Bridging Hydrides in $[H_2Os_3(CO)_{10}]$ and $[(C_2H_3)HOs_3(CO)_{10}]$: a Combined *X*-Ray–Neutron Diffraction Study

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Summary Edge-bridging hydrides in $[RHOs_3(CO)_{10}]$ (R = H or vinyl) have been located by an integrated *X*-ray–neutron diffraction study, which also finds precise positions for the other light atoms.

Edge-bridging hydrides are often postulated in organometallic clusters, but little precise structural evidence has been presented for such M–H–M bridges. Most neutron studies of transition-metal hydrides involve mono- or dinuclear species;[1] only one 'edge-bridged' $[(Bu^tCC)Ru_3(CO)_9H]$[2] and two 'face-bridged' clusters[1] appear to have been investigated. Recent *X*-ray studies[3,4] of $[H_2Os_3(CO)_{10}]$ (I) provide precise Os positions, and indicate tentatively that both hydrides bridge the same Os–Os edge of the Os_3 cluster. We report here studies of (I) and the related vinyl derivative $[(C_2H_3)HOs_3(CO)_{10}]$ (II) by a novel refinement of a single set of positional and thermal parameters to neutron and high-angle *X*-ray data,[5] with the intention of optimising the extraction of structural information.

Crystal data: (I), $C_{10}H_2O_{10}Os_3$, *M* 852·7, triclinic, space group $P\bar{1}$, $a = 8{\cdot}604(2)$, $b = 11{\cdot}887(3)$, $c = 9{\cdot}225(2)$ Å, $\alpha = 80{\cdot}19(2)$, $\beta = 118{\cdot}53(2)$, $\gamma = 98{\cdot}98(2)$°, $Z = 2$, $U = 813{\cdot}8$ Å^3, $\mu(\text{Mo-}K_\alpha) = 225{\cdot}6$ cm^{-1}, $\mu(\text{neutron}) = 0{\cdot}065$ cm^{-1}. (II), $C_{12}H_4O_{10}Os_3$, *M* 878·6, monoclinic, space group $P2_1/n$, $a = 9{\cdot}914(3)$, $b = 14{\cdot}398(5)$, $c = 12{\cdot}416(5)$ Å, $\beta = 99{\cdot}77(4)$°, $Z = 4$, $U = 1746{\cdot}5$ Å^3, $\mu(\text{Mo-}K_\alpha) = 207{\cdot}1$ cm^{-1}, $\mu(\text{neutron}) = 0{\cdot}068$ cm^{-1}. Neutron data [$\lambda = 1{\cdot}1803(5)$ Å] were collected on the Andromache Mk VI 4-circle diffractometer at A.E.R.E. Harwell, profile fitted,[5] and corrected for absorption; an isotropic extinction parameter was refined based on the mean path lengths derived in the absorption calculation.[5] 4-Circle *X*-ray diffractometer data ($\lambda = 0{\cdot}71069$) were collected on a Stoe STADI-4 for (I) and Syntex $P2_1$ for (II), and corrected for absorption. In each case equivalent reflexions were averaged and very weak reflexions excluded.†

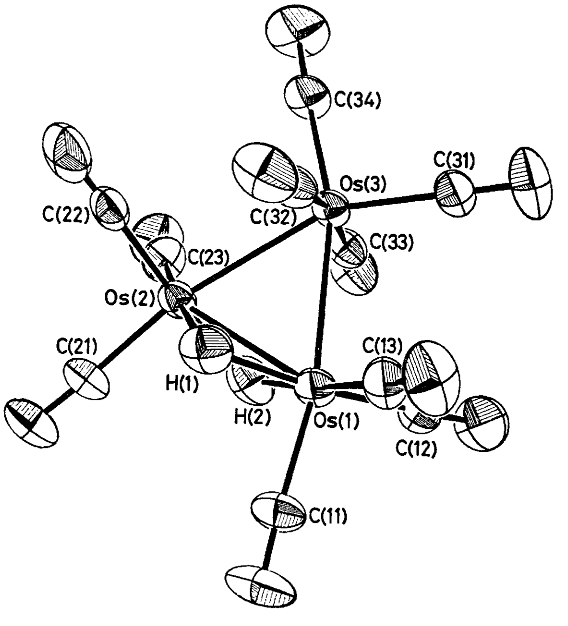

Figure 1. ORTEP plot of $[H_2Os_3(CO)_{10}]$ showing 50% probability thermal ellipsoids. Bond lengths (in addition to those quoted in the text) include: Os(1)–Os(2), 2·680(2); Os(2)–Os(3), 2·812(2); Os(1)–Os(3), 2·818(2); and mean C–O, 1·136 Å.

The structures were initially solved and refined on the *X*-ray data alone; hydrogen atoms were excluded and the other atoms refined anisotropically. The hydrogen atoms were then located as the strong negative peaks in neutron Fourier difference syntheses phased by the *X*-ray parameters. For each structure a single set of positional and anisotropic thermal parameters for all atoms was fitted by least-squares[5] to both neutron and high-angle *X*-ray data ($\sin\theta/\lambda > 0{\cdot}352$). Low-angle *X*-ray data were omitted because they are influenced by bonding electrons. Details of the refinements are presented in the Table. The low residuals indicate satisfactory correction for *X*-ray absorption and neutron extinction, since the combined refinement provides less opportunity than individual *X*-ray or neutron studies for any systematic absorption or extinction errors to be absorbed by changes in the thermal parameters.

