Combined *X*-Ray and Neutron Diffraction Study of $[Os_4(CO)_{11}H_3(CHCHPh)]$†

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The title complex has been prepared by the photolytic reaction of styrene with $[Os_4(CO)_{12}H_4]$. It crystallises in the monoclinic space group $P2_1/c$ with a = 8.720(3), b = 16.338(5), c = 18.144(6) Å, β = 111.60(3)°, and Z = 4. Simultaneous refinement of a single parameter set to fit 2 155 *X*-ray [$(\sin\theta)/\lambda > 0.352$] and 935 neutron data has led to R 0.058 (*X*-ray) and 0.096 (neutron). The Os_4 unit is tetrahedral with three long (mean 2.956 Å) and three short (mean 2.806 Å) Os–Os edges. The styrenyl ligand σ bonds to one Os atom and π bonds to another, asymmetrically bridging a short Os–Os edge. The three hydride ligands bridge two long and one short metal–metal bond with Os–H distances in the range 1.77 to 1.86 Å. The eleven carbonyl ligands are all terminal.

THE reaction of small organic molecules with transition-metal clusters has excited considerable interest because of their possible use as models in catalysis.[1] The position of the hydrogen atoms both on the cluster and on the co-ordinated organic group may be of particular importance. According to their location they may permit or prevent further reaction of the bonded organic molecule. In solution, ^1H n.m.r. gives information on the hydride environment, but in the solid state, hydrides cannot be routinely located by single-crystal *X*-ray diffraction because the scattering is dominated by the heavy-metal atom contribution. Single-crystal neutron diffraction is a much more powerful tool for this type of complex since neutrons are scattered by the nuclei, where the difference in diffracting power between hydrogen and a heavy metal is much smaller. This permits the accurate location of hydrides and other light atoms in transition-metal cluster compounds. Unfortunately neutron-beam fluxes are low and such studies require large crystals and long periods of time for data collection. Consequently there have been few neutron diffraction studies on cluster species. In the determination of the crystal and molecular structure of $[Os_4(CO)_{11}H_3(CHCHPh)]$ reported here we have attempted to optimise the extraction of structural information by fitting a single parameter set to both *X*-ray and neutron data; full details of the method have been given in the recent study of $[Os_3(CO)_{10}H(C_2H_3)]$.[2] Low-angle *X*-ray data are excluded from the refinements because they contain information about bonding electrons as well as inner-core electrons, which are assumed to be centred on the nuclear positions.

The cluster compounds $[Os_4(CO)_{11}H_3(olefin - H)]$ are readily prepared from the direct reaction of $[Os_4(CO)_{12}H_4]$ with the appropriate olefin.[3] In these compounds the Os_4 tetrahedron is retained, and the overall molecular structure in solution has been established by spectroscopic techniques. The structure in the solid state has been confirmed by an *X*-ray structure of the related cyclic olefin complex $[Os_4(CO)_{11}H_3(C_6H_9)]$.[3]

† 1,1,1,2,2,2,3,3,4,4,4-Undecacarbonyl-1,3;2,3;2,4-tri-μ-hydrido-3,4-μ-[1-σ,1—2-η-2-phenylethenyl-$C^1(Os^4),C^{1-2}(Os^3)$]-*tetrahedro*-tetraosmium.

EXPERIMENTAL

X-Ray Data Collection.—Crystals of $[Os_4(CO)_{11}H_3(CHCHPh)]$ were deposited as red blocks from cyclohexane. 4 045 Intensities were recorded on a Syntex $P2_1$ four-circle diffractometer using graphite monochromated Mo-K_α radiation, and a crystal of dimensions *ca.* 0.31 × 0.27 × 0.24 mm. Unit-cell dimensions were determined from the angular measurements of 15 strong reflections with $20 < 2\theta < 30°$. Data were collected in the range $3.0 < 2\theta < 60.0°$, using a 96-step θ—2θ scan procedure; the scan rate was determined from a preliminary 2-s peak count and varied from 0.033 3 to 0.488 3° s^{-1} according to the peak intensity; reflections with intensities of <6 counts s^{-1} were not measured. Two check reflections were monitored periodically throughout data collection and showed no significant variation.

