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JOINT X-RAY AND NEUTRON DIFFRACTION STRUCTURE ANALYSIS OF $[(\mu\text{-H})_3Re_3(CO)_8\{(EtO)_2POP(OEt)_2\}_2]$

DAVID W. PREST, MARTIN J. MAYS,

University Chemical Laboratory, Lensfield Road, Cambri 'ge CB2 1EW (Great Britain)

A. GUY ORPEN *

Department of Inorganic Chemistry, The University, Bristol, BS8 ITS (Great Britain)

and RICHARD K. McMULLAN

Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973 (U.S.A.)

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Summary

The compound $[(\mu\text{-H})_3Re_3(CO)_8\{(EtO)_2POP(OEt)_2\}_2]$ crystallises in the monoclinic space group $P2_1/c$ with a 18.053(6), b 16.211(5), c 14.800(3) Å, $\beta = 102.41(2)°$, and $Z = 4$. Simultaneous refinement of a single parameter set to fit 3212 X-Ray ($\sin\theta/\lambda) > 0.352$ Å^{-1} and 1480 neutron data has led to final weighted residuals $R_w(F)$ of 0.096 (X-Ray) and 0.095 (neutron). The molecule exhibits noncrystallographic C_2 symmetry, with two edges of the Re_3 triangle bridged by $(OEt)_2POP(OEt)_2$ ligands. The hydride ligands lie close to the trimetal plane with each hydride bridging an Re–Re vector. Average molecular parameters involving the hydride ligands are Re–H 1.812(17), Re–Re 3.282(17) Å, Re–H–Re 130(3) and H–Re–H 107.6(27)°. All eight carbonyl ligands are terminal, the ligand polyhedron being derived from that in $H_3Re_3(CO)_{12}$ by substitution of four axial carbonyls by two bidentate phosphite ligands.

Introduction

The $H_3M_3(CO)_{12}$, (M = Mn, Re) trimetal clusters have presented considerable problems in crystallographic characterisation because of difficulties in obtaining suitable crystals. Crystals of these unsubstituted carbonyl clusters are frequently twinned and/or disordered (see Introduction in ref. 2). Such behaviour is typical of many dodecacarbonyl species (e.g. $Fe_3(CO)_{12}$ [3], $Ir_4(CO)_{12}$ [4], $H_4Os_4(CO)_{12}$ [5], $H_6Re_4(CO)_{12}$ [6], $H_2Os_4(CO)_{12}$ [7]) where the highly symmetrical, spheroidal,

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carbonyl arrangement largely determines the molecular packing within the crystal. The (icosahedral or twinned cubo-octahedral) ligand polyhedra can pack in a variety of orientations leading to disorder. Consequently, it has proved impossible to obtain accurate (neutron diffraction) structural information on hydride coordination in these systems. The X-ray structure analysis of $H_3Mn_3(CO)_{12}$ [1] was, however, successful in locating the hydride ligands by a Fourier technique using lower angle data. The hydrides were found to be nearly coplanar with the Mn_3 triangle, given the fairly large uncertainties in the hydrogen coordinates. This conclusion is in agreement with spectroscopic studies on $H_3M_3(CO)_{12}$ (M=Mn, Re) [8] which suggested D_{3h} molecular symmetry for these complexes because of the NMR equivalence of the hydrides and the similarity of their IR spectra to that of $Os_3(CO)_{12}$. Potential energy calculations based on the observed non-hydrogen framework of $H_3Mn_3(CO)_{12}$ also indicate the hydrides to occupy such edge-bridging sites [9]. A recent neutron diffraction study of the equatorially mono-substituted derivative $H_3Re_3(CO)_{11}(PPh_3)$ [2] has provided indirect confirmation of the correctness of this structural model.

The title compound was synthesised in the course of an investigation of the reactions of $H_3Re_3(CO)_{12}$ with diphosphine and diphosphite ligands. A full report of this chemistry including the X-ray structure analysis of this compound has been made elsewhere [10]. The molecule retains the non-hydride ligand polyhedron observed in the related $H_3Mn_3(CO)_{12}$ (and presumably in $H_3Re_3(CO)_{12}$), namely the twinned cubo-octahedron. Four axial sites were found to be substituted by the phosphite ligands, but the hydride ligands were not located in the X-ray study. In order to examine the hydride coordination and determine the other ligand geometries with greater precision a neutron diffraction experiment has been undertaken. Analysis of the structure based on both X-ray and neutron data has permitted comparison of the coordination geometry of the title compound with that in $H_3Mn_3(CO)_{12}$, as well as a description of the likely structure of $H_3Re_3(CO)_{12}$ without the systematic bias in light atom positions inherent in analyses based on X-ray data. In the present case, combined X-ray/neutron data refinement has thus enabled a more complete characterisation of the title complex than would be possible with either data set alone.

Experimental

Crystal data. $C_{24}H_{43}O_{18}P_4Re_3$,M = 1488, space group $P2_1/c$, $Z=4$; a 18.053(6), b 16.211(5), c 14.800(3) Å, β 102.41(2)°, U 4230(2) Å^3 from X-ray measurements at 298 K; D_c 2.04 g cm^{-3}, X-radiation, Mo-K_α, $\lambda = 0.710$ 69 Å, $\mu_{\text{X-ray}}$ 88.6 cm^{-1}; Neutron wavelength $\lambda = 1.1621(5)$ Å based on calibration with KBr crystal ($a=$ 6.6000(1) Å at 298 K), μ_N 1.8 cm^{-1}.

