X-Ray and Neutron Diffraction Studies on $[Ru_4(CO)_8(\mu\text{-}H)_4\{P(OCH_3)_3\}_4]$ † at 293 and 20 K: Characterisation of the Vibrational Behaviour of Two-co-ordinate Hydrogen Atoms

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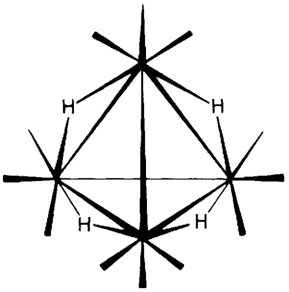
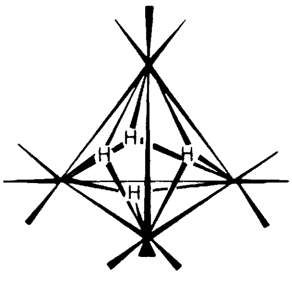
X-Ray and neutron diffraction studies on the complex $[Ru_4(CO)_8H_4\{P(OCH_3)_3\}_4]$ have been carried out at 293 and 20 K respectively. At room temperature the structure is monoclinic, space group $P2_1/c$ with cell parameters a = 15.700(4), b = 11.775(3), c = 21.331(5) Å, β = 100.49(4)°, and Z = 4. At 20 K the structure is triclinic, space group $P\bar{1}$ with a = 15.371(3), b = 11.508(2), c = 21.079(3) Å, α = 90.07(1), β = 100.09(1), γ = 92.09(2)°, and Z = 4. The *X*-ray determination shows the molecular structure to consist of distorted tetrahedral Ru_4 units substituted so that each ruthenium atom is bound to two terminal carbonyl ligands, one trimethyl phosphite ligand, and two hydride ligands. Despite positional disorder affecting four methoxy groups, the μ-hydride ligands spanning four edges of the Ru_4 tetrahedron were located and refined. At low temperature the structure is ordered with two molecules per asymmetric unit, and the neutron analysis provides precise characterization of the molecular structure. All the Ru–H–Ru bridges are symmetrical with mean Ru–H = 1.773(2) Å and show closed three-centre two-electron bonding. Final agreement indices are $R(F)$ = 0.043, $R'(F)$ = 0.038 for 6 647 unique *X*-ray data, and $R(F)$ = 0.048, $R'(F)$ = 0.038 for 8 601 unique neutron data. Analysis of the vibrational behaviour of the hydride hydrogen atoms as determined in the neutron analysis indicates that this motion is consistent with these hydrogens residing in a single-minimum potential well provided by symmetric three-centre, two-electron Ru–H–Ru interactions.

Metal cluster complexes of the type $[M_4(CO)_{12}H_4]$ formed by rhenium, ruthenium, and osmium have been the subject of much interest in recent years.[1-4] In particular, the ruthenium and osmium members of this group are known to undergo carbonyl substitution reactions with a variety of ligands, *e.g.*, PR_3,[5] $P(OR)_3$,[6] and $Ph_2PCH_2CH_2PPh_2$.[7,8] In addition, $[Os_4(CO)_{12}H_4]$ reacts with substituted olefins to give tetranuclear complexes containing bridging vinyl moieties.[9] The deprotonated complex anion $[Ru_4(CO)_{12}H_3]^-$ has been identified as the major carbonyl-containing species present in solutions which catalyze the water-gas shift reaction,[10] and at least two of its isomers have been shown to exist in solution and in the solid state.[11] The products of the reaction of trimethyl phosphite with $[Ru_4(CO)_{12}H_4]$, *i.e.* $[Ru_4(CO)_{12-n}H_4\{P(OCH_3)_3\}_n]$ (n = 1—4), have been found to be dynamic on the n.m.r. time-scale while retaining a ground state conformation closely related to that of the parent carbonyl complex.[6]