A semi-empirical absorption correction based on a pseudo-ellipsoid model and 460 azimuthal scan data from eight independent reflections was applied. Transmission factors ranged from 0.787 to 0.351 for the full data set. Lorentz polarization corrections were also applied, and equivalent reflections averaged to give 2 724 unique observed intensities [$F > 5\sigma(F)$].

Neutron Data Collection.—A large (*ca.* 7.2 mm^3) crystal bounded by the planes {0 0 1}, {1 0 0}, {0 1 0}, and {0 1 1} was grown from dichloromethane–hexane solution by seeding and slow evaporation. Neutron intensities were measured on the Andromache mark VI four-circle diffractometer at A.E.R.E. Harwell with a squashed germanium monochromator and neutron wavelength of 1.1846(5) Å. The crystal was mounted with the diffractometer φ axis collinear with the crystal |010| zone axis. 1 863 Intensities were collected in the range $1 < 2\theta < 60°$ by ω—2θ scans of width 2.4° in ω, of which the extreme 10% on either side was considered to be background intensity. The large scan width was necessitated by the broadness of diffracted peaks, due probably to large mosaic spread in the crystal. The $\bar{4}$ 4 11 reflection was remeasured every 20 reflections to monitor crystal stability and changes in the neutron flux, but no significant variation in intensity was observed. The data were integrated by an orthodox peak-minus-background method. Lorentz and absorption corrections were applied, the latter by numerical (gaussian quadrature) evaluation of attenuation coefficients based on the linear dimensions and indexed faces of the crystal. Transmission coefficients varied between 0.91 and 0.78. Averaging and

sorting of these data gave 935 unique observed intensities [$F > 3\sigma(F)$].

RESULTS

Crystal Data.—$C_{19}H_{10}O_{11}Os_4$, M = 1 175.1, Monoclinic, a = 8.720(3), b = 16.338(5), c = 18.144(6) Å, β = 111.60(3)°, U = 2 403.4 Å^3, $F(000)$ = 2 063.22, D_c = 3.247 g cm^{-3}, Z = 4, D_m = not measured, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 211.3 cm^{-1}; neutrons, λ = 1.184 6(5) Å, μ = 0.76 cm^{-1}. Space group $P2_1/c$ from systematic absences.

Structure Solution and Refinement.—The structure was initially solved and refined with the full X-ray data alone. The four Os atom positions were located by multisolution Σ_2 sign expansion, and all the non-hydrogen atoms from a subsequent difference electron-density synthesis. The structure was refined by blocked full-matrix least squares, with anisotropic thermal parameters for the Os, and carbonyl C and O atoms. A difference synthesis calculated at this stage revealed the positions of the phenyl and ethylene hydrogen atoms, but not the hydridic hydrogens. Refinement continued with these located atoms in idealised positions, riding 1.08 Å away from the relevant carbon atom, with a common isotropic temperature factor assigned to them. In the final cycles of refinement the weighting scheme $w = 0.9003/[\sigma^2(F) + 0.008\ F_o^2]$ was introduced. Final residuals were R = 0.044 and $R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}F_o$ = 0.043. Complex neutral-atom scattering factors were employed throughout the refinement. A final-difference synthesis showed peaks of height *ca.* 1.8 e Å^{-3} close to the Os atoms but did not reveal the positions of the hydrides.