X-Ray data collection

Colourless crystals of $H_3Re(CO)_8(POP)_2$ ((POP) = $(OEt)_2POP(OEt)_2$) were obtained by recrystallisation from slowly evaporated dichloromethane/hexane solution. X-Ray data were collected on a tablet shaped crystal at room temperature as described in ref. 10. These data yielded 2103 with $I > 2\sigma(I)$ and $(\sin\theta/\lambda) >$ 0.352 Å^{-1} for use in combined X-ray/neutron refinement. In view of the relatively poor quality of the initial refinement, a second, more extensive, X-ray data set was collected. The crystal used was ground to an approximately spherical shape (diameter 0.38 ± 0.05 mm), etched with hexane to remove surface powder, and mounted on a glass fibre, in air, using epoxy glue. Crystal quality was checked by oscillation photography and ω (fixed 2θ) and ω-θ scans of several reflections. The orientation matrix and unit-cell dimensions used in data collection were obtained by least-squares fit to the diffractometer setting angles for 20 reflections with $20° < 2\theta < 25°$. Data were collected on a Stoe 4-circle diffractometer at room temperature using a constant width, ω-2θ step scan procedure (width 2.5° in 2θ, 125 steps). A quadrant shell of intensity data with $25° < 2\theta < 42°$ was collected with counting time 0.5 s per step and background measured at the scan extremities for a total time equal to 0.5 of the scan time. A further shell of data were collected in the range $42° < 2\theta < 60°$ with doubled counting times and omitting reflections with pre-scan intensities less than 7 counts s^{-1}. The data were corrected for absorption by a semi-empirical method based on a six parameter fit to 314 azimuthal scan data from 9 independent reflections [11]. The merging residual based on F_0 for these reflections was reduced from 0.073 to 0.039 on applying the correction, transmission coefficients for the full data set varying between 0.215 and 0.140; Lorentz and polarisation corrections were applied to the 8339 data collected and duplicate and equivalent reflections averaged to yield 6949 unique data, of which 3212 with $(\sin \theta/\lambda) > 0.352$ and $I > 1.5\sigma(I)$ were used in the combined refinements described below.

Neutron data collection

A large (ca. 6.0 mm^3) crystal bounded by faces of indices {100}, $(0\bar{1}0)$, $(01\bar{2})$, $(0\bar{1}1)$ and (011) was grown from slowly evaporated, seeded dichloromethane, hexane solution and mounted on a hollow aluminium pin for data collection. Data were collected at room temperature on a 4-circle diffractometer at the Brookhaven High Flux Beam Reactor. Attempts to collect data at lower temperatures were frustrated by crystal disintegration on cooling below ~ 220 K. The orientation matrix used in data collection was derived by least squares fit to the diffractometer setting angles for 32 automatically centred reflections in the range $31° < 2\theta < 40°$. Intensity data were collected by ω-2θ step-scans of width 2.60° (in 2θ), with 65 steps per scan and counting time 2 s per step (exact time determined by a preset monitor count of the direct beam). Two reflections (672 and $6\bar{7}2$) were remeasured after every 50, in order to check instrumental and crystal stability; no variation in their intensities was observed. A full quadrant of data was collected in the range $2° < 2\theta < 50°$, a total of 1861 observations. A further 473 reflections calculated to be most intense after preliminary refinement of the low-angle data, were measured in the range $50 < 2\theta < 75°$. The data were corrected for absorption by the analytical method of De Meulenaer and Tompa [12], using the indexed faces and dimensions of the crystal (μ was calculated from μ/ρ for C, O, Re and P taken from International Tables for X-ray Crystallography [13] and for H taken from ref. 14. Transmission coefficients varied between 0.816 and 0.657. Lorentz corrections were applied and the data averaged to yield 2108 unique data of which 1432 had $I > 2\sigma(I)$ and were used in the combined refinements described below.

Structure solution and refinement

The structure was initially solved and refined using the first X-ray data set [10]. The resultant non-hydrogen atomic parameters were used to phase a difference nuclear scattering density map. The principle features of this map were large negative peaks corresponding to the hydrogen atoms in the structure. The three hydride ligands and the majority of the ethoxy group hydrogen atoms were located from this map. The methylene and methyl hydrogens were placed in idealised, staggered tetrahedral positions with C–H bond lengths fixed at 1.08 Å in the early stages of refinement. In the refinement the methylene (CH_2) geometry was constrained to be tetrahedral, while methyl groups were refined as rigid groups, allowing deviation from perfectly staggered geometry. The thermal parameters varied in the refinements were anisotropic factors for non-hydrogen atoms, individual isotropic factors for the hydride hydrogen atoms and common isotropic factors for each of the 16 methyl and methylene groups. The parameters describing the structure were adjusted by a full-matrix least-squares procedure in which a single set of atomic positional and thermal parameters was simultaneously fitted to both the full neutron data set and the higher angle X-ray data ($\sin\theta/\lambda > 352$ Å^{-1}) as discussed in ref. 11. Refinement with the first X-ray set converged to give residuals $R = 0.172$, $R_w = 0.118$ for the 1430 observed neutron data, and $R = 0.085$, $R_w = 0.075$ * for the 2103 X-ray data with $\sin\theta/\lambda > 0.352$ Å^{-1}.

