

New Mixed-metal Clusters *via* Metal Hydride Coupling. Synthesis and Crystal Structures of $[(\mu_2\text{-H})\text{Os}_3\text{W}(\text{CO})_{12}(\eta^5\text{-C}_5\text{H}_5)]$ and $[(\mu_2\text{-H})_3\text{Os}_3\text{W}(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)]$

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Summary The reaction of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ with the hydrido-complex $[\text{HW}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ under mild conditions yields the heteronuclear metal carbonyl hydride complexes $[(\mu_2\text{-H})\text{Os}_3\text{W}(\text{CO})_{12}(\eta^5\text{-C}_5\text{H}_5)]$ (**1**) and $[(\mu_2\text{-H})_3\text{Os}_3\text{W}(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)]$ (**2**); the complexes have been characterized by X-ray diffraction studies and the locations of the bridging hydride ligands have been ascertained.

THE coupling of metal hydrides to reactive metal cluster species is potentially a general synthetic route to mixed-metal cluster compounds. We have recently reported the utility of this technique in synthesizing rhenium-osmium clusters.¹ Continued efforts in this area have now led to the preparation and structural characterization of some novel tungsten-osmium cluster complexes.

A toluene solution of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]^2$ and a threefold excess of $[\text{HW}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ was heated under reflux for 0.5 h, then cooled and separated into components by preparative t.l.c. (light petroleum-dichloromethane). The major products, crystallized from dichloromethane-methanol, were red $[\text{HOs}_3\text{W}(\text{CO})_{12}(\eta^5\text{-C}_5\text{H}_5)]$ (**1**) and orange $[\text{H}_3\text{Os}_3\text{W}(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)]$ (**2**). These compounds were formulated on the basis of their ¹H n.m.r. spectra and low resolution mass spectra [**1**): τ 4.31 (5H), 28.78 (1H); m/e 1164; and **2**): τ 4.25 (5H), 30.50 (3H, br); m/e 1138]. Their molecular configurations have been established by single-crystal X-ray diffraction studies.

Crystal data for (1): $\text{C}_{17}\text{H}_6\text{O}_{12}\text{Os}_3\text{W}$, $M = 1156.68$, orthorhombic, space group $P2_12_12_1$ (D_2^4 ; No. 19), $a = 9.2707(14)$, $b = 11.8539(23)$, $c = 19.726(3)$ Å, $U = 2167.6(6)$ Å³, $D_c = 3.54$ g cm⁻³, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 230.4$ cm⁻¹. Diffraction data were collected with a Syntex P2₁ diffractometer and were corrected for absorption. The structure was solved *via* a combination of Patterson, difference-Fourier, and least-squares refinement techniques, using a locally

modified version of the Syntex XTL system. The final R -value was 5.5% for those 1446 reflections with $F_o > 3\sigma(F_o)$ and $4^\circ < 2\theta < 45^\circ$ (anisotropic thermal parameters for metal and oxygen atoms; isotropic thermal parameters for carbon atoms).†

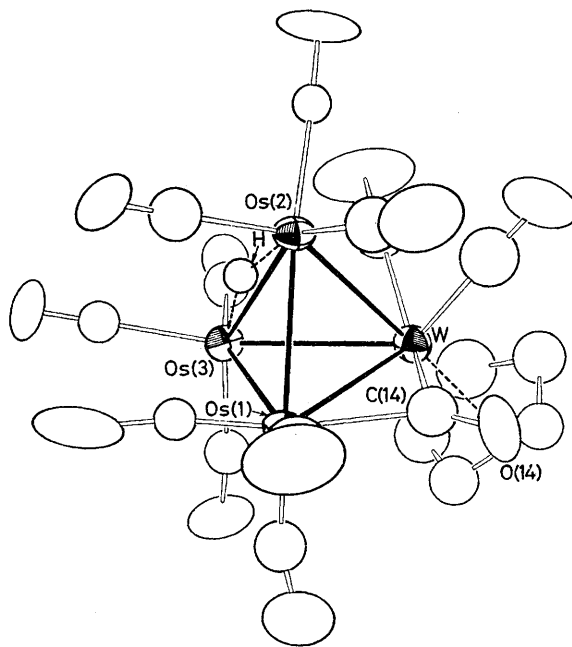


FIGURE 1. Molecular geometry of $[(\mu_2\text{-H})\text{Os}_3\text{W}(\text{CO})_{12}(\eta^5\text{-C}_5\text{H}_5)]$ (**1**), with the hydride ligand shown in its deduced position (ORTEP-II diagram, 50% ellipsoids).