A difference-Fourier synthesis computed using the neutron data and the X-ray thermal and positional parameters for the non-hydrogen atoms revealed the positions of the ten independent hydrogen atoms in the molecule. The structure was refined by blocked full-matrix least squares with independent isotropic temperature factors for the hydrogens, and all other atoms with anisotropic thermal parameters. This single parameter set was fitted simultaneously to the full neutron data [935 reflections with $F > 3\sigma(F)$] and 2 155 X-ray data with $(\sin\theta)/\lambda > 0.352$ and $F > 4\sigma(F)$ (the low-angle X-ray data would have introduced systematic errors arising from the bonding electron distribution). The final model included X-ray and neutron scale factors. The weighting scheme was $w = [\sigma^2(F) + gF_o^2]^{-1}$ with g set to 0.000 55 for X-rays and 0.000 6 for neutrons; the mean value of $w\Delta^2$ was relatively independent of the magnitude of F_o or of $\sin\theta$. X-Ray and neutron scattering factors were taken from ref. 4. The final converged residuals were R = 0.058 (X-ray), 0.096 (neutron) and R' = 0.052 (X-ray), 0.079 (neutron). Final neutron difference maps showed no regions of significant nuclear scattering density, either positive or negative. Attempts to refine neutron extinction and anisotropic thermal parameters for hydrogen led to significantly lowered residuals, but unreasonable values for these parameters. Table 1 lists the final atomic co-ordinates from the combined refinement. Details of anisotropic thermal parameters, molecular least-squares planes, and observed and calculated structure factors for both X-ray and neutron data may be found in Supplementary Publication No. SUP 22996 (19 pp.).*

Neutron data reduction was carried out at A.E.R.E. Harwell but all the remaining computing was performed on the University of Cambridge I.B.M. 370/165 computer with programs written by Professor G. M. Sheldrick.

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

TABLE 1

Atom co-ordinates ($\times 10^4$)

Atom	x/a	y/b	z/c
Os(1)	6 590(1)	1 962(1)	3 562(1)
Os(2)	5 708(1)	3 024(1)	4 553(1)
Os(3)	3 706(1)	2 863(1)	2 849(1)
Os(4)	6 721(1)	3 731(1)	3 290(1)
C(11)	8 861(13)	1 834(7)	4 198(7)
O(11)	10 212(17)	1 749(8)	4 586(8)
C(12)	6 183(11)	923(7)	3 900(6)
O(12)	5 889(16)	267(9)	4 083(8)
C(13)	6 794(11)	1 602(7)	2 596(7)
O(13)	6 865(15)	1 370(9)	2 010(8)
C(21)	7 845(13)	2 968(8)	5 346(7)
O(21)	9 138(17)	2 928(11)	5 854(8)
C(22)	4 960(13)	2 090(8)	4 933(7)
O(22)	4 499(16)	1 501(9)	5 137(8)
C(23)	4 805(14)	3 818(8)	5 077(7)
O(23)	4 318(20)	4 284(11)	5 378(9)
C(31)	1 547(12)	2 516(7)	2 727(6)
O(31)	247(14)	2 349(8)	2 675(8)
C(32)	3 322(10)	2 603(7)	1 781(6)
O(32)	3 105(15)	2 414(9)	1 146(9)
C(41)	9 048(14)	3 575(8)	3 910(7)
O(41)	10 384(17)	3 514(10)	4 247(9)
C(42)	7 073(13)	4 898(9)	3 327(7)
O(42)	7 293(22)	5 586(12)	3 336(11)
C(43)	7 066(11)	3 521(7)	2 307(7)
O(43)	7 167(15)	3 388(8)	1 732(7)
C(1)	4 241(12)	4 082(7)	2 565(7)
C(2)	2 942(14)	4 216(7)	2 791(8)
C(3)	1 283(12)	4 500(7)	2 204(8)
C(4)	758(15)	4 333(9)	1 410(8)
H(4)	1 541(39)	3 992(18)	1 163(19)
C(5)	−700(16)	4 640(10)	871(8)
H(5)	−1 012(33)	4 496(15)	233(19)
C(6)	−1 690(18)	5 175(9)	1 110(1)
H(6)	−2 772(43)	5 358(20)	703(20)
C(7)	−1 153(15)	5 344(9)	1 928(12)
H(7)	−1 925(37)	5 732(18)	2 168(17)
C(8)	333(13)	5 033(8)	2 502(8)
H(8)	676(36)	5 202(19)	3 069(20)
H(1)	3 983(28)	4 258(15)	1 948(17)
H(2)	3 090(28)	4 324(15)	3 393(17)
H(13)	4 359(25)	1 840(13)	3 104(13)
H(23)	3 663(27)	3 129(14)	3 837(14)
H(24)	6 211(23)	3 944(12)	4 128(12)