Further refinements were conducted using the second X-ray data set. The weighting scheme used was $w = (\sigma^2(F_0) + gF^2)^{-1}$ with $g = 0.0004$ for the X-ray data and $g = 0.0$ for neutron. The increased number of observed high angle data available gave improved standard deviations in the positional parameters, but the residuals increased, being 0.175 and 0.119 for neutron data, and 0.116, 0.099 for the 3212 X-ray data with $\sin\theta/\lambda > 0.352$. Positive nuclear scattering density difference syntheses indicated poorly fitted regions near the oxygen and carbon atoms particularly those of O–CH_2 groups. The larger data: parameters ratio available using the second X-ray dat set enabled refinement of anisotropic thermal parameters for all oxygen atoms and the carbon atoms of these groups. Constraints were applied as above to hydrogen atom positions in order to reduce the number of parameters refined.

In the final stages of refinement the neutron scattering length of Re and an isotropic secondary extinction parameter for the neutron data were included as adjustable parameters. Refinement converged to $R = 0.143$, $R_w = 0.095$ for the 1480 neutron data and $R = 0.112$, $R_w = 0.095$ for the 3212 observed X-ray data with $\sin\theta/\lambda > 0.352$ Å^{-1}. The refined value of the neutron extinction parameter corresponds to 90 seconds of arc r.m.s. mosaic spread. The neutron scattering length of rhenium refined to a value of 9.41(5) fm agreeing within 2σ with the value of 9.2(1) fm given in ref. 15, the source of the neutron scattering lengths used in these refinements; complex neutral atom X-ray scattering factors were taken from ref. 13. Final difference nuclear scattering density maps showed no chemically significant features.

The molecular geometry is illustrated in Fig. 1 and an alternative view of the core of the molecule showing the metal coordination spheres is shown in Fig. 2. Final atomic positional parameters are given in Table 1 and the derived bond lengths and angles in Tables 2 and 3. Atomic thermal parameters and tables of observed and calculated structure factors are available on request from the authors. Calculations were performed with programs of the CRYSNET system ** and with programs written by G.M. Sheldrick.

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* $R = \sum|F_0 - |F_c||\sum F_0$; $R_w = \sum w^{1/2}|F_0 - |F_c||/\sum w^{1/2}F_0$.

** Described briefly in E.O. Schlemper, W.C. Hamilton and S.J. LaPlaca, J. Chem. Phys., 54 (1971) 3990.

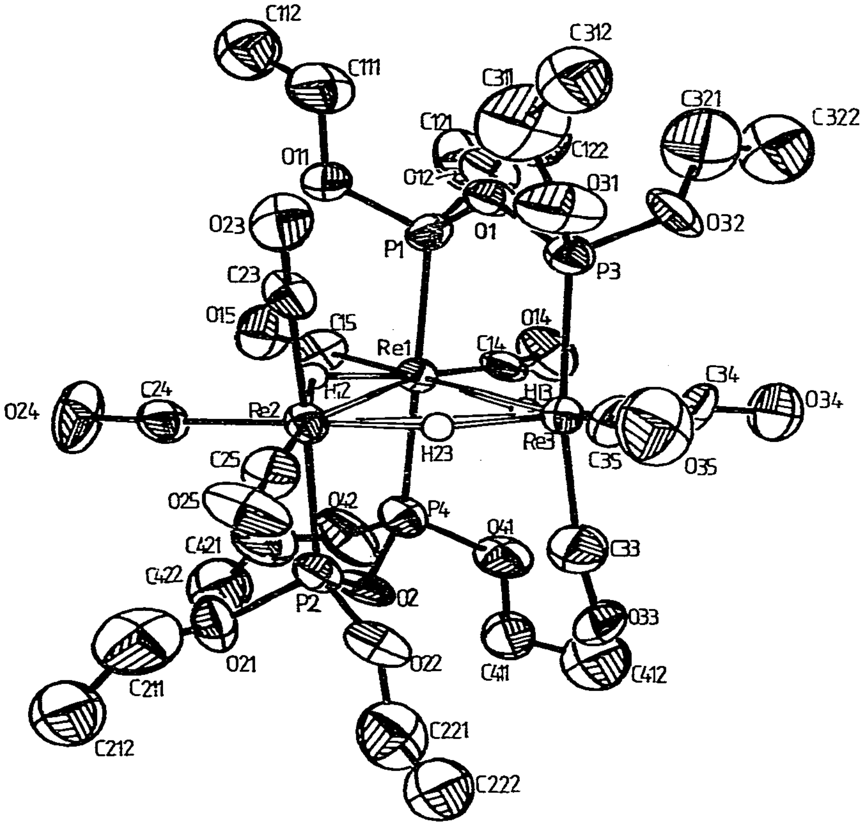

Fig. 1. Perspective view of $H_3Re_3(CO)_8((OEt)_2POP(OEt)_2)_2$ showing the labelling scheme; thermal ellipsoids [19] are drawn to enclose 40% probability and hydride hydrogens as spheres of arbitrary size. Ethoxy hydrogen atoms are omitted for clarity.

