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X-RAY AND NEUTRON DIFFRACTION ANALYSIS OF THE STRUCTURES OF $H_3Re_3(CO)_{11}[P(C_6H_5)_3]$ AND $H_4Os_4(CO)_{11}[P(OCH_3)_3]$ *

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Summary

The molecular structures of $H_4Os_4(CO)_{11}P(OMe)_3$ and the equatorial isomer of $H_3Re_3(CO)_{11}(PPh_3)$ have been analyzed by single-crystal X-ray and neutron diffraction techniques. Both molecules have edge-bridging H atoms, with approximate D_{2d} and D_{3h} symmetries for the H_4Os_4 and H_3Re_3 cores, respectively. The average molecular parameters determined by neutron diffraction are as follows: for $H_4Os_4(CO)_{11}P(OMe)_3$, Os—H = 1.787(3) Å, Os—Os = 2.966(4) Å, Os—H—Os = 112.2(4)°, H—Os—H = 104(2)°; for *eq*-$H_3Re_3(CO)_{11}(PPh_3)$, Re—H = 1.822(8) Å, Re—Re = 3.262(12) Å, Re—H—Re = 127.1(5)°, H—Re—H = 112.7(3)°. Final agreement factors for the neutron analyses, $R(F)$, are 0.104 for $H_4Os_4(CO)_{11}P(OMe)_3$ (2576 reflections) and 0.092 for $H_3Re_3(CO)_{11}(PPh_3)$ (2331 reflections).

Introduction

We have been seeking the structure of $H_3Re_3(CO)_{12}$ for quite some time. First prepared by Kaesz and coworkers in 1964 [1], it was assigned a D_{3h} structure (with edge-bridging H atoms) largely on the basis of its infra-red spectrum, which greatly resembled that of $Os_3(CO)_{12}$. All attempts at growing suitable crystals of $H_3Re_3(CO)_{12}$, however, met with failure. From most solvents, $H_3Re_3(CO)_{12}$ crystallizes as beautiful colorless square tiles, apparently perfect

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* Dedicated to the memory of Professor Paolo Chini.

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but horrendously disordered as revealed by X-ray photographs [2]. After a few years of fruitless attempts with a wide variety of solvents, we finally gave up on the problem.

In the meantime, we turned out attention to the manganese analog, $H_3Mn_3(CO)_{12}$, which yielded more satisfactory results. In an X-ray structure determination carried out several years ago [3], we showed that it had the D_{3h} structure predicted for $H_3Re_3(CO)_{12}$, with edge-bridging H atoms (located and refined). Subsequent potential energy calculations by Orpen [4], based on a consideration of non-bonding contact interactions, also indicated that the edge-bridging positions are the most stable sites for the H atoms in $H_3Mn_3(CO)_{12}$.

In this paper we return to the rhenium problem, this time using a phosphine derivative to overcome the disorder problems that plagued our earlier analysis of the parent compound. This manuscript describes the neutron diffraction study of the equatorial isomer of $H_3Re_3(CO)_{11}(PPh_3)$, which not only confirms beyond any reasonable doubt the original structure proposed for $H_3Re_3(CO)_{12}$ [1], but also provides a more accurate measurement of the central H_3M_3 core than was possible in the X-ray work on $H_3Mn_3(CO)_{12}$ [3].

Also described in this paper is the neutron diffraction analysis of $H_4Os_4(CO)_{11}P(OMe)_3$. Once again, a substituted molecule was chosen to circumvent the disorder problem that we experienced in our recent X-ray study of the ruthenium analog $H_4Ru_4(CO)_{12}$ [5]. The background literature on the structures of the $H_4Os_4(CO)_{12}/H_4Ru_4(CO)_{12}$ family of molecules was thoroughly covered in that earlier article [5] and in a recent review of ours [6], and will not be repeated here.

Experimental section

All reactions were carried out under nitrogen, while chromatographic steps were performed in air.

Preparation of eq-$H_3Re_3(CO)_{11}(PPh_3)$

This was carried out using the procedure of Andrews [7]. A mixture of $H_3Re_3(CO)_{12}$ (1.5 g, 1.67 mmol), prepared by the published method [1], and PPh_3 (0.47 g, 1.79 mmol) was refluxed in n-octane (250 ml, redistilled from CaH_2 under N_2) for about 1 hour to give an orange solution. After cooling to room temperature, the solvent was removed on a rotary evaporator and the tan residue chromatographed on a 1.5 × 55 cm column of silica gel packed in hexane. First eluted (with hexane) were three colorless bands: $Re_2(CO)_{10}$, $H_3Re_3(CO)_{12}$, and a mixture of $Re_2(CO)_9(PPh_3)$ and $HRe(CO)_4(PPh_3)$. Next, a long pale yellow band [$H_3Re_3(CO)_{11}(PPh_3)$] was eluted with 9/1 hexane/CH_2Cl_2, and then a short bright yellow band [$H_3Re_3(CO)_{10}(PPh_3)_2$] with 2/1 hexane/$CH_2Cl_2$. The yellow powder which was obtained after removal of the solvent from the pale yellow fraction was recrystallized (by carefully layering hexane over a dichloromethane solution) to yield plate-like yellow crystals of *eq*-$H_3Re_3(CO)_{11}(PPh_3)$ (34% yield). Spectral details for this compound match those previously reported [7]: Proton NMR spectrum (in $CDCl_3$): τ 25.90 ppm (doublet), J(P—H) 17.5 Hz; τ 27.11 ppm (singlet); 27.20 ppm (singlet). Infra-red spectrum (in cyclohexane): 2113w, 2089m, 2050w, 2020vs, 2010m, 2002s, 1974s, 1969(sh), 1955w, 1942w cm^{-1}.

X-ray diffraction analysis of eq-$H_3Re_3(CO)_{11}(PPh_3)$

A plate-like yellow crystal of *eq*-$H_3Re_3(CO)_{11}(PPh_3)$ with dimensions 0.22 × 0.08 × 0.22 mm was used for the X-ray diffraction measurements. Unit-cell parameters and other crystallographic details are given in Table 1. Two quadrants of reciprocal space ($\pm h$, $\pm k$, $+l$) were sampled at room temperature. Data were collected on a Syntex $P2_1$ four-circle automated diffractometer, with the ω-scan technique using Mo-K_α graphite-monochromatized radiation up to a 2θ limit of 45°. A total of 9611 reflections were collected with a minimum scan speed of 2.0°/min. Three check reflections were monitored at 50-reflection intervals and exhibited no significant variation during the period of data collection. Integrated raw intensities were corrected for Lorentz, polarization and absorption effects, and merged to give 3419 reflections having $F_0^2 > 3\sigma(F_0^2)$. Direct methods [8] were employed to provide initial positions of the Re atoms. Subsequent difference-Fourier maps [9] revealed the remaining non-hydrogen atoms. Several cycles of full-matrix least-squares refinement (in which anisotropic thermal parameters were assigned to the Re and P atoms, and isotropic ones to the C and O atoms) resulted in the final agreement factors of $R(F)$ = 0.041 and $R(wF)$ = 0.050 [10]. In the last cycle, all shifts were less than 0.1 of their estimated standard deviations.