DISCUSSION

The structure consists of isolated molecules of [$Os_4(CO)_{11}H_3(CHCHPh)$] separated by typical van der Waals distances. Figure 1 is an ORTEP plot of a molecule, and an alternative view of the cluster is shown in Figure 2. Interatomic distances and angles are given in Tables 2 and 3. The molecule contains an Os_4 tetrahedron with three long (mean 2.956 Å) and three short (2.806 Å) metal–metal edges. Hydrides bridge the long Os(2)–Os(3) and Os(2)–Os(4) edges and the short Os(1)–Os(3) edge, while the organic ligand asymmetrically bridges the short Os(3)–Os(4) edge. All eleven carbonyl groups are terminal, two are bound to Os(3) and three each to the other three metal atoms.

The arrangement of the hydrides in this complex is unusual in that one of them, H(13), bridges a short metal–metal bond. It has been found that, in the absence of other bridging groups, the presence of a bridging hydride is generally associated with a ' long ' metal–metal bond.[5] This has been used as a criterion in determining the

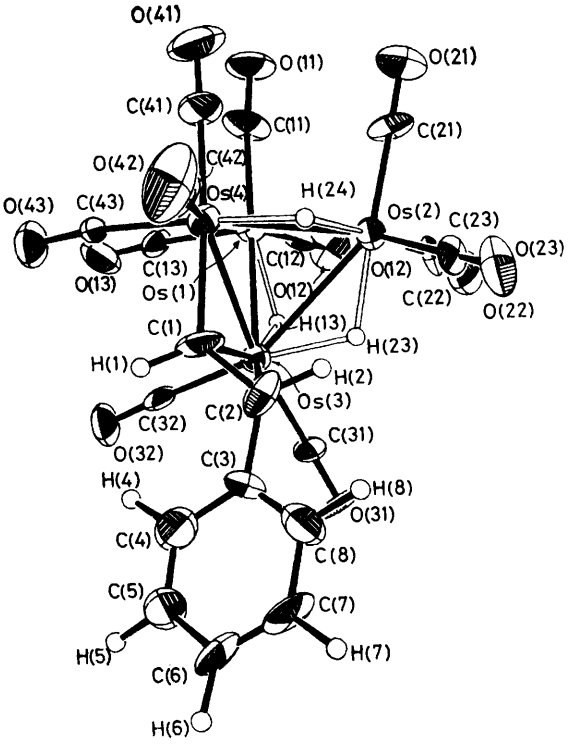

FIGURE 1 The molecular structure of $[Os_4(CO)_{11}H_3(CHCHPh)]$ showing the atom-numbering scheme adopted

positions of hydrides in cluster structures where they have not been directly located in the *X*-ray analysis. However, the lengthening of the metal–metal bond is always associated with a bending away of the adjacent carbonyl ligands from the bridged edge to accommodate the steric requirements of the hydride ligand. In this complex there is no perturbation of the carbonyls adjacent to the ' long ' Os(1)–Os(4) edge, but the average

TABLE 2

Bond lengths (Å)