Structural studies on these complexes have concentrated on the distribution of hydride and carbonyl ligands around the quasi-tetrahedral M_4 core. Two major structural forms have been identified for the neutral dodecacarbonyltetrahydrides [(I) and (II) below]. Form (I) is characterized by D_{2d} molecular symmetry, staggering of the carbonyl ligands relative to the M–M vectors, and edge-bridging of the hydride ligands. This is the configuration adopted by the ruthenium [2] and osmium [3] analogues and the majority of their simply substituted derivatives. In contrast, form (II) has T_d molecular symmetry with carbonyls eclipsed relative to the M–M vectors and three-co-ordinate, face-bridging hydride ligands. This geometry is found for $[Re_4(CO)_{12}H_4]$.[1] This variety of structural forms has been the subject of a theoretical analysis [4] which rationalized the preference of $[Re_4(CO)_{12}H_4]$ for form (II) on the basis of valence electron count {56 e^- *versus* 60 e^- for $[Os_4(CO)_{12}H_4]$}. The analysis also suggested a low-energy mechanism for hydride rearrangement in (I) *via* a face-bridging intermediate.



(I)



(II)

The broad structural features of this class of complexes have been established by *X*-ray diffraction studies on the dodecacarbonyltetrahydrides and a number of their substituted derivatives. The problems associated with the location of hydrogen atoms from *X*-ray diffraction data alone are well known. In particular, for heavy-metal cluster complexes, the hydride parameters determined from these data are subject to systematic as well as large random errors. In order to obtain precise structural parameters for a complex representative of form (I), we have undertaken structure analyses of $[Ru_4(CO)_8H_4\{P(OCH_3)_3\}_4]$ at 20 K by neutron diffraction methods and, as a preliminary, at room temperature by *X*-ray methods. The low-temperature neutron data permit character-

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† 1,1,2,2,3,3,4,4-Octacarbonyl-1,2;1,4;2,3;3,4-tetra-μ-hydrido-1,2,3,4-tetrakis(trimethyl phosphite)-*tetrahedro*-tetraruthenium.

Supplementary data available (No. SUP 23477, 91 pp.): structure factors and thermal parameters for both *X*-ray and neutron diffraction. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Standard deviations in quoted parameters given in parentheses in the text are externally estimated as in Table 1 except where individual dimensions are reported.