TABLE 1

SUMMARY OF CRYSTAL DATA AND REFINEMENT RESULTS FOR $H_3Re_3(CO)_{11}(PPh_3)$

Space group $P2_1/n$
$Z = 4$
Mol wt. = 1131.9
ρ(obsd) [a] = 2.32 g cm^{-3}

	X-ray	neutron
Unit cell parameters	a = 8.895(2) Å	8.907(9) Å
	b = 22.311(5) Å	22.320(22) Å
	c = 16.355(3) Å	16.369(16) Å
	β = 78.47(1)°	78.41(3)°
	V = 3180(1) Å^3	3188(6) Å^3
ρ(calc)	2.36 g cm^{-3}	2.36 g cm^{-3}
Wavelength used	0.71069 Å (Mo-K_α)	1.048(1) Å
Absorption coefficient, μ	119.4 cm^{-1}	1.121 cm^{-1}
($\sin\theta/\lambda$) limit	0.538 Å^{-1} ($2\theta = 45°$)	0.441 Å^{-1} ($2\theta = 55°$) [b]
Total no. of reflections measured	9503	3095
No. of unique reflections	4229	2864
No. of reflections used in the structure analysis	3419 ($I > 3\sigma$)	2331 ($I > \sigma$)
No. of variable parameters	197	396
Final agreement factors $R(F)$	0.041	0.092
$R(wF)$	0.050	0.057
$R(F^2)$	—	0.116
$R(wF^2)$	—	0.107

[a] Obtained via flotation from a solution of bromoform and carbon tetrachloride. [b] Selected strong reflections were sampled out to 2θ = 90°.

Neutron diffraction analysis of eq-$H_3Re_3(CO)_{11}(PPh_3)$

A crystal of *eq*-$H_3Re_3(CO)_{11}(PPh_3)$ with a volume of 5.91 mm^3 (approximate dimensions 4.1 × 1.2 × 1.0 mm) was mounted roughly along its [1 0 1] axis. Neutron diffraction data were collected at room temperature at the Brookhaven High Flux Beam Reactor [11]. The wavelength used was 1.048(1) Å, calibrated with Al_2O_3 powder (hexagonal, a = 4.758, c = 12.991 Å at 25°C). The $\pm h, +k, +l$ quadrant of reciprocal space was sampled using the $\theta/2\theta$ step-scan technique up to a maximum 2θ value of 90° *. A fixed scan width of 2.8° in 2θ was used for $2\theta < 55°$ and a variable scan width was used in the range $55° < 2\theta < 90°$. The step size (0.04 to 0.06°) was adjusted so that there were about 65 steps (40 000 incident beam monitor counts per step, corresponding to approximately 2 seconds/step) in each scan. Two check reflections were monitored at 100-reflection intervals; no significant change in their intensities occurred over the course of data collection.

The cell constants (Table 1) were determined from a least-squares fit to the centered 2θ angles of 32 reflections. Raw intensities of 3095 reflections were measured, with background corrections based on the counts of 5 steps on either end of each scan. The squared observed structure factors were obtained by applying Lorentz and absorption corrections to the raw intensity data. The absorption corrections were based on numerical integration over a Gaussian grid of points. Calculated transmission coefficients ranged from 0.840 to 0.897. Data for symmetry-equivalent reflections were averaged to give 2864 unique F^2 values, of which 2331 were greater than one e.s.d. and were included in the subsequent structure analysis. Agreement factors for data averaging (based on F^2 values) are R = 0.055 and R_w = 0.026.

Neutron scattering lengths used are b(Re) = 0.92, b(P) = 0.513, b(O) = 0.5803, b(C) = 0.6648, and b(H) = −0.3741 (× 10^{-12} cm). Initial atomic positions of the non-hydrogen atoms were taken from the X-ray structure determination. A difference-Fourier map [9] revealed the positions of the three hybride ligands (corresponding to the three largest negative peaks) and six other H atoms. Several cycles of refinement by an automated differential synthesis procedure, followed by inspection of difference maps, gave the positions of the remaining H atoms. The entire structure was then refined on F^2 by block-matrix least-squares techniques, employing anisotropic thermal parameters for H and O atoms, and isotopic factors for Re, P and C. The final agreement factors are $R(F)$ = 0.092, $R(wF)$ = 0.057, $R(F^2)$ = 0.116 and $R(wF^2)$ = 0.107; all parameters shifts were within their e.s.d.'s.

Preparation of $H_4Os_4(CO)_{12}$

The direct hydrogenation procedure of Kaesz and coworkers [12] was employed. It was found that yields could be doubled by raising the temperature from that of refluxing octane (120°C) to that of a mixture of refluxing xylenes (137—144°C). Pure hydrogen gas (dried with 98% H_2SO_4) was bubbled through the refluxing solution of $Os_3(CO)_{12}$ (699 mg, 0.77 mmol) in xylene (300 ml). The reaction was monitored by infrared spectroscopy and was

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* For high-angle data ($55° < 2\theta < 90°$), only those reflections whose intensities were predicted to be strong were measured.

stopped after all $Os_3(CO)_{12}$ and $H_2Os_3(CO)_{10}$ disappeared (approx. 90 hours). After cooling, the solvent was removed and the brown solid was suspended in 10 ml of hexane and chromatographed on a silica gel column. The product $H_4Os_4(CO)_{12}$ was eluted as a pale-yellow band with 5/1 hexane/CH_2Cl_2 and obtained as a yellow powder (415 mg; 65% yield) after removing the solvent by evaporation.