Os(2)–Os(1)	2.802(3)	Os(3)–Os(1)	2.787(3)
Os(4)–Os(1)	2.942(3)	C(11)–Os(1)	1.902(11)
C(12)–Os(1)	1.883(12)	C(13)–Os(1)	1.918(13)
H(13)–Os(1)	1.823(20)	Os(3)–Os(2)	2.950(2)
Os(4)–Os(2)	2.977(3)	C(21)–Os(2)	1.891(10)
C(22)–Os(2)	1.886(15)	C(23)–Os(2)	1.938(15)
H(23)–Os(2)	1.786(21)	H(24)–Os(2)	1.816(22)
Os(4)–Os(3)	2.830(3)	C(31)–Os(3)	1.900(12)
C(32)–Os(3)	1.889(13)	C(1)–Os(3)	2.151(13)
C(2)–Os(3)	2.299(13)	H(13)–Os(3)	1.772(22)
H(23)–Os(3)	1.858(27)	C(41)–Os(4)	1.941(12)
C(42)–Os(4)	1.927(16)	C(43)–Os(4)	1.945(14)
C(1)–Os(4)	2.154(10)	H(24)–Os(4)	1.769(25)
O(11)–C(11)	1.137(17)	O(12)–C(12)	1.178(20)
O(13)–C(13)	1.152(21)	O(21)–C(21)	1.167(16)
O(22)–C(22)	1.155(22)	O(23)–C(23)	1.109(24)
O(31)–C(31)	1.136(18)	O(32)–C(32)	1.139(20)
O(41)–C(41)	1.103(18)	O(42)–C(42)	1.139(26)
O(43)–C(43)	1.101(21)	C(2)–C(1)	1.356(20)
H(1)–C(1)	1.096(33)	C(3)–C(2)	1.519(15)
H(2)–C(2)	1.067(35)	C(4)–C(3)	1.368(20)
C(8)–C(3)	1.437(20)	H(4)–C(4)	1.097(41)
C(5)–C(4)	1.382(18)	H(5)–C(5)	1.111(38)
C(6)–C(5)	1.405(25)	H(6)–C(6)	1.006(34)
C(7)–C(6)	1.409(29)	H(7)–C(7)	1.122(40)
C(8)–C(7)	1.424(18)	H(8)–C(8)	1.000(39)

TABLE 3

Bond angles (°)