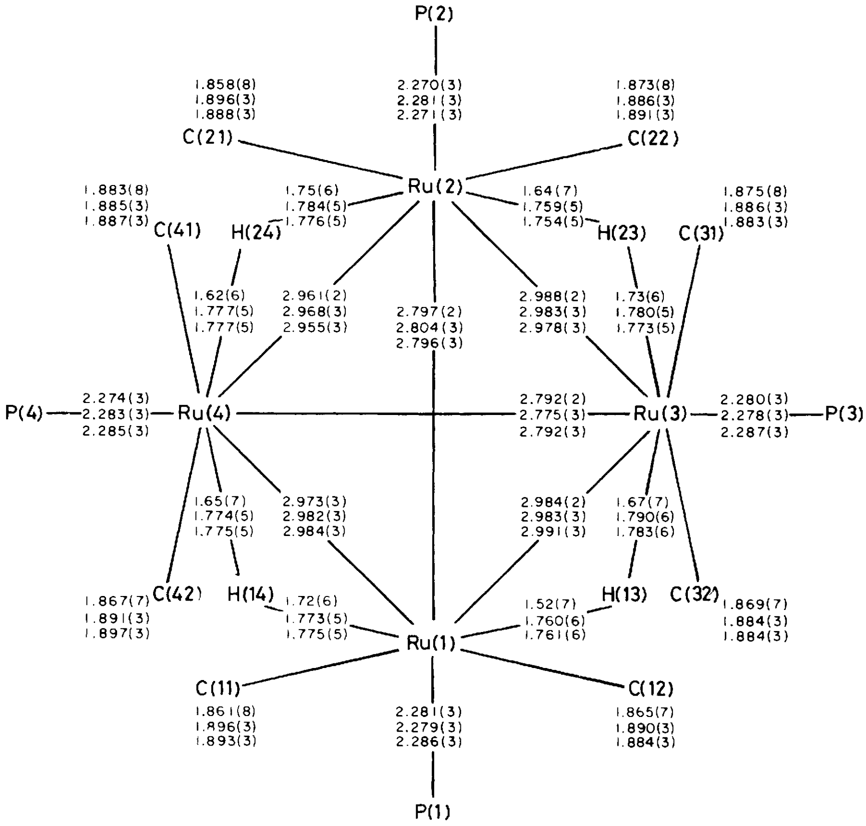

Figure 1. The core of $[Ru_4(CO)_8H_4\{P(OCH_3)_3\}_4]$ shown schematically with key to atom labelling. Bond distances (Å) listed in columns are *X*-ray values (upper) and neutron values (molecules A and B)

ization both of the geometry and of the vibrational motion of the molecules, in particular of the internal vibronic modes involving the hydride hydrogen atoms. Such characterization provides the data necessary to test the accepted picture of the M-H-M three-centre, two-electron bond as an inherently symmetrical interaction with a single-minimum potential well in which the bridging hydrogen moves. A report of the synthesis and spectroscopic properties of this compound has appeared.[6] During the course of the work reported here, the neutron diffraction study on the related cluster $[Os_4(CO)_{11}H_4\{P(OCH_3)_3\}]$ has shown its core to have configuration (I) above.[12]

Results

A summary of the various classes of chemically related bond lengths and interbond angles is given in Table 1; individual values are listed in Table 2 for bond lengths and in Table 3 for bond angles. The atomic co-ordinates obtained by *X*-ray and neutron diffraction methods are given in Tables 5 and 6 respectively. Selected thermal parameters are given in Table 7. Figures 1 and 2 show the labelling scheme adopted for designating chemically equivalent atoms in $[Ru_4(CO)_8H_4\{P(OCH_3)_3\}_4]$. The non-equivalent molecules in the triclinic cell are distinguished by letters A and B suffixed to atom indices. The hydride atoms are given double indices that identify the ruthenium atoms to which they are bonded. For other ligand atoms, the first digit also specifies the metal atom to which the group is attached; the following digits if any distinguish between atoms of the same type in a particular ligand. In Table 5 one set of the disordered oxygen atoms within a phosphite group of the monoclinic structure are suffixed A to distinguish the alternative conformations, of which A is shown in Figure 2.*

The three different observations on the molecule show major conformational changes only in the methoxy groups as a result of differing crystal environments. The Ru_4 cluster and its immediate co-ordination sphere are characterized by non-crystallographic D_{2d} symmetry. Each ruthenium atom is approximately octahedrally co-ordinated by one trimethyl phosphite, two carbonyl, one ruthenium atom, and two hydride ligands which bridge to one further ruthenium atom each. The spatial arrangement of these groups in the cluster is clearly illustrated in Figure 3 for molecule A. This geometry is related to that of the parent $[Ru_4(CO)_{12}H_4]$ by replacement of the four carbonyls *cisoid* to the μ-hydride ligands by phosphite groups. With the ordering in phosphite groups 2 and 4 (numbered according to their P atoms) between 293 and 20 K, the molecule appears to achieve a single preferred packing arrangement in the crystal, since the order-disorder transformation between the monoclinic and triclinic lattices is observed to be reversible. It is noted that one of the alternative conformations found for phosphite group 4 at 293 K is not represented in either molecule at 20 K. A similar case of temperature-dependent lattice transformation probably also occurs in crystals of the related $[Ru_4(CO)_{11}H_4\{P(OCH_3)_3\}]$ cluster, which were found to undergo a destructive transformation that prevented low-temperature neutron diffraction analysis.

The dimensions in the $Ru_4C_8H_4P_4$ core determined from the *X*-ray and neutron analyses are compared in Figure 1.

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* The thermal ellipsoids were drawn using ORTEP (C. K. Johnson, Report ORNL-5138, ORTEP-II, Oak Ridge National Laboratory, Tennessee, 1972).

