

Synthesis of a novel planar hexaosmium carbonyl cluster: crystal structure of $[\text{HOs}_6(\text{CO})_{20}(\mu\text{-}\eta^2\text{-NC}_5\text{H}_4\text{CH=CH})]$

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Abstract

The alkylidyne cluster $[\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-CNC}_5\text{H}_4\text{CH=CH}_2)]$ (**1**) reacts with the triosmium cluster $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ to yield the 94-electron organometallic cluster $[\text{HOs}_6(\text{CO})_{20}(\mu\text{-}\eta^2\text{-NC}_5\text{H}_4\text{CH=CH})]$ (**3**). Complex **3** has been shown by X-ray structure analysis to possess an unprecedented planar Os_6 metal geometry in which an open triosmium chain is fused to an edge of an osmium triangle through two Os–Os bonds and a bridging hydride.

Keywords: Synthesis; Carbonyl cluster; Crystal structure; Alkylidyne cluster

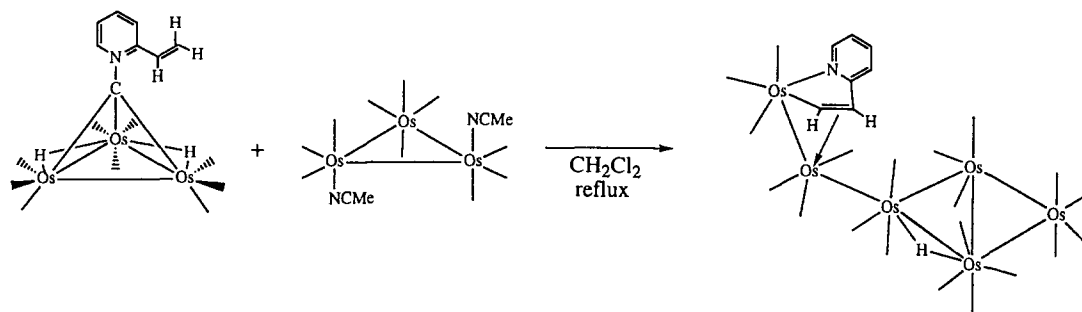
We have recently reported the preparation of a triosmium alkylidyne cluster $[\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-CNC}_5\text{H}_4\text{CH=CH}_2)]$ (**1**) and show that **1** readily undergoes thermal rearrangement to afford an alkylidene cluster $[\text{HOs}_3(\text{CO})_9(\mu\text{-C(H)NC}_5\text{H}_4\text{-}\eta^2\text{-CH=CH}_2)]$ (**2**), the structure of which reveals the presence of an η^2 coordination from the vinyl group to one osmium atom [1]. Lewis and coworkers [2] have also shown that the complex $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ readily reacts with 2-vinylpyridine with C–H bond cleavage at the vinyl carbon atom to give the trinuclear cluster $[\text{HOs}_3(\text{CO})_9\text{-L}(\text{NC}_5\text{H}_4\text{CH=CH})]$ (L = CO or PMe_2Ph) with an open structure. In light of this observation, investigation of the possibility of linking two cluster units by treating **1** with $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ under thermolytic conditions was pursued. In this way, it is hoped that isolation of good intermediates in the synthesis of high nuclearity cluster complexes can be achieved. In this communication, we report the synthesis and full characterization of a novel 94 electron Os_6 carbonyl cluster, which contains a rare open planar metal framework.

The reaction of $[\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-CNC}_5\text{H}_4\text{CH=CH}_2)]$ (**1**) with a slight excess of the activated cluster

$[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ in refluxing CH_2Cl_2 for 16 h gives the hexanuclear cluster $[\text{HOs}_6(\text{CO})_{20}(\mu\text{-}\eta^2\text{-NC}_5\text{H}_4\text{CH=CH})]$ (**3**) with a moderate yield (34%) after purification by thin layer chromatography on silica with *n*-hexane: CH_2Cl_2 (70:30, v/v) as eluent (Scheme 1). Several other compounds with low yields in this reaction remain unidentified. Complex **3** was initially characterized¹ on the basis of the parent molecular ion at 1807 in its mass spectrum. The IR spectrum shows the absence of any bridging carbonyl ligands. The ¹H NMR spectrum in CD_2Cl_2 shows four signals for the heterocycle, which hence remains intact, and two coupled doublets (δ -5.76 and 9.29 ppm) for the CH=CH group. The coupling of 7 Hz between these two protons and their chemical shifts indicates that the two hydrogen atoms in the CH=CH group are in *cis* configuration. In order to establish the overall geometry of the cluster and