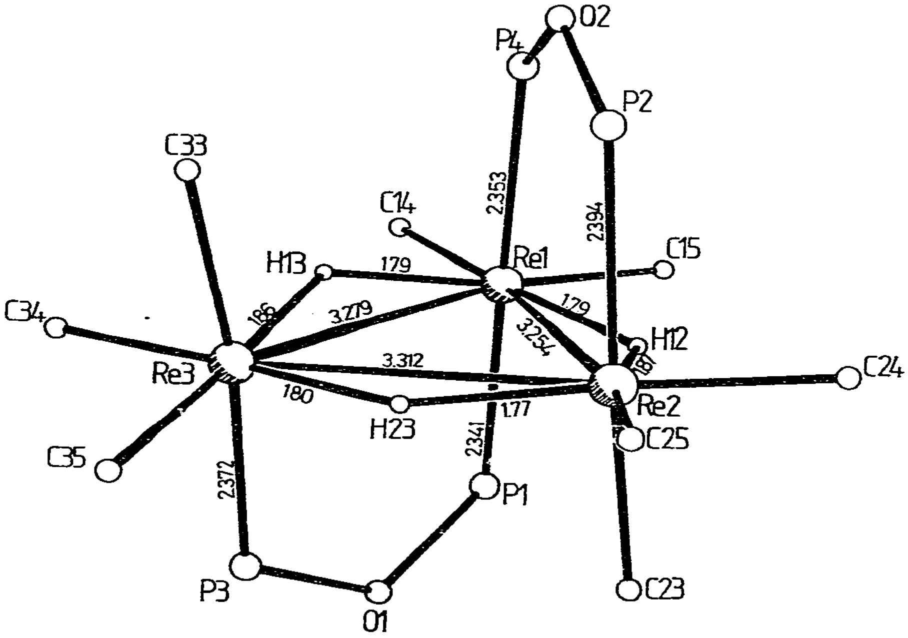

Fig. 2. The core of $H_3Re_3(CO)_8((OEt)_2POP(OEt)_2)_2$ showing the coordination geometry around the metal atoms, and some important bond lengths.

Discussion

The crystal structure consists of dicrete molecules of $H_3Re_3(CO)_8(POP)_2$, which show approximate C_2 molecular symmetry, the diad axis passing through Re(1) and H(23) (see Fig. 1 and 2). The geometry of the non-hydrogen frame-work as revealed by the combined X-ray/neutron refinement does not differ significantly from that obtained in the original X-ray analysis [10], except in that the standard deviations in light-atom coordinates are approximately halved here. The metal atoms form an isoceles triangle, the two shorter edges of which are bridged by the POP ligands, all three edges being spanned by hydride ligands. If direct metal–metal interactions are ignored the metal atoms are approximately octahedrally coordinated by two *cis*-(CO) ligands, two *cis*-hydride ligands and two axial ligands (one (CO) and one phosphorus for Re(2) and Re(3) and two phosphorus ligands for Re(1)).

The molecular geometry is closely related to that observed for the unsubstituted congeneric cluster $H_3Mn_3(CO)_{12}$. Thus the ligand polyhedron, as defined by the phosphorus atoms and (CO) groups, approximates to a twinned cubo-octahedron, the same form as found in $Os_3(CO)_{12}$ and for the non-hydrogen ligands of $H_3Mn_3(CO)_{12}$ [1]. In a regular twinned cubo-octahedral ligand arrangement the six equatorial ligating atoms lie in a plane which coincides with the tri-metal plane for such tri-metal clusters. In the case of $H_3Mn_3(CO)_{12}$ the three μ-hydride ligands must also lie in this plane if the molecule is to show full D_{3h} symmetry. In $H_3Re_3(CO)_8(POP)_2$ the ligand polyhedron is somewhat distorted by the bridging POP ligands; this distortion is reflected in the r.m.s. deviation of the equatorial (CO) ligands from the tri-metal plane (0.208, c.f. 0.056 Å for $H_3Mn_3(CO)_{12}$). This distortion is a result of the P ··· P distance within POP ligands being considerably shorter than the Re–Re distances bridged (mean values are 2.87 and 3.267 Å respectively); thus the associated axial coordination sites are pulled together in order to minimise the strain on the extended P–O–P linkages. As a consequence the POP bridged Re–Re distances are shorter than that bridged by hydride alone (mean 3.267(5) vs. 3.312(4) Å). In addition the other 'octahedral' sites on the POP bridged rhenium atoms are affected so that the equatorial site bridging the same Re–Re vector as the POP ligand is forced out of the tri-metal plane, and away from the POP moiety. Thus H(12) and H(13) lie +0.26 and −0.38 Å out of plane respectively, whilst H(23) lies only +0.04 Å from the Re_3 plane. It therefore seems reasonable to assume that in the absence of such distortions (e.g. in $H_3M_3(CO)_{12}$ (M=Mn, Re)) the μ-H ligands would lie very close to the tri-metal plane and these molecules would therefore have molecular D_{3h} symmetry. This is in accord with spectroscopic observations [8] and the X-ray structure analysis of $H_3Mn_3(CO)_{12}$ [1]. A similar conclusion has been reached in the recently reported neutron diffraction study of the equatorially substituted isomer of $H_3Re_3(CO)_{11}PPh_3$ [2], where the out of plane distortions of the equatorial ligands are much smaller (largest deviation of μ-H 0.07 Å). The slightly puckered arrangement of equatorial ligands here present is also reflected in the fact that the H–Re–H and Re–H–Re angles sum to 712.7° (cf. 719.3° in $H_3Re_3(CO)_{11}$(eq-PPh_3) [2] and 720° for perfect planarity of the $(\mu\text{-H})_3Re_3$ unit).