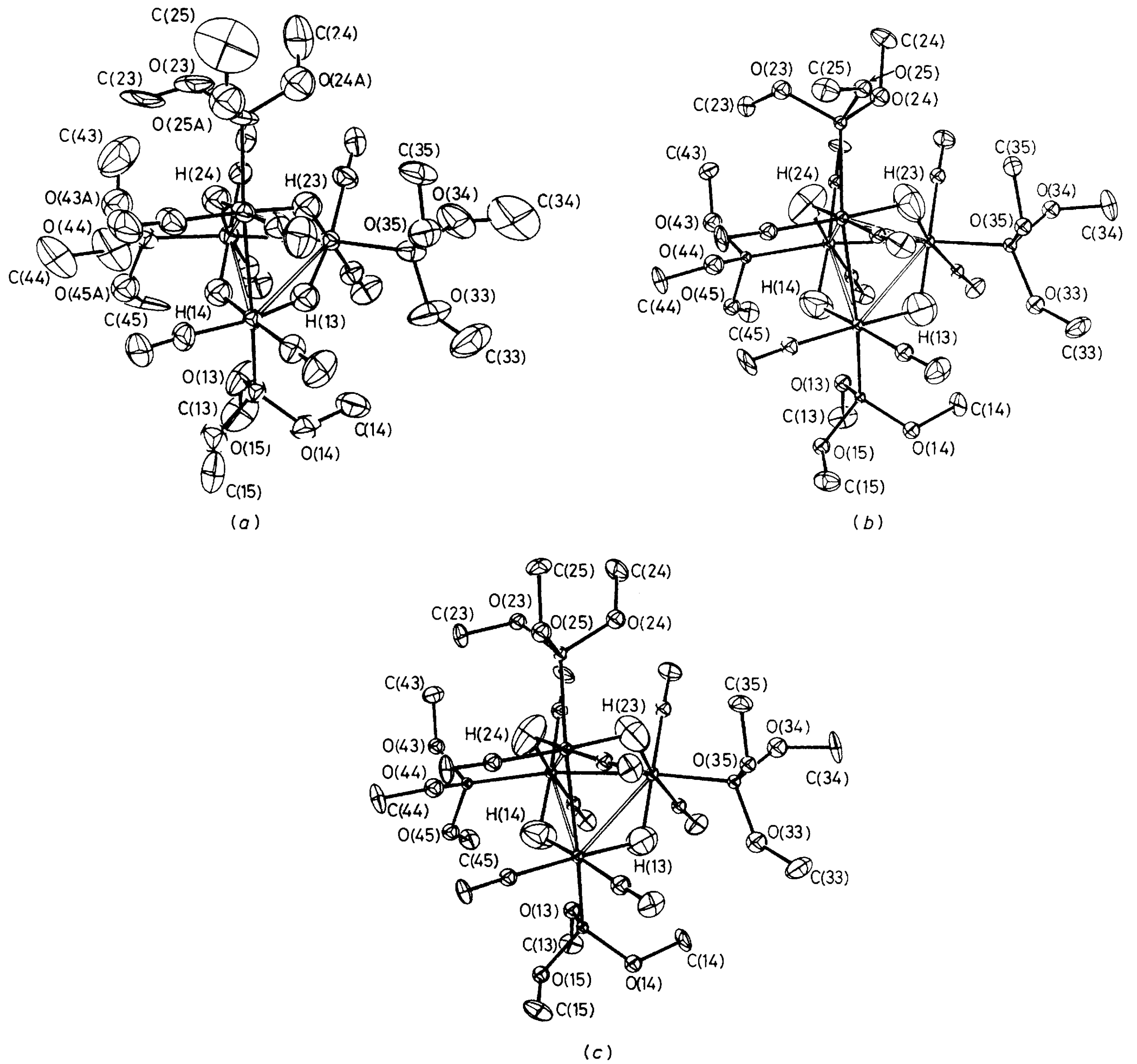

Figure 2. Perspective view of $[Ru_4(CO)_8H_4\{P(OCH_3)_3\}_4]$ with labelling of hydride and peripheral methoxy carbon and oxygen atoms (*cf.* Figure 1). Methoxy hydrogen atoms are omitted. One conformation is shown in (*a*) for disordered $P(OCH_3)_3$ groups 2 and 4. The thermal ellipsoids are drawn to enclose 40% probability in (*a*) from the 293 K *X*-ray analysis, and 98% in (*b*), molecule A, and (*c*), molecule B, from the 20 K neutron analysis