Preparation of $H_4Os_4(CO)_{11}P(OMe)_3$

This synthesis was adapted from that of $H_4Ru_4(CO)_{11}P(OMe)_3$ [13], with the added feature of using trimethylamine oxide to facilitate the removal of carbonyl ligands. To a suspension of $H_4Os_4(CO)_{12}$ (335.2 mg, 0.304 mmol) in dry, degassed and freshly distilled THF (30 ml) was added $P(OMe)_3$ (0.035 ml, 0.304 mmol) and Me_3NO (34 mg, 0.304 mmol). This suspension was stirred at room temperature for 50 minutes, after which time all the $H_4Os_4(CO)_{12}$ had dissolved. Evaporation of the solvent to dryness gave a yellow product which contained the mono-substituted derivative and some other osmium clusters. The yellow solid was dissolved in CH_2Cl_2 and chromatographed on a silica gel column (60—80 mesh) with a 4/1 CH_2Cl_2/hexane solvent mixture as eluant. Three well-separated bands developed: the first consisting of unreacted $H_4Os_4(CO)_{12}$, the second a mixture of various neutral substituted derivatives, and the third some uncharacterized anionic cluster species. The solid obtained by evaporation of the second band was dissolved in CH_2Cl_2/hexane (1/4) and chromatographed on silica gel. Elution with 1/4 CH_2Cl_2/hexane produced three bands, containing in succession $H_4Os_4(CO)_{11}P(OMe)_3$, $H_4Os_4(CO)_{10}[P(OMe)_3]_2$, and $H_4Os_4(CO)_9[P(OMe)_3]_3$. After two such chromatographic runs, the compound was found to be very pure. Crystals of $H_4Os_4(CO)_{11}P(OMe)_3$ were obtained by cooling, at −20°C, a solution of the compound in CH_2Cl_2/hexane *. Yield: 32%. Analysis Found: C, 13.98; H, 1.02; Os, 63.82; P, 2.71. $C_{14}H_{13}O_{14}Os_4P$ Calcd;: C, 14.04; H, 1.08; O, 18.72; Os, 63.54; P, 2.59%. Proton NMR spectrum (in $CDCl_3$): τ 30.38 ppm (doublet), J(P—H) 4.1 Hz. Infrared spectrum (in pentane): 2095w, 2070vs, 2060vs, 2020s, 2000s, 1990 w cm^{-1}.

X-ray diffraction analysis of $H_4Os_4(CO)_{11}P(OMe)_3$

The air-stable compound crystallized as plate-like bright yellow crystals. X-ray diffraction data were obtained and reduced to F_0^2 values in a manner similar to that described above for *eq*-$H_3Re_3(CO)_{11}(PPh_3)$. Unit cell parameters and other relevant crystallographic details are given in Table 2. At the end of data reduction, 3014 unique reflections with $F_0^2 > 3\sigma(F_0^2)$ remained for the subsequent structure analysis. The initial positions of the four Os atoms were derived from a Patterson map. Subsequent difference-Fourier maps revealed the remaining non-hydrogen atoms. The structure was then refined (with anisotropic thermal parameters for the Os and P atoms and isotropic ones for the C and O atoms) to yield the final agreement factors of $R(F) = 0.048$ and $R(wF) = 0.052$. In the last cycle, all shifts were less than 0.1 of their e.s.d.'s .

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* For the neutron diffraction work, crystals were grown by layering heptane over a concentrated dichloromethane solution.

TABLE 2

SUMMARY OF CRYSTAL DATA AND REFINEMENT RESULTS FOR $H_4Os_4(CO)_{11}P(OCH_3)_3$

Space group $P\bar{1}$
$Z = 2$
Mol. wt. = 1197.0

		X-ray	neutron
Unit cell parameters		$a = 11.241(6)$ Å	11.206(1) Å
		$b = 13.897(4)$ Å	13.842(14) Å
		$c = 8.735(2)$ Å	8.715(9) Å
		$\alpha = 95.54(2)°$	95.55(1)°
		$\beta = 111.95(3)°$	111.97(1)°
		$\gamma = 94.54(4)°$	94.47(1)°
		$V = 1249.8(9)$ Å^3	1238(2) Å^3
ρ(calc)		3.18 g cm^{-3}	3.21 g cm^{-3}
Wavelength used		0.71069 Å	1.160(1) Å
Absorption coefficient, μ		216.0 cm^{-1}	0.991 cm^{-1}
($\sin\theta/\lambda$) limit		0.595 Å^{-1} ($2\theta = 50°$)	0.525 Å^{-1} ($2\theta = 75°$) [a]
Total no. of reflections measured		4978	3627
No. of unique reflections		3968	3129
No. of reflections used in the structure analysis		3014 ($I > 3\sigma$)	2576 ($I > \sigma$)
No. of variable parameters		158	338
Final agreement factors	$R(F)$	0.048	0.104
	$R(wF)$	0.052	0.074
	$R(F^2)$	—	0.129
	$R(wF^2)$	—	0.143

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[a] Selected strong reflections were sampled out to $2\theta = 100°$.

Neutron diffraction analysis of $H_4Os_4(CO)_{11}P(OMe)_3$

A thin plate-like crystal of $H_4Os_4(CO)_{11}P(OMe)_3$ with a volume of 9.45 mm^3 (approximate dimensions 4.4 × 1.8 × 1.2 mm), mounted approximately along the c^* direction, was used for the neutron diffraction experiment. Data were obtained and reduced to F_0^2 values in a manner similar to that described above for *eq*-$H_3Re_3(CO)_{11}(PPh_3)$. Counts were accumulated for approximately 1 second per step, and the wavelength of the neutron beam was 1.160(1) Å. Three intense reflections were measured at 50-reflection intervals to monitor the experiment, and automatic recentering was applied as soon as significant variations of the monitor intensities were observed. This was necessary since some slippage of the crystal occurred during data collection. Any off-centered reflections were remeasured after each recentering. Three slightly different orientation matrices were utilized during the experiment, yielding three batches of data (1039, 402 and 2186 reflections) which were processed separately. In the absorption correction, calculated transmission coefficients ranged from 0.768 to 0.943. After sorting and averaging, 3129 unique reflections remained, of which 2576 with $F_0^2 > \sigma(F_0^2)$ were included in the subsequent structure analysis. Agreement factors for data averaging (based on F^2) are $R = 0.039$ and $R_w = 0.019$. The cell constants given in Table 2 were determined from a least-squares fit to the average centered 2θ angles of 48 Friedel pairs. The unit cell lengths are slightly, but systematically shorter than those determined by X-ray diffraction, possibly reflecting a small error in the neutron wavelength calibration.