Table. Refinement details.[a]

		Combined	
Compound	*X*-Ray alone	High-angle *X*-ray	Neutron
$[H_2Os_3(CO)_{10}]$	$R = 0{\cdot}044$ $R' = 0{\cdot}049$ $N = 3132$	$R = 0{\cdot}041$ $R' = 0{\cdot}039$ $N = 2602$	$R = 0{\cdot}030$ $R' = 0{\cdot}026$ $N = 713$
$[(C_2H_3)HOs_3(CO)_{10}]$	$R = 0{\cdot}032$ $R' = 0{\cdot}029$ $N = 2463$	$R = 0{\cdot}037$ $R' = 0{\cdot}032$ $N = 1927$	$R = 0{\cdot}029$ $R' = 0{\cdot}029$ $N = 1197$

[a] N = No. of reflexions employed in refinement. $R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_0|$.

In (I) (Figure 1) the proposed[3,4] hydride locations bridging the shortest edge of the Os_3 triangle are confirmed; the Os–H–Os units are symmetrical within experimental error, with mean Os–H 1·850(5) Å, mean ∠Os–H–Os 92·9(2)°, and H ··· H 2·397(8) Å. Our Os–Os distances agree with those of Churchill, Hollander, and Hutchison[3] to within 0·001 Å, but differ by up to 0·01 Å from those of

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† 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.

Allen, Mason, and Hitchcock,[4] possibly a consequence of the inaccurate unit-cell determined photographically by the latter. The structure of (II) (Figure 2) is similar to that of the μ-but-1-enyl analogue,[6] the hydride and vinyl groups bridging the same edge of the Os_3 triangle. The Os–H–Os bridge is significantly asymmetric with Os(2)–H(1) 1·813(4) and Os(3)–H(1) 1·857(4) Å, and ∠Os–H–Os 101·6(2)°. The vinyl group and σ-bonded Os(3) are coplanar to within 0·15 Å, the maximum deviations being shown by H(2) and H(3), which bend away from Os(2) slightly. A relatively weak vinyl π interaction with Os(2) is consistent with the asymmetry of the hydride bridge; the C–C bond [1·396(3) Å] is *ca.* 0·07 Å longer than expected for a normal C=C double bond. All *trans* H–Os–C angles in (I) and (II) fall in the narrow range 172·8—174·2°, close to linear, which supports the description of the Os–H–Os bridges as 'open' 2-electron 3-centre bent bonds.[1]

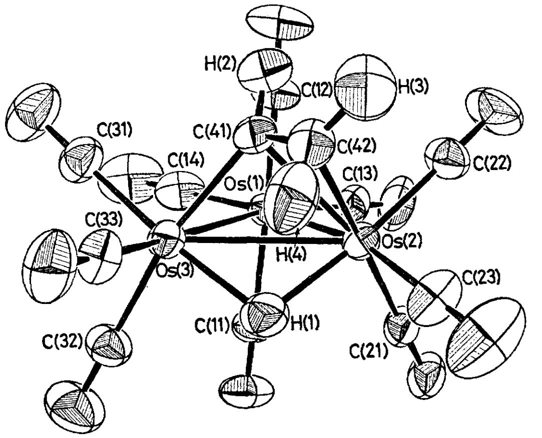

FIGURE 2. ORTEP plot of $[(C_2H_3)HOs_3(CO)_{10}]$ showing 50% probability thermal ellipsoids. Bond lengths (in addition to those quoted in the text) include: Os(1)–Os(2), 2·917(2); Os(2)–Os(3), 2·845(2); Os(1)–Os(3), 2·857(2); Os(2)–C(41), 2·273(3); Os(3)–C(41), 2·107(3); Os(2)–C(42), 2·362(3); and mean C–O, 1·135 Å.

The combination of X-ray and neutron data provides C and O positions 4—10 times more precise than found in studies of Os clusters by X-rays alone, because the Os atoms dominate the X-ray scattering. This enhanced precision enables consistent *trans* effects to be noted. The mean axial Os–C(O) distance [1·946 Å in both (I) and (II)] and the mean Os–C distance for carbonyl group *trans* to Os [1·924 (I) and 1·912 Å (II)] are similar to the values of 1·946 and 1·912 Å respectively in $[Os_3(CO)_{12}]$.[7] Os–C bonds in (I) *trans* to H are short [mean 1·897(3) Å]; in (II) there is a short Os–C bond [1·887(4) Å] *trans* to the long Os–H bond and longer Os–C bond [1·921(3) Å] *trans* to the short Os–H. Similarly the Os–C [1·907(3) Å] *trans* to the vinyl π-bond is shorter than that *trans* to the vinyl σ-bond [1·941(3) Å].

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