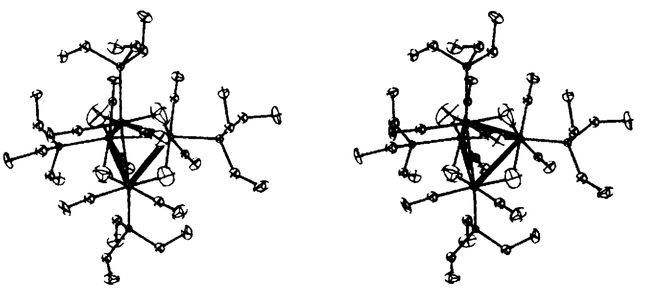

Figure 3. Stereoscopic diagram of $[Ru_4(CO)_8H_4\{P(OCH_3)_3\}_4]$, molecule A, in the orientation shown in Figure 2(*b*). The vibration ellipsoids enclose 98% probability

Except where discussed below, the *X*-ray and neutron derived molecular parameters are in good agreement. The latter are uniformly more precise and will be used in further descriptions of the structure. A half-normal probability plot [14] comparing bond lengths in molecules A and B has a slope of 1.3 which indicates an overall satisfactory estimate of the assigned errors in these parameters, given the somewhat different crystal environments of the two molecules. Subject to the same reservation, the averaging of chemically equivalent bond lengths (Table 1) yields 'external' estimates of error in the internuclear distances.

The Ru_4 core of the molecule is distinctly distorted from T_d to D_{2d} tetrahedral geometry. The Ru–Ru distances fall into two groups of four long, hydride-bridged vectors with mean lengths of 2.978(4) Å and two shorter, unbridged Ru–Ru bonds with mean lengths of 2.792(6) Å. At individual ruthenium atoms, there are large distortions from idealized octa-

Table 1. A summary of bond lengths (Å) and angles (°) for $[Ru_4(CO)_8H_4\{P(OCH_3)_3\}_4]$

	Number		Average [a]		Range [b]	
(*a*) Distances	Neutron	*X*-ray	Neutron	*X*-ray	Neutron	*X*-ray
Ru-Ru (unbridged)	4	2	2.792(6)	2.795(3)	2.775(3)—2.792(3)	2.792(2)—2.797(2)
Ru-Ru (bridged)	8	4	2.978(4)	2.977(6)	2.955(3)—2.991(3)	2.961(2)—2.988(2)
Ru-P	8	4	2.281(2)	2.276(3)	2.271(3)—2.286(3)	2.270(3)—2.281(3)
Ru-H	16	8	1.773(2)	1.68(3)	1.754(5)—1.790(6)	1.52(7)—1.75(6)
Ru-C(O)	16	8	1.889(1)	1.869(3)	1.883(3)—1.897(3)	1.858(8)—1.883(8)
C-O (carbonyl)	16	8	1.151(1)	1.144(4)	1.146(3)—1.158(4)	1.130(9)—1.157(10)
P-O	24	8 [c]	1.604(2)	1.600(8)	1.586(4)—1.620(4)	1.549(6)—1.608(5)
O-C (methoxy)	24	8 [c]	1.440(1)	1.408(7)	1.430(3)—1.450(3)	1.38(1)—1.440(8)
C-H	69 [d]		1.083(1)		1.042(8)—1.111(5)	
(*b*) Angles						
Ru-H-Ru	8	4	114.2(3)	128(4)	112.6(3)—115.2(3)	123(4)—139(4)
H-Ru-H	8	4	101.8(13)	94(2)	98.9(2)—107.5(2)	91(3)—98(3)
H-Ru-P (*cis*)	16	8	82.7(10)	88(2)	74.0(2)—88.5(2)	82(2)—95(2)
H-Ru-C (*cis*)	16	8	82.8(5)	87(2)	79.0(2)—85.5(2)	81(2)—92(2)
C-Ru-P	16	8	96.1(9)	96.1(9)	89.9(1)—100.8(1)	92.8(2)—99.5(2)
C-Ru-C	8	4	92.7(6)	91.6(11)	91.3(1)—95.3(1)	89.2(3)—93.3(3)
P-Ru-Ru (*trans*)	8	4	166.4(8)	166.7(8)	163.8(1)—169.6(1)	164.7(1)—167.9(1)
Ru-C-O	16	8	177.7(3)	177.8(4)	176.1(2)—179.4(2)	176.6(6)—178.9(6)
P-O-C (methoxy)	24	8 [c]	121.6(5)	126(2)	117.9(2)—126.9(2)	120.2(5)—132.4(6)