Neutron scattering lengths used are $b(\mathrm{Os}) = 1.08$, $b(\mathrm{P}) = 0.513$, $b(\mathrm{O}) = 0.5803$, $b(\mathrm{C}) = 0.6648$, and $b(\mathrm{H}) = -0.3741$ ($\times 10^{-12}$ cm). Initial atomic positions of non-hydrogen atoms were taken from the X-ray structure determination. The four hydride ligand positions were readily located from a difference-Fourier map, but the H atoms of the disordered methyl groups were less easily found and caused some difficulty in the structure analysis. The structure was eventually refined on F^2 by imposing rigid-body constraints [14] on the disordered methyl groups, assuming idealized sp^3-hybridized geometries, C—H bond lengths of 1.05 Å, and individual isotropic thermal parameters. The rest of the molecule was unconstrained, with anisotropic thermal parameters for all atoms. The final agreement factors are $R(F) = 0.104$, $R(wF) = 0.074$, $R(F^2) = 0.129$, and $R(wF^2) = 0.143$, with all parameter shifts within their e.s.d.'s.

Results and discussion

$H_3Re_3(CO)_{11}(PPh_3)$

A full molecular plot of *eq*-$\mathrm{H_3Re_3(CO)_{11}(PPh_3)}$ is given in Fig. 1, and a view of the equatorial plane is shown in Fig. 2. Interatomic distances and angles from the neutron study are listed in Tables 3 and 4, and final atomic positions and thermal parameters are available [15]. The structure of the molecule very closely resembles that of $\mathrm{H_3Mn_3(CO)_{12}}$ [3], except, of course, for the phosphine ligand. The average geometrical parameters for the $\mathrm{H_3M_3}$ core (Re—H = 1.822(8) Å, Re—Re = 3.262(12) Å, Re—H—Re = 127.1(5)°, H—Re—H = 112.7-

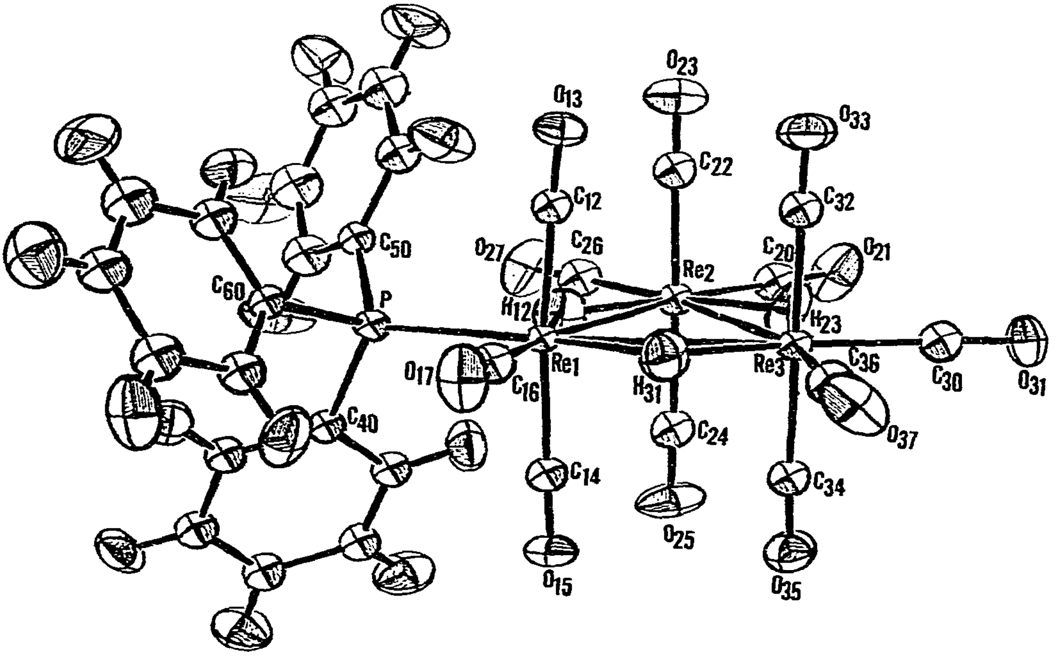

Fig. 1. A full molecular plot of *eq*-$\mathrm{H_3Re_3(CO)_{11}(PPh_3)}$. In this and all other plots, atoms are drawn as 30% probability ellipsoids [35].

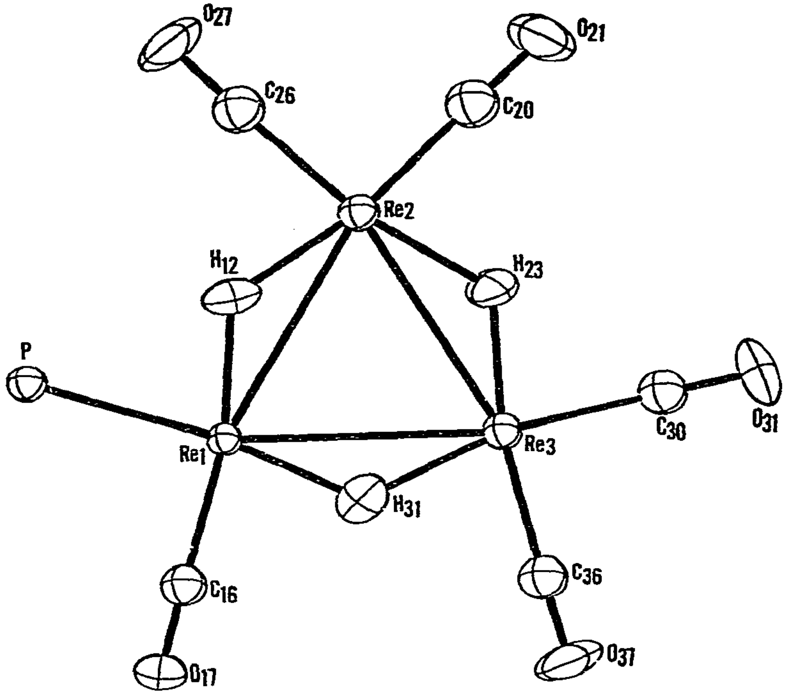

Fig. 2. The core of $H_3Re_3(CO)_{11}(PPh_3)$, viewed normal to the equatorial plane.

(3)°] are consistent with those in $H_3Mn_3(CO)_{12}$ [Mn—H = 1.72(3) Å, Mn—Mn = 3.111(2) Å, Mn—H—Mn = 131(7)°, H—Mn—H = 108(6)°], provided that the difference in covalent radii between Re and Mn is taken into account. These parameters also match very well those from a recent neutron diffraction analysis of $H_3Re_3(CO)_8[(EtO)_2POP(OEt)_2]_2$ (Re—H = 1.81(2) Å, Re—Re = 3.282-(17) Å, Re—H—Re = 130(3)° [16].