All Re–Re distances show substantial lengthening as compared to that expected for a single Re–Re bond (3.041(1) Å in $Re_2(CO)_{10}$ [16]). This is a typical feature of μ-hydride bridged transition metal complexes [17], and consistent with the reduction

TABLE 1

ATOM COORDINATES ($\times 10^4$)

Atom	x/a	y/b	z/c
Re(1)	6859(1)	4666(1)	3150(1)
Re(2)	8650(1)	4571(1)	3100(1)
Re(3)	7564(1)	6029(1)	1929(1)
H(12)	7810(11)	4327(12)	3607(14)
H(13)	6801(13)	5376(15)	2214(17)
H(23)	8414(11)	5457(13)	2400(14)
P(1)	7096(5)	5626(5)	4360(6)
P(2)	8223(6)	3680(5)	1802(7)
P(3)	7629(6)	6869(5)	3256(7)
P(4)	6665(6)	3704(5)	1932(8)
O(1)	7541(7)	6494(6)	4202(8)
O(2)	7361(6)	3441(7)	1464(9)
C(14)	5790(7)	4913(7)	2856(9)
O(14)	5162(9)	5053(11)	2783(14)
C(15)	6724(7)	3863(8)	3997(9)
O(15)	6595(10)	3359(11)	4579(13)
C(23)	9023(7)	5267(7)	4208(10)
O(23)	9277(8)	5653(9)	4789(12)
C(24)	9039(7)	3642(7)	3845(9)
O(24)	9259(10)	3088(9)	4325(13)
C(25)	9592(7)	4679(8)	2750(9)
O(25)	10 165(9)	4731(11)	2501(13)
C(33)	7409(8)	5441(8)	711(10)
O(33)	7235(12)	5176(10)	−30(10)
C(34)	6747(10)	6700(9)	1343(9)
O(34)	6288(12)	7097(12)	907(14)
C(35)	8326(11)	6754(9)	1585(10)
O(35)	8723(14)	7187(12)	1344(16)
O(11)	7628(8)	5304(8)	5322(9)
C(111)	7880(8)	5839(8)	6085(13)
H(111)	8457(8)	6028(8)	6104(13)
H(112)	7520(8)	6377(8)	6017(13)
C(112)	7844(8)	5409(10)	6916(13)
H(113)	8048(8)	5807(10)	7502(13)
H(114)	8222(8)	4887(10)	6947(13)
H(115)	7282(8)	5193(10)	6934(13)
O(12)	6413(8)	6106(9)	4690(11)
C(121)	5939(12)	5719(10)	5071(14)
H(121)	5824(12)	5119(10)	4755(14)
H(122)	6176(12)	5647(10)	5802(14)
C(122)	5241(13)	6187(12)	4944(13)
H(123)	4885(13)	5998(12)	5407(13)
H(124)	4965(13)	6038(12)	4241(13)
H(125)	5337(13)	6844(12)	5005(13)
O(21)	8524(8)	2741(10)	1886(12)
C(211)	9258(16)	2552(15)	2090(14)
H(211)	9558(16)	2959(15)	1714(14)
H(212)	9475(16)	2630(16)	2824(14)
C(212)	9378(11)	1673(15)	1828(13)
H(213)	9977(11)	1603(15)	2121(13)
H(214)	9264(11)	1501(15)	1107(13)
H(215)	9059(11)	1279(15)	2194(13)

TABLE 1 (continued)

