster is 60, which from PSEP<sup>9</sup> theory is consistent with the observed tetrahedral framework.

The indenyl group is essentially coplanar with the triangular metal face  $[\text{Os}(1)\text{Os}(2)\text{Os}(4)]$ , the interplanar angle being  $4.5^\circ$ . Unlike the situation in  $[\text{Ru}_4(\text{CO})_9(\text{C}_9\text{H}_7)(\text{C}_9\text{H}_9)]$ <sup>7</sup> the indenyl group in  $[\text{Os}_4\text{H}(\text{CO})_9(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^5\text{-C}_{13}\text{H}_{15})]$  deviates only slightly from planarity. There is no evidence of slippage of the  $\eta^5$  ring, with  $\Delta = 0.005 \text{ \AA}$ <sup>§10</sup> and the fold and hinge angles<sup>¶</sup> being  $1.3^\circ$  and  $5.2^\circ$ , respectively. An analysis of the C-C bond lengths in the indenyl six membered ring does not conclusively prove that there is alternation between short and long bonds, as found in the benzene ring of  $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_6)]$ <sup>2</sup> as the difference between the bond lengths is slightly less than three times their standard deviation and cannot be considered significant. The <sup>1</sup>H NMR spectrum of the cluster shows that the protons attached to the six membered ring are allylic in character, this, coupled with the bond length analysis suggests



**Fig. 1** The molecular structure of  $[\text{Os}_4\text{H}(\text{CO})_9(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^5\text{-C}_{13}\text{H}_{15})]$  showing the atom numbering scheme. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): Os(1)-Os(2) 2.7945(13), Os(1)-Os(3) 2.8379(14), Os(1)-Os(4) 2.897(2), Os(2)-Os(3) 2.675(2), Os(2)-Os(4) 2.9350(12), Os(3)-Os(4) 2.9538(14), Os(1)-C(1) 2.21(2), Os(1)-C(2) 2.33(2), Os(2)-C(3) 2.27(2), Os(2)-C(4) 2.20(2), Os(4)-C(5) 2.29(2), Os(4)-C(6) 2.25(2), Os(4)-C(7) 2.23(2), Os(4)-C(8) 2.28(2), Os(4)-C(9) 2.26(2), C(2)-C(1)-C(8) 116(2), C(1)-C(2)-C(3) 125(2), C(4)-C(3)-C(2) 119(2), C(3)-C(4)-C(9) 117(2), C(9)-C(5)-C(6) 104(2), C(7)-C(6)-C(5) 109(2), C(6)-C(7)-C(8) 110(2), C(7)-C(8)-C(9) 107(2), C(7)-C(8)-C(1) 132(2), C(9)-C(8)-C(1) 121(2), C(8)-C(9)-C(4) 122(2), C(8)-C(9)-C(5) 110(2), C(4)-C(9)-C(5) 128(2).



**Fig. 2** The intermolecular packing between the discrete molecules of  $[\text{Os}_4\text{H}(\text{CO})_9(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^5\text{-C}_{13}\text{H}_{15})]$

that there is in fact significant electron localisation into the cyclohexatriene configuration within this ring.

The crystal structure shows that the discrete molecules pack with the indenyl groups adjacent and parallel (Fig. 2). The intermolecular separation between these groups is *ca.* 3.5 Å which suggests graphitic packing. A similar type of interaction has been observed in a number of arene-substituted clusters<sup>11</sup> but this is the first example involving an indenyl ligand.

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### Footnotes

† Spectroscopic data for [Os<sub>4</sub>H(CO)<sub>9</sub>(μ<sub>3</sub>-η<sup>2</sup>-η<sup>2</sup>-η<sup>5</sup>-C<sub>13</sub>H<sub>15</sub>)]: IR (CH<sub>2</sub>Cl<sub>2</sub>) ν<sub>CO</sub>/cm<sup>-1</sup> 2065s, 2013s, 1999vs, 1970m; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz) δ 5.38 (s, 1H), 4.92 (dd, 2H, J<sub>H1H2</sub> 3.9, J<sub>H1H3</sub> 2.4 Hz), 4.46 (dd, 2H, J<sub>H1H2</sub> 3.9, J<sub>H2H3</sub> 2.5 Hz), 1.65 (q, 2H, J 7.5 Hz), 1.13 (q, 2H, J 7.5 Hz), 1.11 (t, 6H), -13.02 (s, 1H); FAB MS: *m/z* 1192 (1192, M<sup>+</sup>).

‡ Crystal data for [Os<sub>4</sub>H(CO)<sub>9</sub>(μ<sub>3</sub>-η<sup>2</sup>-η<sup>2</sup>-η<sup>5</sup>-C<sub>13</sub>H<sub>15</sub>)]: C<sub>22</sub>H<sub>16</sub>O<sub>9</sub>Os<sub>4</sub>, *M* = 1185.15, monoclinic, space group *P*2<sub>1</sub>/*c* (no. 14), *a* = 13.460(5), *b* = 11.069(8), *c* = 17.216(5) Å, β = 111.27(2)°, *U* = 2390(2) Å<sup>3</sup>, *D<sub>c</sub>* = 3.293 Mg m<sup>-3</sup>, *Z* = 4, Mo-Kα radiation, λ = 0.710 73 Å, μ(Mo-Kα) = 21.245 mm<sup>-1</sup>, *T* = 293(2) K. Siemens R3mV four-circle diffractometer, 3384 unique reflections collected 5 < 2θ < 45°, semi-empirical absorption correction applied (minimum and maximum transmission factors 0.127 and 0.314 respectively), 3129 unique (*R*<sub>int</sub> = 0.0151). Structure solved by direct methods (Os atoms) and refined by full-matrix least squares methods based on *F*<sup>2</sup>. With Os and O atoms anisotropic and aromatic and aliphatic hydrogen atoms in fixed positions refinement converged at *R*<sub>1</sub> = 0.0477,

*wR*<sub>2</sub> = 0.1116 for 2581 reflections with *F* > 4σ(*F*) and *R*<sub>1</sub> = 0.0613 and *wR*<sub>2</sub> = 0.1197 (all data). In the final Δ*F* synthesis no feature layout with +2.69 and -1.96 e Å<sup>-3</sup>.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ The slippage parameter is defined as follows: Δ = {[M-C(8) + M-C(9)]/2} - {[M-C(5) + M-C(7)]/2}, where M-C(*n*) is the metal-carbon bond length, and is used as an indicator of the degree of η<sup>3</sup> or η<sup>5</sup> character in the coordination of the indene.

¶ The hinge angle shows the deviation from coplanarity of the planes defined by C(5)C(6)C(7) and C(5)C(9)C(8)C(7).

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