Os(3)–Os(1)–Os(2)	63.7(1)	Os(4)–Os(1)–Os(2)	62.4(1)
Os(4)–Os(1)–Os(3)	59.1(1)	C(11)–Os(1)–Os(2)	98.6(4)
C(11)–Os(1)–Os(3)	154.2(3)	C(11)–Os(1)–Os(4)	96.6(3)
C(12)–Os(1)–Os(2)	102.7(4)	C(12)–Os(1)–Os(3)	112.4(3)
C(12)–Os(1)–Os(4)	164.6(4)	C(12)–Os(1)–C(11)	88.9(4)
C(13)–Os(1)–Os(2)	156.3(3)	C(13)–Os(1)–Os(3)	96.3(3)
C(13)–Os(1)–Os(4)	97.2(3)	C(13)–Os(1)–C(11)	95.4(5)
C(13)–Os(1)–C(12)	96.5(5)	H(13)–Os(1)–Os(2)	82.1(7)
H(13)–Os(1)–Os(3)	38.5(7)	H(13)–Os(1)–Os(4)	97.6(6)
H(13)–Os(1)–C(11)	164.3(8)	H(13)–Os(1)–C(12)	75.7(7)
H(13)–Os(1)–C(13)	89.5(8)	Os(3)–Os(2)–Os(1)	57.9(1)
Os(4)–Os(2)–Os(1)	61.1(1)	Os(4)–Os(2)–Os(3)	57.0(1)
C(21)–Os(2)–Os(1)	91.8(4)	C(21)–Os(2)–Os(3)	146.1(4)
C(21)–Os(2)–Os(4)	96.7(4)	C(22)–Os(2)–Os(1)	87.0(4)
C(22)–Os(2)–Os(3)	99.2(3)	C(22)–Os(2)–Os(4)	146.7(4)
C(22)–Os(2)–C(21)	93.4(5)	C(23)–Os(3)–Os(1)	170.4(3)
C(23)–Os(2)–Os(3)	112.5(3)	C(23)–Os(2)–Os(4)	114.0(4)
C(23)–Os(2)–C(21)	97.1(5)	C(23)–Os(2)–C(22)	96.0(6)
H(23)–Os(2)–Os(1)	91.6(8)	H(23)–Os(2)–Os(3)	36.8(9)
H(23)–Os(2)–Os(4)	84.4(9)	H(23)–Os(2)–C(21)	176.5(9)
H(23)–Os(2)–C(22)	87.5(9)	H(23)–Os(2)–C(23)	79.4(9)
H(24)–Os(2)–Os(1)	94.2(7)	H(24)–Os(2)–Os(3)	76.7(6)
H(24)–Os(2)–Os(4)	33.4(7)	H(24)–Os(2)–C(21)	92.2(7)
H(24)–Os(2)–C(22)	174.2(6)	H(24)–Os(3)–C(23)	81.9(8)
H(24)–Os(2)–H(23)	86.8(10)	Os(2)–Os(3)–Os(1)	58.4(1)
Os(4)–Os(3)–Os(1)	63.2(1)	Os(4)–Os(3)–Os(2)	62.0(1)
C(31)–Os(3)–Os(1)	125.6(3)	C(31)–Os(3)–Os(2)	109.1(3)
C(31)–Os(3)–Os(4)	163.7(4)	C(32)–Os(3)–Os(1)	98.4(3)
C(32)–Os(3)–Os(2)	155.2(3)	C(32)–Os(3)–Os(4)	101.4(3)
C(32)–Os(3)–C(31)	91.1(4)	C(1)–Os(3)–Os(1)	111.2(3)
C(1)–Os(3)–Os(2)	94.1(3)	C(1)–Os(3)–Os(4)	48.9(2)
C(1)–Os(3)–C(31)	122.8(4)	C(1)–Os(3)–C(32)	86.3(5)
C(2)–Os(3)–Os(1)	136.5(3)	C(2)–Os(3)–Os(2)	90.7(3)
C(2)–Os(3)–Os(4)	75.8(3)	C(2)–Os(3)–C(31)	91.4(5)
C(2)–Os(3)–C(32)	103.3(5)	C(2)–Os(3)–C(1)	35.3(5)
H(13)–Os(3)–Os(1)	39.8(6)	H(13)–Os(3)–Os(2)	78.5(6)
H(13)–Os(3)–Os(4)	102.9(7)	H(13)–Os(3)–C(31)	87.6(8)
H(13)–Os(3)–C(32)	88.5(8)	H(13)–Os(3)–C(1)	149.2(8)
H(13)–Os(3)–C(2)	168.2(8)	H(23)–Os(3)–Os(1)	90.6(7)