Atom	x/a	y/b	z/c
O(22)	8477(11)	4016(10)	895(12)
C(221)	8255(10)	3556(9)	42(16)
H(221)	8424(10)	2917(9)	137(16)
H(222)	7650(10)	3590(9)	−225(16)
C(222)	8675(9)	3985(10)	−574(14)
H(223)	8400(9)	3601(10)	−1143(14)
H(224)	9283(9)	3945(10)	−496(14)
H(225)	8496(9)	4618(10)	−709(14)
O(31)	8409(14)	7345(11)	3560(13)
C(311)	8807(18)	7622(15)	4343(17)
H(311)	8426(18)	7744(15)	4799(17)
H(312)	9200(18)	7141(15)	4636(17)
C(312)	9209(10)	8301(11)	4291(11)
H(313)	9110(10)	8766(11)	4774(11)
H(314)	9296(10)	8595(11)	3667(11)
H(315)	9707(10)	7947(11)	4597(11)
O(32)	7048(14)	7596(8)	3120(12)
O(321)	6716(17)	7987(15)	3600(18)
H(321)	6664(17)	7595(15)	4173(18)
H(322)	7070(17)	8510(15)	3854(18)
C(322)	6028(18)	8282(16)	3240(18)
H(323)	5579(18)	7844(16)	3255(18)
H(324)	5994(18)	8487(16)	2538(18)
H(325)	5968(18)	8806(16)	3670(18)
O(41)	6034(8)	4018(8)	1011(10)
C(411)	5846(10)	3546(10)	237(13)
H(411)	6361(10)	3341(10)	47(13)
H(412)	5528(10)	3018(10)	385(13)
C(412)	5419(13)	3965(13)	−488(18)
H(413)	5282(13)	3504(13)	−1026(18)
H(414)	5742(13)	4454(13)	−714(18)
H(415)	4902(13)	4214(13)	−344(18)
O(42)	6304(12)	2851(9)	2074(17)
C(421	6679(14)	2292(14)	2516(17)
H(421)	7260(14)	2390(14)	2465(17)
H(422)	6629(14)	2381(14)	3224(17)
C(422)	6526(12)	1472(16)	2336(15)
H(423)	6900(12)	1077(16)	2818(15)
H(424)	6546(12)	1298(16)	1637(15)
H(425)	5953(12)	1407(16)	2435(15)

of the metal–metal bond order on going from two-centre two-electron bonding to the three-centre two-electron bonding found here. As judged by the orientation of the equatorial carbonyl ligands (i.e. those *trans* to μ-H) all these 3c-2e systems are 'closed' [18]; the angles between pairs of *trans* CO ligands are 147, 143 and 151° for hydrides H(12), H(13) and H(23) as compared with Re–H–Re angles of 125(1), 128(1) and 136(1)° respectively. The large values of the H–Re–H angles (mean 108(3)°) compared with the ideal octahedral value of 90° are also indicative of 'closed' Re–H–Re interactions involving substantial Re–Re orbital overlap. The

TABLE 2

BOND LENGTHS (Å)[a]

Re–Re		P–O	
Re(1)–Re(2)	3.254(5)	P(1)–O(1)	1.662(15)
Re(1)–Re(3)	3.279(5)	P(3)–O(1)	1.566(17)
Re(2)–Re(3)	3.312(4)	P(2)–O(2)	1.576(16)
	⟨3.282(17)⟩	P(4)–O(2)	1.617(18)
			⟨1.605(25)⟩
Re–H			
Re(1)–H(12)	1.790(19)	P–O	(ethoxy)
Re(1)–H(13)	1.786(26)	P(1)–O(11)	1.624(15)
Re(2)–H(12)	1.874(22)	P(1)–O(12)	1.620(20)
Re(2)–H(23)	1.769(22)	P(2)–O(21)	1.612(19)
Re(3)–H(13)	1.857(26)	P(2)–O(22)	1.604(23)
Re(3)–H(23)	1.798(20)	P(3)–O(31)	1.584(26)
	⟨1.812(17)⟩	P(3)–O(32)	1.561(22)
		P(4)–O(41)	1.658(17)
Re–P		P(4)–O(42)	1.563(21)
Re(1)–P(1)	2.341(10)		⟨1.603(11)⟩
Re(1)–P(4)	2.353(11)		
Re(2)–P(2)	2.394(11)	O–C	(ethoxy)
Re(3)–P(3)	2.372(11)	O(11)–C(111)	1.420(21)
	⟨2.365(14)⟩	O(12)–C(121)	1.285(28)
		O(21)–C(211)	1.330(32)
Re–C		O(22)–C(221)	1.447(28)
Re(1)–C(14)	1.927(13)	O(31)–C(311)	1.306(31)
Re(1)–C(15)	1.860(14)	O(32)–C(321)	1.202(37)
Re(2)–C(23)	1.985(14)	O(41)–C(411)	1.358(24)
Re(2)–C(24)	1.909(12)	O(42)–C(421)	1.231(29)
Re(2)–C(25)	1.888(15)		⟨1.322(30)⟩
Re(3)–C(33)	2.004(15)		
Re(3)–C(34)	1.888(16)	C–C	
Re(3)–C(35)	1.957(19)	C(111)–C(112)	1.428(27)
	⟨1.927(18)⟩	C(121)–C(122)	1.448(31)
		C(211)–C(212)	1.505(34)
C–O	(carbonyl)	C(221)–C(222)	1.480(30)
C(14)–O(14)	1.139(21)	C(311)–C(312)	1.329(34)
C(15)–O(15)	1.244(24)	C(321)–C(322)	1.331(41)
C(23)–O(23)	1.083(21)	C(411)–C(412)	1.361(29)
C(24)–O(24)	1.160(20)	C(421)–C(422)	1.372(35)
C(25)–O(25)	1.175(24)		⟨1.407(24)⟩
C(33)–O(33)	1.157(21)		
C(34)–O(34)	1.134(24)		
C(35)–O(35)	1.116(31)		
	⟨1.151(17)⟩		

[a] The C–H distances in the ethoxy groups are contrained to 1.08 Å. The e.s.d.'s in ⟨⟩ are from $[\Sigma(d_i-\bar{d})^2.n(n-1)]^{1/2}$; e.s.d.'s in () are from positional errors and standard errors in cell parameters.