As mentioned in the Introduction, the original geometry suggested for $H_3Re_3(CO)_{12}$ [1], with H atoms bridging the edges of the Re_3 triangle, is essentially confirmed by the present result. The central H_3Re_3 fragment in $H_3Re_3(CO)_{11}(PPh_3)$ is planar with ±0.07 Å *, and each H atom is displaced by an average of 0.81 Å from the center of the corresponding Re—Re vector (c.f. 0.7 Å in $H_3Mn_3(CO)_{12}$[3]). One striking feature about the equatorial PPh_3 ligand is that the Re—H bond *trans* to it [Re(1)—H(31) = 1.78(1) Å] is markedly shorter than all the other Re—H distances in the molecule [range 1.82(1)—1.83(1) Å]. This may be related to the fact that PPh_3 is a poorer π-acceptor than CO [17]. The molecule is, incidentally, somewhat fluxional in solution. Although both axial and equatorial forms of $H_3Re_3(CO)_{11}(PPh_3)$ can be isolated,

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* For the least-squares plane defined by the six-atom H_3Re_3 unit, the deviations, (in Å) are as follows: Re(1), —0.03(1); Re(2), 0.04(1); Re(3), 0.05(1); H(12), 0.01(1); H(23), —0.07(1); H(31), 0.00(1). For the plane defined by the Re_3 triangle, the out-of-plane deviations (in Å) are: H(12), 0.02(1); H(23), —0.13(1); H(31), 0.00(1). The dihedral angles between the central Re_3 plane and various Re—H—Re planes are as follows: Re(1)H(12)Re(2), 1.7°, Re(2)H(23)Re(3), 8.9°; Re(3)-H(31)Re(1), 0.1°.

TABLE 3

SELECTED BOND DISTANCES (Å) IN $H_3Re_3(CO)_{11}(PPh_3)$ (NEUTRON RESULTS)

Re—Re			
Re(1)—Re(2)	3.279(5)	*C—O*	
Re(1)—Re(3)	3.239(5)	C(12)—O(13)	1.15(1)
Re(2)—Re(3)	3.268(6)	C(14)—O(15)	1.15(1)
		C(16)—O(17)	1.15(1)
Mean	3.262(12) [a]	C(20)—O(21)	1.17(1)
		C(22)—O(23)	1.12(1)
		C(24)—O(25)	1.13(1)
		C(26)—O(27)	1.16(1)
H—Re		C(30)—O(31)	1.14(1)
H(12)—Re(1)	1.829(14)	C(32)—O(33)	1.13(1)
H(12)—Re(2)	1.823(14)	C(34)—O(35)	1.12(1)
H(23)—Re(2)	1.833(14)	C(36)—O(37)	1.12(1)
H(23)—Re(3)	1.832(14)		
H(31)—Re(1)	1.782(14)	Mean	1.140(5) [a]
H(31)—Re(3)	1.832(13)		
Mean	1.822(8) [a]	*P—C*	
		P—C(40)	1.83(1)
Re—P		P—C(50)	1.82(1)
Re(1)—P	2.42(1)	P—C(60)	1.83(1)
		Mean	1.825(3) [a]
Re—C			
Re(1)—C(12)	1.98(1)		
Re(1)—C(14)	1.98(1)		
Re(1)—C(16)	1.93(1)		
Re(2)—C(20)	1.92(1)		
Re(2)—C(22)	2.00(1)		
Re(2)—C(24)	2.00(1)		
Re(2)—C(26)	1.95(1)		
Re(3)—C(30)	1.93(1)		
Re(3)—C(32)	2.00(1)		
Re(3)—C(34)	2.00(1)		
Re(3)—C(36)	1.95(1)		
Mean	1.97(1) [a]		

[a] In this and all subsequent tables, standard deviations of mean values are calculated as $\sigma(\bar{x}) = [\Sigma(x_i - \bar{x})^2/n(n-1)]^{1/2}$, where $\bar{x}$ is the average value and x_i are individual values.

the two isomers interconvert slowly in solution (over a period of days) to give an equilibrium mixture consisting of 71% of the equatorial form [7,18] *.

The other members of the 48-electron Re_3 family, the deprotonated clusters $[H_2Re_3(CO)_{12}]^-$ [19] and $[HRe_3(CO)_{12}]^{2-}$ [20], have very similar structures, with two and one edge-bridging H atoms, respectively. In contrast, the 46-electron clusters $[H_4Re_3(CO)_{10}]^-$ [21] and $[H_3Re_3(CO)_{10}]^{2-}$ [22] have distinctly different geometries, with one edge being doubly-bridged $[M(\mu\text{-}H)_2M]$. Finally, the novel 42-electron cluster $H_3Rh_3[P(OMe)_3]_6$, recently analyzed by neutron diffraction [23], has a H_3M_3 core very different from that of $H_3Re_3(CO)_{11}(PPh_3)$. In contrast to the near-planar H_3M_3 skeleton in the latter compound,

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* The energy of activation for the equatorial → axial conversion is 25 ± 2 kcal/mol and the half-life of this process is 2.1 days [7b].

TABLE 4

SELECTED BOND ANGLES (deg.) IN $H_3Re_3(CO)_{11}(PPh_3)$ (NEUTRON RESULTS)

Re—H—Re		*Re—Re—Re*	
Re(1)—H(12)—Re(2)	127.7(8)	Re(2)—Re(1)—Re(3)	60.2(1)
Re(2)—H(23)—Re(3)	126.1(8)	Re(1)—Re(2)—Re(3)	59.3(1)
Re(1)—H(31)—Re(3)	127.3(8)	Re(1)—Re(3)—Re(2)	60.5(1)
Mean	127.1(5)	Mean	60.0(4)
H—Re—H		*P—Re—C*	
H(12)—Re(1)—H(31)	113.0(6)	P—Re(1)—C(12)	93.7(3)
H(12)—Re(2)—H(23)	112.1(6)	P—Re(1)—C(14)	92.8(3)
H(23)—Re(3)—H(31)	113.1(6)	P—Re(1)—C(16)	93.4(4)
Mean	112.7(3)	Mean	93.3(3)
		H—Re—C	
		H(12)—Re(1)—C(12)	92.3(5)
H—Re—P		H(12)—Re(1)—C(14)	92.2(5)
H(12)—Re(1)—P	74.8(5)	H(12)—Re(1)—C(16)	168.1(5)
H(31)—Re(1)—P	172.1(5)	H(31)—Re(1)—C(12)	87.3(5)
		H(31)—Re(1)—C(14)	85.9(5)
C—Re—C		H(31)—Re(1)—C(16)	78.8(5)
C(12)—Re(1)—C(14)	172.9(4)	H(12)—Re(2)—C(20)	168.6(6)
C(12)—Re(1)—C(16)	86.7(3)	H(12)—Re(2)—C(22)	88.7(5)
C(14)—Re(1)—C(16)	90.0(4)	H(12)—Re(2)—C(24)	88.7(5)
C(20)—Re(2)—C(22)	92.0(4)	H(12)—Re(2)—C(26)	79.3(5)
C(20)—Re(2)—C(24)	90.8(4)	H(23)—Re(2)—C(20)	79.3(5)
C(20)—Re(2)—C(26)	89.3(4)	H(23)—Re(2)—C(22)	87.1(5)
C(22)—Re(2)—C(24)	177.1(4)	H(23)—Re(2)—C(24)	92.6(5)
C(22)—Re(2)—C(26)	89.6(4)	H(23)—Re(2)—C(26)	168.0(6)
C(24)—Re(2)—C(26)	91.2(4)	H(23)—Re(3)—C(30)	80.0(5)
C(30)—Re(3)—C(32)	90.2(4)	H(23)—Re(3)—C(32)	86.8(5)
C(30)—Re(3)—C(34)	89.4(4)	H(23)—Re(3)—C(34)	91.5(6)
C(30)—Re(3)—C(36)	89.8(4)	H(23)—Re(3)—C(36)	169.7(5)
C(32)—Re(3)—C(34)	178.4(5)	H(31)—Re(3)—C(30)	166.9(6)
C(32)—Re(3)—C(36)	91.0(4)	H(31)—Re(3)—C(32)	89.8(5)
C(34)—Re(3)—C(36)	90.6(4)	H(31)—Re(3)—C(34)	90.9(5)
		H(31)—Re(3)—C(36)	77.0(5)