As shown in Figure 1, complex (**1**) has a tetrahedral heterometallic core in which the tungsten atom is co-

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

ordinated to an η^5 -cyclopentadienyl ring and to two terminal carbonyl ligands, while each of the osmium atoms is linked to three terminal carbonyl ligands; the twelfth carbonyl ligand is involved in an asymmetric bridge between W and Os(1) [Os(1)-C(14) = 2.12(5) and W-C(14) = 2.29(5) Å; \angle Os(1)-C(14)-O(14) = 144(4)°]. Metal-metal

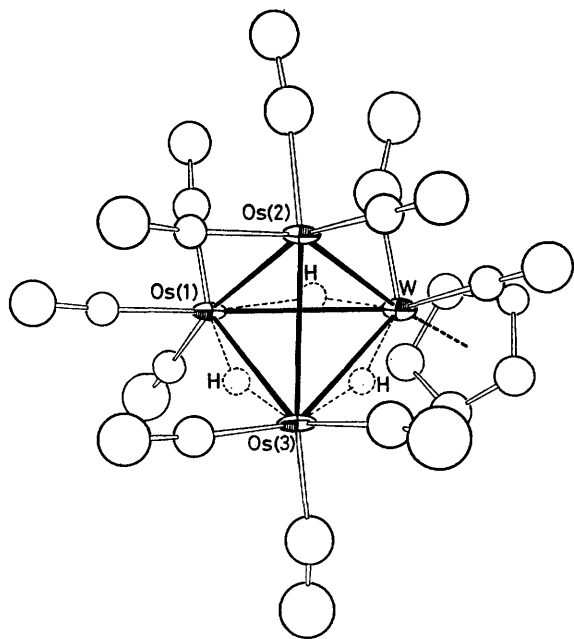


FIGURE 2. Molecular geometry of $[(\mu_2\text{-H})_3\text{Os}_3\text{W}(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)]$ (**2**), with the three hydride ligands shown in their deduced positions (ORTEP-II diagram, 50% ellipsoids).

distances within the tetrahedral core are W-Os(1) = 2.914(3), W-Os(2) = 2.935(3), W-Os(3) = 2.908(3), Os(1)-Os(2) = 2.783(2), Os(1)-Os(3) = 2.798(3), and Os(2)-Os(3) = 2.933(3) Å. This last metal-metal vector is lengthened

by ca. 0.14 Å relative to the other osmium-osmium bonds in the molecule and is thus clearly identified as the site for a μ_2 -hydride ligand (*cf.* ref. 3).

Crystal data for (2): $\text{C}_{16}\text{H}_8\text{O}_{11}\text{Os}_3\text{W}$, $M = 1130.68$, monoclinic, space group $P2_1$ (C_2^2 ; No. 4), $a = 8.385(2)$, $b = 14.682(4)$, $c = 8.872(2)$ Å, $\beta = 104.60(2)^\circ$, $U = 1057.0(4)$ Å³, $D_c = 3.55$ g cm⁻³, $Z = 2$, $\mu(\text{Mo-}K\alpha) = 232.5$ cm⁻¹. Solution and refinement of the structure [as for (**1**), above] led to an R -value of 5.4% for 1433 reflections with $F_o > 3\sigma(F_o)$ and $4^\circ < 2\theta < 45^\circ$ (anisotropic thermal parameters for metal atoms; isotropic thermal parameters for all other atoms). The molecule is illustrated in Figure 2. The structure of (**2**) closely resembles that of (**1**), but no longer possesses an asymmetrically bridging (or 'semi-bridging') carbonyl ligand. Metal-metal distances within molecule (**2**) are: W-Os(1) = 3.073(2), W-Os(2) = 2.880(3), W-Os(3) = 3.082(3), Os(1)-Os(2) = 2.825(2), Os(1)-Os(3) = 2.941(2), and Os(2)-Os(3) = 2.827(2) Å. Three of these vectors [W-Os(1), W-Os(3), and Os(1)-Os(3)] are lengthened by ca. 0.13 Å relative to the analogous normal metal-metal bonds and are thus identified as bonds bridged by μ_2 -hydride ligands in this structure. The three μ_2 -hydride ligands occupy the edges of one triangular face of the heterometallic tetrahedral core of (**2**).†

Contrary to its solid-state configuration, compound (**2**) displays only one hydride resonance near room temperature; the dynamic processes responsible are being investigated. Compound (**1**) can be converted in good yield directly into (**2**) by treatment with hydrogen in refluxing toluene. Further reactions of (**1**) under these conditions are being examined. Related mixed-metal clusters $\{[\text{HOs}_3\text{Mo}(\text{CO})_{12}(\text{C}_5\text{H}_5)]$, $[\text{H}_3\text{Os}_3\text{Mo}(\text{CO})_{11}(\text{C}_5\text{H}_5)]$, and $[\text{HRu}_3\text{W}(\text{CO})_{12}(\text{C}_5\text{H}_5)]\}$ have been prepared by analogous reactions.

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¹ J. R. Shapley, G. A. Pearson, M. Tachikawa, G. E. Schmidt, M. R. Churchill, and F. J. Hollander, *J. Amer. Chem. Soc.*, **1977**, **99**, 8064.

² M. Tachikawa and J. R. Shapley, *J. Organometallic Chem.*, **1977**, **124**, C19.

³ M. R. Churchill, B. G. DeBoer, and F. J. Rotella, *Inorg. Chem.*, **1976**, **15**, 1843.