¹ Spectroscopic data for $[\text{HOs}_6(\text{CO})_{20}(\mu\text{-}\eta^2\text{-NC}_5\text{H}_4\text{CH=CH})]$ (**3**). IR (CH_2Cl_2): $\nu(\text{CO})$ 2123 w, 2106vw, 2083s, 2073m, 2050s, 2039vs, 2017s, 2006s, 1981m cm^{-1} . ¹H NMR (CD_2Cl_2): δ 9.29 (d, 1H, $J = 7.0$ Hz, CH=CH), 8.59 (m, 1H, $\text{C}_5\text{H}_4\text{N}$), 7.62 (m, 1H, $\text{C}_5\text{H}_4\text{N}$), 7.33 (m, 1H, $\text{C}_5\text{H}_4\text{N}$), 6.69 (m, 1H, $\text{C}_5\text{H}_4\text{N}$), 5.76 (d, 1H, $J = 7.0$ Hz, CH=CH), -13.88 (s, 1H, OsH) ppm. Positive fast atom bombardment mass spectroscopy (nitrobenzyl alcohol as matrix): m/z 1807 (1807 simulated).

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Scheme 1.

the mode of coordination of the organic group, single-crystal X-ray analysis was undertaken².

Red crystals of **3** suitable for diffraction experiment were grown by slow evaporation of a solution of **3** in CH_2Cl_2 –MeOH at room temperature for a period of 3 days. The molecular structure of **3** is illustrated in Fig. 1, together with some important bond parameters. The metal framework consists of an almost planar hexa-osmium geometry (maximum deviation from the least-squares plane, 0.069 Å) in which an open triosmium chain is fused to one edge of an osmium triangle through two Os–Os bonds and a hydride bridge. The formation of **3** is accompanied by the coupling of two Os_3 units with the opening out of an Os–Os edge. Such a metal framework is previously unknown in osmium cluster chemistry. The two metal–metal distances Os(1)–Os(2), 2.823(3) Å, and Os(2)–Os(3), 2.897(3) Å, are within the range expected for Os–Os single bonds, and the Os(1)–Os(2)–Os(3) fragment deviates from a linear geometry (Os(1)–Os(2)–Os(3), 159.5(1)°). The 20 carbonyl ligands are terminally bound to the metals; four each to Os(5) and Os(6) and three each to Os(1), Os(2), Os(3) and Os(4). The hydride ligand, inferred by its signal in the ^1H NMR spectrum of **3** was revealed from difference Fourier technique at final stage of refinement of the structure and was found to bridge the relatively long Os(3)–Os(6) edge (Os(3)–Os(6),

3.041(3) Å). The bending of the Os(1)–Os(2)–Os(3) chain away from linearity is probably the result of the $\text{NC}_5\text{H}_4\text{CH}=\text{CH}$ bridge with the η^2 -bonding mode at the Os(2) atom. The $\text{NC}_5\text{H}_4\text{CH}=\text{CH}$ ligand forms two σ bonds to Os(1) (Os(1)–N(1), 2.12(4) Å; Os(1)–C(21), 2.14(5) Å) and a π bonds to Os(2) (Os(2)–C(21), 2.26(5) Å). Thus it is a five-electron donor. The resulting five-membered metallocycle is nearly planar (maximum deviation, 0.22 Å) and the dihedral angle between the Os_6 plane and the $\text{NC}_5\text{H}_4\text{CH}=\text{CHOs}$ plane is 39.3°. Metallation at the vinyl carbon of 2-vinylpyridine to afford a five-membered chelate ring is frequently observed in transition metal chemistry such as in $[\text{RhCl}_2(\text{NC}_5\text{H}_4\text{CH}=\text{CH})(\text{PBu}_3)_2]$ [5], $[\text{Re}(\text{NC}_5\text{H}_4\text{CH}=\text{CH})(\text{CO})_4]$ [6] and $[\text{HOs}_3(\text{CO})_9\text{L}(\text{NC}_5\text{H}_4\text{CH}=\text{CH})]$ (L = CO or PMe_2Ph) [2] but with the C=C bond coordinated to an adjacent metal atom in the cluster. In terms of electron counting, the complex