well defined nature of the rhenium coordination geometry in this compound suggests an alternative means of defining the 'openness' of the hydride bridges based on the deviation of the hydride from the planes defined by the axial ligands and the CO *trans* to the hydride (e.g. in the case of H(12) the planes defined by C(25), C(23),

(Continued on p. 406)

TABLE 3

BOND ANGLES (°) ^{a}

Re(1)–Re(2)–Re(3)	59.9(1)	H(12)–Re(2)–C(23)	87.0(7)	C(23)–Re(2)–P(2)	177.5(4)
Re(3)–Re(1)–Re(2)	60.9(1)	H(23)–Re(2)–C(23)	91.0(7)	C(33)–Re(3)–P(3)	171.8(4)
Re(2)–Re(3)–Re(1)	59.2(1)	H(23)–Re(3)–C(33)	92.7(8)		⟨174.7(28)⟩
	⟨60.0(5)⟩	H(13)–Re(3)–C(33)	88.1(4)		
			⟨89.7(13)⟩	P(1)–Re(1)–P(4)	178.1(4)
Re(1)–H(12)–Re(2)	125.2(11)				
Re(1)–H(13)–Re(3)	128.3(12)	H(12)–Re(1)–P(1)	85.0(7)	C(14)–Re(1)–Re(3)	102.9(4)
Re(2)–H(23)–Re(3)	136.4(13)	H(13)–Re(1)–P(1)	97.8(8)	C(15)–Re(1)–Re(2)	104.9(4)
	⟨130.0(33)⟩	H(12)–Re(1)–P(4)	93.4(7)	C(24)–Re(2)–Re(1)	105.5(4)
		H(13)–Re(1)–P(4)	81.9(8)	C(25)–Re(2)–Re(3)	104.9(4)
H(12)–Re(1)–Re(3)	87.8(7)	H(12)–Re(2)–P(2)	92.6(6)	C(34)–Re(3)–Re(1)	106.5(5)
H(13)–Re(3)–Re(2)	81.9(7)	H(23)–Re(2)–P(2)	91.4(7)	C(35)–Re(3)–Re(2)	101.2(5)
H(23)–Re(2)–Re(1)	81.9(7)	H(23)–Re(3)–P(3)	95.1(7)		⟨104.3(8)⟩
H(12)–Re(2)–Re(3)	85.4(6)	H(13)–Re(3)–P(3)	92.6(8)		
H(23)–Re(3)–Re(1)	80.7(7)		⟨91.2(19)⟩	O(14)–Re(1)–Re(2)	163.1(4)
H(13)–Re(1)–Re(2)	84.6(8)			O(15)–Re(1)–Re(3)	165.0(4)
	⟨83.7(11)⟩	C(14)–Re(1)–C(15)	91.6(5)	O(24)–Re(2)–Re(3)	165.4(4)
		C(24)–Re(2)–C(25)	89.5(6)	O(25)–Re(2)–Re(1)	163.6(4)
H(13)–Re(1)–C(15)	168.3(8)	C(34)–Re(3)–C(35)	93.3(7)	O(34)–Re(3)–Re(2)	165.4(5)
H(12)–Re(1)–C(14)	168.9(8)	C(23)–Re(2)–C(24)	87.3(5)	O(35)–Re(3)–Re(1)	157.7(4)
H(12)–Re(2)–C(25)	169.6(7)	C(23)–Re(2)–C(25)	90.5(5)		⟨163.4(12)⟩
H(23)–Re(2)–C(24)	172.6(8)	C(33)–Re(3)–C(34)	85.2(6)		
H(23)–Re(3)–C(34)	172.7(9)	C(33)–Re(3)–C(35)	91.2(6)	C(23)–Re(2)–Re(1)	96.7(4)
H(13)–Re(3)–C(35)	176.8(8)		⟨89.8(10)⟩	C(23)–Re(2)–Re(3)	94.8(3)
	⟨171.5(13)⟩			C(33)–Re(3)–Re(1)	100.4(4)
		C(14)–Re(1)–P(1)	92.5(4)	C(33)–Re(3)–Re(2)	94.8(4)
H(12)–Re(1)–C(15)	77.6(8)	C(15)–Re(1)–P(1)	88.7(5)		⟨96.7(13)⟩
H(13)–Re(1)–C(14)	78.5(8)	C(14)–Re(1)–P(4)	89.3(4)		
H(12)–Re(2)–C(24)	80.3(7)	C(24)–Re(2)–P(2)	90.2(4)	H(12)–Re(1)–H(13)	112.5(10)
H(23)–Re(2)–C(25)	83.3(8)	C(25)–Re(2)–P(2)	89.4(5)	H(12)–Re(2)–H(23)	106.9(9)
H(23)–Re(3)–C(35)	79.7(8)	C(34)–Re(3)–P(3)	86.8(8)	H(13)–Re(3)–H(23)	103.4(10)
H(13)–Re(3)–C(34)	83.5(9)	C(35)–Re(3)–P(3)	87.6(5)		⟨107.6(27)⟩
	⟨80.5(10)⟩		⟨89.6(7)⟩		