the H-atom arrangement in $H_3Rh_3[P(OMe)_3]_6$ is skewed: one H atom is in the plane of the Rh_3 ring, one is above, and the other is below the Rh_3 plane [the displacements in the three cases are 0.20(2), 1.13(2) and −1.03(2) Å]. The difference between $H_3Re_3(CO)_{11}(PPh_3)$ and $H_3Rh_3[P(OMe)_3]_6$ may well be a consequence of their different electron configurations: the coordination of each metal atom is approximately octahedral in $H_3Re_3(CO)_{11}(PPh_3)$ but square planar in $H_3Rh_3[P(OMe)_3]_6$.

$H_4Os_4(CO)_{11}P(OMe)_3$

Two views of $H_4Os_4(CO)_{11}P(OMe)_3$ are shown in Figs. 3 and 4. The interatomic distances and angles from the neutron study are given in Tables 5 and 6, and final atomic positions and thermal parameters are available [15]. The H_4Os_4 core of the molecule has approximate D_{2d} symmetry (Fig. 4), and has the characteristic four-long/two-short pattern of metal—metal distances invariably found in the $H_4Os_4(CO)_{12}$/$H_4Ru_4(CO)_{12}$ family of clusters [5,6]. As expected, these H atoms are found to bridge the long Os—Os edges, with the

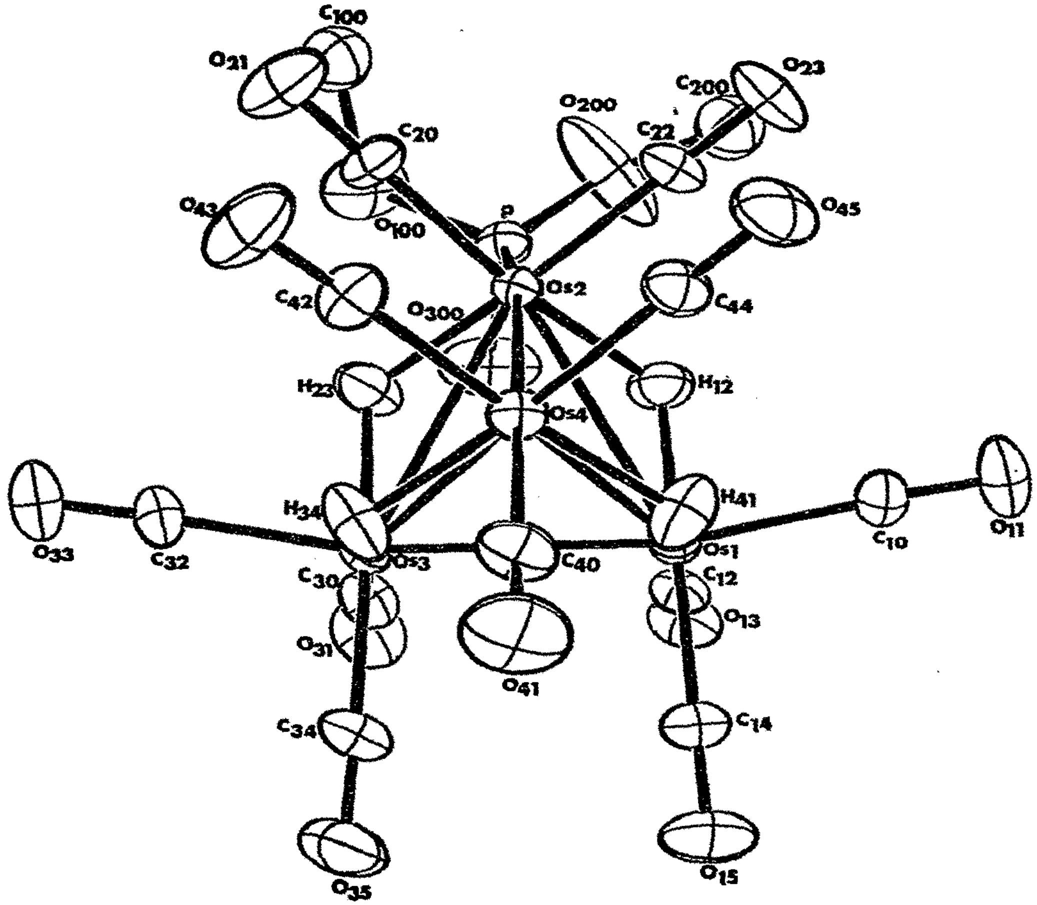

Fig. 3. A molecular plot of $H_4Os_4(CO)_{11}P(OMe)_3$, viewed approximately in a direction perpendicular to one of the faces of the tetrahedron. The H atoms of the methyl groups have been omitted for clarity, and methoxy carbon C(300) is hidden.

following average geometry: Os—H = 1.787(3) Å, Os—Os = 2.966(4) Å, Os—H—Os = 112.2(4)°, H—Os—H = 104(2)°. The Os—H bond length found here is in good agreement with those of other tetranuclear osmium carbonyl clusters (1.805(5) Å in $H_3Os_4(CO)_{11}$ (HC=CHPh) [24] and 1.788(4) Å in $H_3Os_4(CO)_{12}I$ [25]), and also with the Ru—H distance of 1.773(2) Å found in the closely related molecule $H_4Ru_4(CO)_8[P(OMe)_3]_4$ [26].