H(23)–Os(3)–Os(2)	35.1(7)	H(23)–Os(3)–Os(4)	87.5(7)
H(23)–Os(3)–C(31)	79.1(8)	H(23)–Os(3)–C(32)	169.4(7)
H(23)–Os(3)–C(1)	95.6(8)	H(23)–Os(3)–C(2)	73.2(8)
H(23)–Os(3)–H(13)	95.0(10)	Os(2)–Os(4)–Os(1)	56.5(1)
Os(3)–Os(4)–Os(1)	57.7(1)	Os(3)–Os(4)–Os(2)	61.0(1)
C(41)–Os(4)–Os(1)	82.5(4)	C(41)–Os(4)–Os(2)	92.6(4)
C(41)–Os(4)–Os(3)	139.6(4)	C(42)–Os(4)–Os(1)	168.9(3)
C(42)–Os(4)–Os(2)	116.5(4)	C(42)–Os(4)–Os(3)	128.7(3)
C(42)–Os(4)–C(41)	89.5(5)	C(43)–Os(4)–Os(1)	90.5(3)
C(43)–Os(4)–Os(2)	145.8(3)	C(43)–Os(4)–Os(3)	95.4(3)
C(43)–Os(4)–C(41)	91.5(5)	C(43)–Os(4)–C(42)	97.5(5)
C(1)–Os(4)–Os(1)	105.8(3)	C(1)–Os(4)–Os(2)	93.3(4)
C(1)–Os(4)–Os(3)	48.8(3)	C(1)–Os(4)–C(41)	171.5(5)
C(1)–Os(4)–C(42)	82.5(4)	C(1)–Os(4)–C(43)	86.9(4)
H(24)–Os(4)–Os(1)	90.7(6)	H(24)–Os(4)–Os(2)	34.4(6)
H(24)–Os(4)–Os(3)	80.8(6)	H(24)–Os(4)–C(41)	93.9(7)
H(24)–Os(4)–C(42)	82.1(8)	H(24)–Os(4)–C(43)	174.6(6)
H(24)–Os(4)–C(1)	87.7(7)	O(11)–C(11)–Os(1)	178.9(13)
O(12)–C(12)–Os(1)	177.5(9)	O(13)–C(13)–Os(1)	177.5(10)
O(21)–C(21)–Os(2)	177.6(14)	O(22)–C(22)–Os(2)	177.1(13)
O(23)–C(23)–Os(2)	178.4(14)	O(31)–C(31)–Os(3)	176.0(12)
O(32)–C(32)–Os(3)	177.3(12)	O(41)–C(41)–Os(4)	177.0(15)
O(42)–C(42)–Os(4)	178.6(16)	O(43)–C(43)–Os(4)	175.8(10)
Os(4)–C(1)–Os(3)	82.2(4)	C(2)–C(1)–Os(3)	78.3(7)
C(2)–C(1)–Os(4)	128.4(9)	H(1)–C(1)–Os(3)	120.4(15)
H(1)–C(1)–Os(4)	118.4(16)	H(1)–C(1)–C(2)	112.7(16)
C(1)–C(2)–Os(3)	66.4(7)	C(3)–C(2)–Os(3)	120.7(7)
C(3)–C(2)–C(1)	121.5(12)	H(2)–C(2)–Os(3)	100.8(15)
H(2)–C(2)–C(1)	122.4(16)	H(2)–C(2)–C(3)	113.1(17)
C(4)–C(3)–C(2)	122.7(12)	C(8)–C(3)–C(2)	116.9(11)
C(8)–C(3)–C(4)	120.1(10)	H(4)–C(4)–C(3)	120.9(18)
C(5)–C(4)–C(3)	122.5(14)	C(5)–C(4)–H(4)	116.4(20)
H(5)–C(5)–C(4)	118.0(20)	C(6)–C(5)–C(4)	121.1(14)
C(6)–C(5)–H(5)	120.7(18)	H(6)–C(6)–C(5)	118.3(28)
C(7)–C(6)–C(5)	116.3(12)	C(7)–C(6)–H(6)	125.1(29)
H(7)–C(7)–C(6)	120.3(18)	C(8)–C(7)–C(6)	124.1(16)
C(8)–C(7)–H(7)	115.6(21)	C(7)–C(8)–C(3)	115.9(13)
H(8)–C(8)–C(3)	124.0(20)	H(8)–C(8)–C(7)	120.1(23)
Os(3)–H(13)–Os(1)	101.6(10)	Os(3)–H(23)–Os(2)	108.1(14)
Os(4)–H(24)–Os(2)	112.3(10)		