P(1)–Re(1)–Re(2)	91.7(3)	P(1)–O(1)–P(3)	126.3(8)	O(11)–C(111)–O(112)	109.7(15)
P(1)–Re(1)–Re(3)	86.9(2)	P(2)–O(2)–P(4)	127.1(9)	O(12)–(121)–O(122)	109.3(16)
P(4)–Re(1)–Re(2)	86.3(3)		⟨126.7(4)⟩	O(21)–C(211)–O(212)	110.6(19)
P(4)–Re(1)–Re(3)	92.0(3)			O(22)–C(221)–O(222)	102.2(14)
P(2)–Re(2)–Re(1)	84.0(3)	O(1)–P(1)–O(11)	100.5(7)	O(31)–C(311)–(312)	115.9(22)
P(2)–Re(2)–Re(3)	87.6(2)	O(1)–P(1)–O(12)	93.3(8)	O(32)–C(321)–O(322)	119.6(24)
P(3)–Re(3)–Re(1)	83.5(7)	O(1)–P(3)–O(31)	100.9(10)	O(41)–C(411)–O(412)	112.4(16)
P(3)–Re(3)–Re(2)	93.4(2)	O(1)–P(3)–O(32)	102.3(11)	O(42)–C(421)–O(422)	123.0(21)
	⟨88.2(13)⟩	O(2)–P(2)–O(21)	94.9(8)		⟨112.8(23)⟩
		O(2)–P(2)–O(22)	105.0(10)		
Re(1)–C(14)–O(14)	172.6(15)	O(2)–P(4)–O(41)	100.9(9)		
Re(1)–C(15)–O(15)	175.7(13)	O(2)–P(4)–O(42)	102.2(11)		
Re(2)–C(23)–O(23)	174.4(14)		⟨100.0(14)⟩		
Re(2)–C(24)–O(24)	177.2(15)				
Re(2)–C(25)–O(25)	177.4(13)	O(11)–P(1)–O(12)	103.6(9)		
Re(3)–C(33)–O(33)	170.4(14)	O(21)–P(2)–O(22)	103.5(11)		
Re(3)–C(34)–O(34)	172.5(17)	O(31)–P(3)–O(32)	101.6(11)		
Re(3)–C(35)–O(35)	172.4(17)	O(41)–P(4)–O(42)	98.6(10)		
	⟨174.5(9)⟩		⟨101.8(12)⟩		
Re(1)–P(1)–O(1)	118.0(6)	P(1)–O(11)–C(111)	121.9(10)		
Re(1)–P(4)–O(2)	120.1(6)	P(1)–O(12)–C(121)	121.3(13)		
Re(2)–P(2)–O(2)	122.0(8)	P(2)–O(12)–C(211)	122.6(15)		
Re(3)–P(3)–O(1)	121.4(6)	P(2)–O(22)–C(221)	118.6(14)		
	⟨120.4(9)⟩	P(3)–O(31)–C(311)	135.0(23)		
		P(3)–O(32)–C(321)	136.7(18)		
Re(1)–P(1)–O(11)	115.7(6)	P(4)–O(41)–C(411)	121.5(12)		
Re(1)–P(1)–O(12)	121.7(7)	P(4)–O(42)–C(421)	121.7(19)		
Re(1)–P(4)–O(41)	112.9(7)		⟨124.9(24)⟩		
Re(1)–P(4)–O(42)	118.7(11)				
Re(2)–P(2)–O(21)	117.5(8)				
Re(2)–P(2)–O(22)	111.4(7)				
Re(3)–P(3)–O(31)	113.4(10)				
Re(3)–P(3)–O(32)	114.5(8)				
	⟨115.7(12)⟩				

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[a] Hydrogen atoms of the ethoxy groups are contrained to tetrahedral positions.

P(2) and Re(2), and C(14), P(1), P(4) and Re(1)). Defining a positive deviation from these coordination planes as implying the hydride to lie on the opposite side of the plane from the rhenium atom to which it bridges, it is clear that for the bridge to be 'closed' both deviations associated with a hydride must be positive. This is indeed the case for the three hydrides here, the deviations being +0.35 and +0.27 Å for H(12), +0.35 and +0.10 Å for H(13), and +0.22 and +0.18 Å for H(23).

The improved precision of the present study relative to the X-ray only analysis [10] allows discussion of structural *trans* influence as indicated by the Re-ligating atom distances. In particular the Re–C bond lengths show the expected trends in that those *trans* to hydride ligands (i.e. the six equatorial (CO) ligands) show shorter Re–C distances (mean 1.905(14) Å) than the two axial (CO) ligands which are *trans* to the POP ligands (mean Re–C 1.995(15) Å). Conversely those Re–P bonds *trans* to (CO) are longer than those mutually *trans* (mean 2.383(11) vs. 2.348(7) Å); these effects are attributable to competition between *trans* ligands for metal π-donor electron density and show the carbonyls to be the strongest π-acid ligands present, followed by the POP ligands. The Re–H bond lengths are broadly similar to those determined in the complete room temperature neutron diffraction analysis of $H_3Re_3(CO)_{11}(PPh_3)$ [2], the mean value here being 1.812(17) Å (c.f. 1.822(8) Å) [2]. Other molecular dimensions from the present study are unremarkable and do not differ significantly from those determined in the X-ray structure analysis [10].

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