The particular orientation of the $P(OMe)_3$ ligand relative to the H_4Os_4 core (Fig. 4) (i.e., one in which the phosphite is *cis* to two Os—H—Os edges and *trans* to an Os—Os bond) is, in fact, the one predicted by Knox and Kaesz for the ruthenium analog $H_4Ru_4(CO)_{11}P(OMe)_3$ [13] and confirmed crystallographically by us recently [5].

The H_4M_4 family of clusters is now known to exist in two predominant geometries: a D_{2d} form (I), and a C_s form (II) [6] *. In addition, their

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* Besides the edge-bridging structures I and II, a few examples of compounds having face-bridging H atoms are also known: e.g., $H_4Co_4(C_5H_5)_4$ [27a] and $H_4Re_4(CO)_{12}$ [27b]. The bonding in H_4M_4-type clusters has been discussed by Hoffmann, Schilling et al. [28].

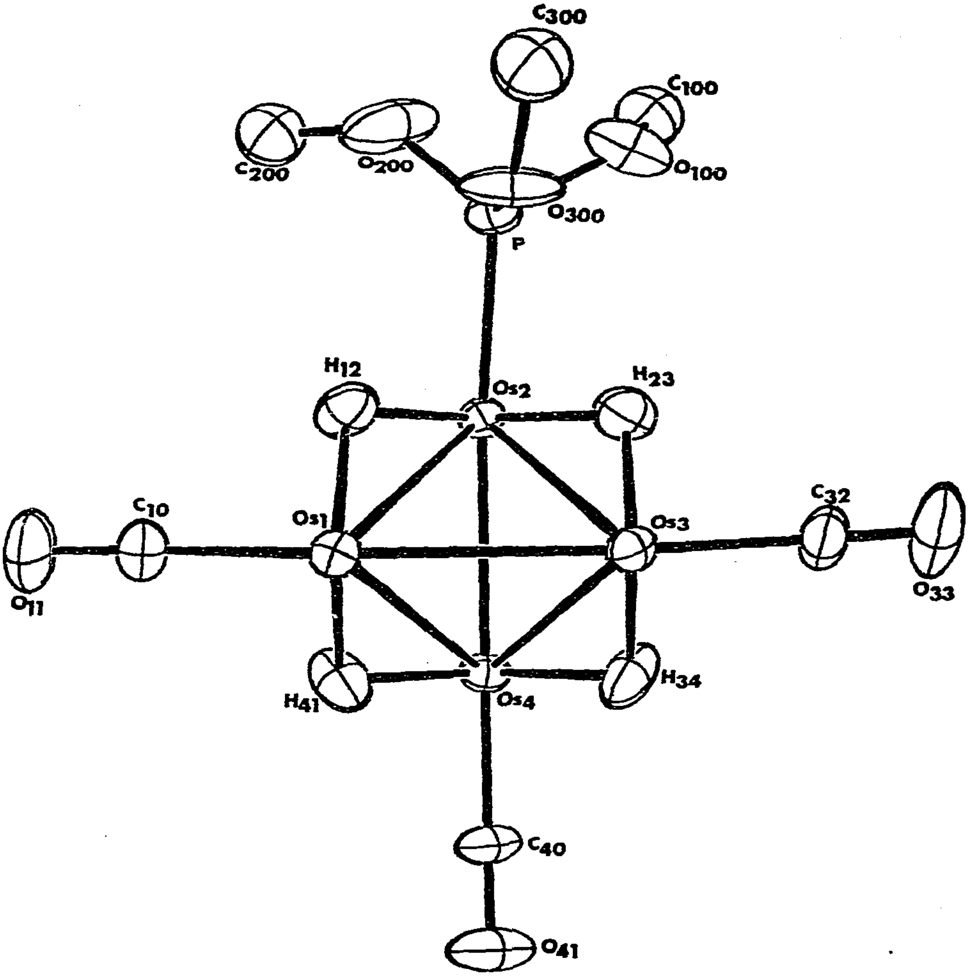
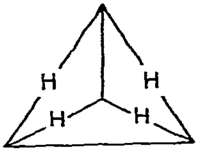
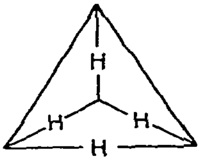


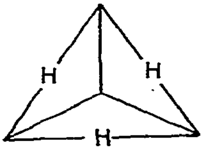
Fig. 4. The D_{2d} core of $H_4Os_4(CO)_{11}P(OMe)_3$, showing the two unbridged Os—Os edges lying opposite one another. Eight carbonyl ligands have been removed for clarity.



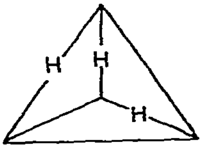
I (D_{2d})



II (C_s)



III (C_{3v})



IV (C_2)

TABLE 5

SELECTED BOND DISTANCES (Å) IN $H_4Os_4(CO)_{11}P(OMe)_3$ (NEUTRON RESULTS)

Os—Os(long)		*Os—C*	
Os(1)—Os(2)	2.957(5)	Os(1)—C(10)	1.919(7)
Os(1)—Os(4)	2.976(5)	Os(1)—C(12)	1.893(6)
Os(2)—Os(3)	2.965(3)	Os(1)—C(14)	1.913(6)
Os(3)—Os(4)	2.968(4)	Os(2)—C(20)	1.883(8)
		Os(2)—C(22)	1.890(6)
Mean	2.966(4)	Os(3)—C(30)	1.900(6)
Os—Os(short)		Os(3)—C(32)	1.911(8)
Os(1)—Os(3)	2.818(5)	Os(3)—C(34)	1.901(6)
Os(2)—Os(4)	2.810(4)	Os(4)—C(40)	1.915(6)
		Os(4)—C(42)	1.895(8)
Mean	2.814(4)	Os(4)—C(44)	1.902(6)
H—Os		Mean	1.902(3)
H(12)—Os(1)	1.79(1)		
H(12)—Os(2)	1.79(1)	*C—O(carbonyl)*	
H(23)—Os(2)	1.79(1)	C(10)—O(11)	1.12(1)
H(23)—Os(3)	1.77(1)	C(12)—O(13)	1.14(1)
H(34)—Os(3)	1.77(1)	C(14)—O(15)	1.13(1)
H(34)—Os(4)	1.80(1)	C(20)—O(21)	1.15(1)
H(41)—Os(1)	1.78(1)	C(22)—O(23)	1.14(1)
H(41)—Os(4)	1.79(1)	C(30)—O(31)	1.13(1)
		C(32)—O(33)	1.13(1)
Mean	1.787(3)	C(34)—O(35)	1.13(1)
Os—P		C(40)—O(41)	1.12(1)
Os(2)—P	2.293(7)	C(42)—O(43)	1.13(1)
P—O		C(44)—O(45)	1.13(1)
P—O(100)	1.59(1)	Mean	1.130(2)
P—O(200)	1.51(1)	*O—C(methoxy)*	
P—O(300)	1.57(1)	O(100)—C(100)	1.39(1)
		O(200)—C(200)	1.31(1)
Mean	1.56(3)	O(300)—C(300)	1.39(1)
		Mean	1.36(3)