cis Os–Os–C(carbonyl) angle for the three hydride bridged bonds is 115.0° compared to a value of 95.1° for the unbridged ones. Potential-energy calculations, based on the non-bonding interactions between the ligands, on this complex and the related $[Os_4(CO)_{11}H_3(C_6H_9)]$ [6] placed the hydrides along the same Os–Os edges as have been found in this neutron study.

The unusual, ' short ', hydride-bridged metal–metal distance [Os(1)–Os(3)] [*cf.* the ' long ' unbridged metal–metal bond, Os(1)–Os(4)] is probably due to complex electronic effects involving multi-centre metal interactions in the Os_4 tetrahedron. It may be of significance

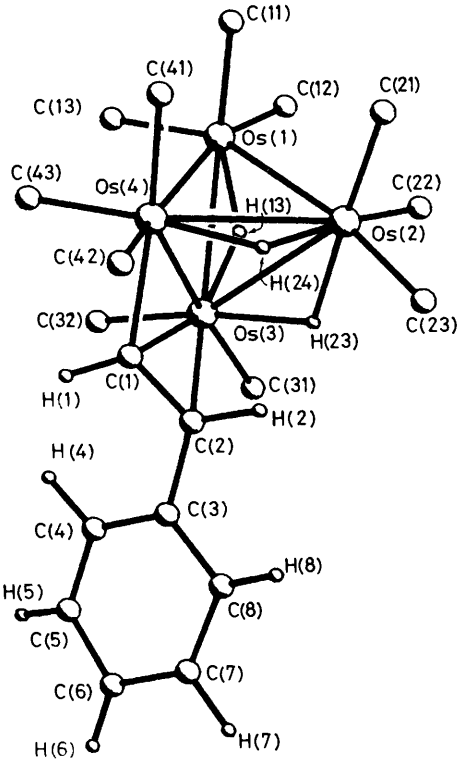

FIGURE 2 A view of the molecule showing the co-ordination mode of the organic group. The carbonyl oxygens have been omitted for clarity

that atoms Os(1) and Os(2) have equivalent environments except that the bridged Os(1)–Os(3) bond is shorter than the Os(2)–Os(3) bond. This equivalence suggests that the imbalance is centred on Os(3) rather than Os(1), and may be connected to the presence of the co-ordinated styrenyl ligand. The variations of electronic effects within the Os_4 tetrahedron may also be illustrated by an analysis of metal–metal interactions present in the bridged M–H–M units. A bridged metal–metal bond is described as ' open ' if the O→C→M vectors *trans* to the bridging atom point at this atom, and ' closed ' if these vectors point towards the centre of the triangle formed by the two metals and the bridging atom. In the former case there is little direct orbital overlap between the metals, but in the latter the bonding orbitals of the metals and the ligand may all overlap, suggesting that there is significant metal–metal interaction. In this complex the orientation of the C(11)→Os(1) vector indicates the Os(1)–H(13)–Os(3) bridge is ' closed ' with respect to Os(1); that is it points towards the centre of the HOs_2 triangle. In contrast, the slightly acute H(13)–Os(3)–C(31) and H(13)–Os(3)–C(32) angles suggest that the Os(3) orbital involved in bonding with H(13) points along the edge of the triangle, implying only slight Os(1)–Os(3) orbital overlap.

The other two hydride ligands, H(23) and H(24), participate in typical M–H–M three-centre two-electron bonds,[7] although the distinction between ' open ' and ' closed ' bonds is unclear here. The deviation of the hydride ligand from the appropriate metal co-ordination planes provides an alternative description of the ' openness ' or otherwise of the M–H–M unit. In the case of H(23), the hydride lies 0.10(4) Å from the plane defined by Os(2), C(21), and C(22). The positive sign of the deviation means that the hydride is on the opposite side of the relevant plane from the second Os atom to which it is bonded. A large positive deviation for both planes related to each hydride indicates that the M–H–M bond is ' closed ', and a significantly large negative deviation indicates that the bond is ' open '. The Os(2)–H(24)–Os(4) system is also intermediate between ' open ' and ' closed ', with deviations of only 0.05(3) and 0.02(4) Å from the Os(2) and Os(4) equatorial planes. The M–H–M angle is the same as the inter-*trans* carbonyl angle of 112°. This is in contrast to the markedly ' open ' geometries observed for a number of triangular Os_3 clusters.[2,8,9]

The average Os–H distance is somewhat shorter, at 1.805 Å, than the range of distances in the Os_3 clusters (1.83—1.85 Å), but slightly longer than the average value of 1.79 Å in $[Os_4(CO)_{12}H_3I]$.[10] The asymmetries observed in these Os–H–Os bridges are of marginal significance.

The mean C–H and C–O bond lengths of 1.07(2) Å and 1.138(8) Å, respectively, fall in the expected ranges.

Discussion of structural *trans* effects is limited by the fairly high estimated standard deviations in the Os–C bond lengths and the distorted co-ordination geometries found here. These distortions are presumably required to achieve the optimum balance between bonding and non-bonding interactions.

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