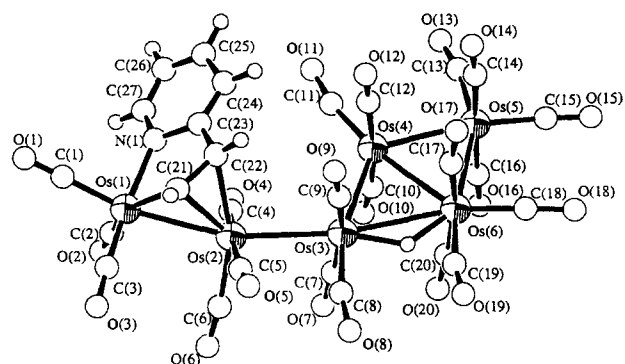


Fig. 1. Molecular structure of **3**, showing the atom-numbering scheme, with selected bond distances and angles: Os(1)–Os(2), 2.823(3) Å; Os(2)–Os(3), 2.897(3) Å; Os(3)–Os(4), 2.914(4) Å; Os(4)–Os(5), 2.813(4) Å; Os(4)–Os(6), 2.923(4) Å; Os(5)–Os(6), 2.961(4) Å; Os(3)–Os(6), 3.041(3) Å; Os(1)–N(1), 2.12(4) Å; Os(1)–C(21), 2.14(5) Å; Os(2)–C(21), 2.26(5) Å; Os(2)–C(22), 2.33(6) Å; C(21)–C(22), 1.40(7) Å; Os(1)–Os(2)–Os(3), 159.5(1)°; Os(2)–Os(3)–Os(4), 110.1(1)°; Os(3)–Os(4)–Os(5), 124.8(1)°; Os(3)–Os(4)–Os(6), 62.82(9)°; Os(5)–Os(4)–Os(6), 62.1(1)°; Os(4)–Os(5)–Os(6), 60.76(9)°; Os(4)–Os(6)–Os(5), 57.11(9)°; Os(1)–C(21)–Os(2), 79(1)°; N(1)–Os(1)–C(21), 80(1)°; C(21)–Os(2)–C(22), 35(1)°.

² Crystal data for **3**: $\text{C}_{27}\text{H}_7\text{NO}_{20}\text{Os}_6\text{CH}_2\text{Cl}_2$; $M = 1806.51$ (1891.48 with CH_2Cl_2); monoclinic; space group, $P2_1/c$ (No. 14); $a = 9.934(5)$, $b = 13.164(4)$, and $c = 30.383(7)$ Å; $\beta = 97.63(4)^\circ$; $U = 3937(2)$ Å³; $Z = 4$; $D_c = 3.190$ g cm⁻³; $F(000) = 3336$; Mo K α radiation ($\lambda = 0.71073$ Å); $\mu(\text{Mo K}\alpha) = 194.87$ cm⁻¹; red needles of dimensions of 0.15 × 0.18 × 0.34 mm; 5431 unique data measured at 298 K on a Rigaku AFC7R diffractometer ($2\theta_{\text{max}} = 45^\circ$); absorption corrected by Ψ scan method; 2202 observed ($I > 3\sigma(I)$). Structure solved by direct methods (SIR88) [5] and Fourier difference techniques, refined by full-matrix least-squares analysis (Os and Cl anisotropic) to $R = 0.076$ and $R_w = 0.086$, $w = 4F_o^2 / [\sigma^2(F_o^2) + 0.024(F_o^2)^2]$; program used TeXsan [4]. Atomic coordinates, thermal parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

$[\text{HOs}_6(\text{CO})_{20}(\mu\text{-}\eta^2\text{-NC}_5\text{H}_4\text{CH=CH})]$ (**3**) is a 94-electron system with seven metal–metal bonds. This is in accordance with the effective atomic number rule and it has four more electrons than the 90-electron $[\text{Os}_6\text{S}(\text{CO})_{19}]$ [7] complex with rhombic six-atom-raft geometry. We are currently investigating the mechanism for this cluster coupling reaction, which involves a CH_2 fragment loss from the starting alkylidyne cluster, and the reactivity of the title complex.

Acknowledgements

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