[a] Distances in this table were computed using the more precise unit cell parameters derived from the X-ray analysis.

deprotonated analogs H_3M_4 can form structures of either C_{3v} (III) or C_2 (IV) symmetry [29]. Of these, I is by far the most common, being found in $H_4Ru_4(CO)_{12}$ [5], $H_4Ru_4(CO)_{11}P(OMe)_3$ [30], $H_4Ru_4(CO)_{10}(PPh_3)_2$ [5], $H_4Ru_4(CO)_8[P(OMe)_3]_4$ [26], $[H_4Rh_4(C_5Me_5)_4]^{2+}$ [31], and the present compound. The C_s structure II has been found in $H_4Ru_4(CO)_{10}(Ph_2PCH_2CH_2PPh_2)$ [32] and $[H_4Re_4(CO)_{13}]^{2-}$ [33]. Structures III and IV have been discovered as two isomeric forms of the anion $[H_3Ru_4(CO)_{12}]^-$ [29b]. The existence of this rich variety of structural forms (I—IV) suggests that the energy differences between the various configurations are small, a conclusion which is supported by the fact that the H atoms in H_3Ru_4- and H_4Ru_4-type clusters are fluxional on the NMR time scale [13,29a, 34].

Usually, the locations of the H atoms in structures I—IV can be inferred reliably from the positions of the longer metal—metal edges, and our result confirms the general usefulness of such correlations. However, if other bridging ligands are present (e.g., unsaturated organic fragments), this correlation may break down. In the case of the cyclohexenyl complex $H_3Os_4(CO)_{11}(C_6H_9)$, po-

TABLE 6

SELECTED BOND ANGLES (deg) IN $H_4Os_4(CO)_{11}P(OMe)_3$ (NEUTRON RESULTS)

Os—H—Os		*H—Os—C*	
Os(1)—H(12)—Os(2)	111.1(5)	H(12)—Os(1)—C(10)	84.4(4)
Os(2)—H(23)—Os(3)	112.4(7)	H(12)—Os(1)—C(12)	79.4(4)
Os(3)—H(34)—Os(4)	112.4(5)	H(12)—Os(1)—C(14)	172.5(4)
Os(1)—H(41)—Os(4)	112.8(7)	H(23)—Os(2)—C(30)	83.4(5)
		H(41)—Os(1)—C(12)	172.2(5)
Mean	112.2(4)	H(41)—Os(1)—C(14)	79.5(4)
H—Os—H		H(12)—Os(2)—C(20)	172.4(3)
H(12)—Os(1)—H(41)	108.0(5)	H(12)—Os(2)—C(22)	83.2(4)
H(12)—Os(2)—H(23)	99.0(5)	H(23)—Os(2)—C(20)	85.6(5)
H(23)—Os(3)—H(34)	104.5(5)	H(23)—Os(2)—C(22)	176.2(4)
H(34)—Os(4)—H(41)	104.2(5)	H(23)—Os(2)—C(30)	83.2(4)
		H(23)—Os(3)—C(32)	81.6(5)
Mean	104(2)	H(23)—Os(3)—C(34)	173.8(4)
Os—Os—Os		H(34)—Os(3)—C(30)	172.0(5)
Os(2)—Os(1)—Os(3)	61.7(1)	H(34)—Os(3)—C(32)	83.8(5)
Os(2)—Os(1)—Os(4)	56.5(1)	H(34)—Os(3)—C(34)	81.2(4)
Os(3)—Os(1)—Os(4)	61.6(1)	H(34)—Os(4)—C(40)	82.7(4)
Os(1)—Os(2)—Os(3)	56.8(1)	H(34)—Os(4)—C(42)	81.5(5)
Os(1)—Os(2)—Os(4)	62.1(1)	H(34)—Os(4)—C(44)	173.2(5)
Os(3)—Os(2)—Os(4)	61.8(1)	H(41)—Os(4)—C(40)	84.0(4)
Os(1)—Os(3)—Os(2)	61.4(1)	H(41)—Os(4)—C(42)	174.2(4)
Os(1)—Os(3)—Os(4)	61.8(1)	H(41)—Os(4)—C(44)	82.2(4)
Os(2)—Os(3)—Os(4)	56.6(1)		
Os(1)—Os(4)—Os(2)	61.4(1)	*C—Os—C*	
Os(1)—Os(4)—Os(3)	56.6(1)	C(10)—Os(1)—C(12)	95.0(3)
Os(2)—Os(4)—Os(3)	61.7(1)	C(10)—Os(1)—C(14)	95.9(3)
		C(12)—Os(1)—C(14)	93.1(3)
Mean	60.0(7)	C(20)—Os(2)—C(22)	91.9(3)
H—Os—P		C(30)—Os(3)—C(32)	95.4(3)
H(12)—Os(2)—P	80.3(4)	C(30)—Os(3)—C(34)	91.0(3)
H(23)—Os(2)—P	78.7(4)	C(32)—Os(3)—C(34)	96.6(3)
		C(40)—Os(4)—C(42)	96.8(3)
Mean	79.5(8)	C(40)—Os(4)—C(44)	95.9(3)
P—Os—C		C(42)—Os(4)—C(44)	92.0(3)
P—Os(2)—C(20)	94.7(3)		
P—Os(2)—C(22)	98.7(2)	Mean	94.4(7)
Mean	97(2)		

tential energy calculations predicted H atoms to bridge, not the three longest Os—Os edges, but the first, second and fourth longest [4]. This prediction was indirectly confirmed by a neutron diffraction analysis of the closely related molecule $H_3Os_4(CO)_{11}(CH{=}CHC_6H_5)$ [24].

Acknowledgements

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$R(F^2) = \Sigma |F_0^2 - |F_c|^2| / \Sigma F_0^2$; $R(wF^2) = \{\Sigma w |F_0^2 - |F_c|^2|^2 / \Sigma w F_0^4\}^{1/2}$.
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