[a] The estimated standard deviations (e.s.d.s) in parentheses are from $[\sum_{i=1}^{n} (d_i - \bar{d})^2/n(n-1)]$. [b] The e.s.d.s in parentheses are from least-squares positional errors and standard errors in cell parameters. [c] Four distances and angles involving disordered oxygen sites are excluded; these bond lengths were constrained during refinement (see text). [d] Three distances involving C(24A) are excluded; these librationally shortened distances are 0.984, 0.981, and 1.000(10) Å.

hedral geometry, particularly in the H-Ru-H angles, as seen in Table 3. All eight carbonyl ligands are terminal and approximately linear with the mean Ru-C-O angle being 177.7(3)°. The Ru-H-Ru bridges are markedly bent, with a mean angle of 114.2(3)°, and are very nearly symmetric, although the Ru-H distances in the extremes 1.754(5) and 1.790(6) Å differ significantly. The most marked asymmetry in each molecule (Figure 1) occurs at H(13) and H(23), both of which are involved in the shortest $H(CH_3) \cdots H$(hydride) contacts, these being 2.233 Å for H(141A) $\cdots$ H(13A), 2.215 Å for H(142B) $\cdots$ H(13B), 2.207 Å for H(351A) $\cdots$ H(23A), and 2.233 Å for H(351B) $\cdots$ H(23B).

Discussion

The molecular structure of $[Ru_4(CO)_8H_4\{P(OCH_3)_3\}_4]$ has the characteristic core geometry of the $[M_4(CO)_{12}H_4]$ complexes previously described as form (I). The cluster has 60 valence electrons implying a total of six metal-metal bonds according to the effective atomic number rule. In this crude description the bonds fall into two classes; two-centre, two-electron (Ru-Ru) bonds and longer [by 0.186(6) Å] three-centre, two-electron (Ru-H-Ru) interactions. These features are very similar to those observed for a number of related complexes studied by *X*-ray diffraction, *i.e.* $[Ru_4(CO)_{12}H_4]$,[2] $[Ru_4(CO)_{11}H_4\{P(OCH_3)_3\}]$,[1] $[Ru_4(CO)_{10}H_4(PPh_3)_2]$,[2,5] $[Os_4(CO)_{12}H_4]$,[3] and $[Os_4(CO)_{11}(CNCH_3)H_4]$.[15] Only for the last of these was location and refinement of the hydride ligands possible, although in the others their edge-bridging sites were clearly indicated by the geometry of the non-hydrogen framework. Three other cluster complexes in this area have been the subject of neutron diffraction analyses, $[Ru_3(CO)_9(CCBu^t)H]$,[16] $[(PPh_3NPPh_3)]^+[FeRu_3(CO)_{13}H]^-$,[17] and $[Os_4(CO)_{11}H_4\{P(OCH_3)_3\}]$.[12] The last shows the greatest resemblance to the present complex, both in core geometry [mean Os-H 1.787(3), Os-Os (H-bridged) 2.966(4), Os-Os (unbridged) 2.814(4) Å, and Os-H-Os 112.2(4)° at 298 K] and in the ligand distribution, the phosphite ligand being *cisoid* to two hydride ligands. The mean Ru-H distance observed in $[Ru_4(CO)_8H_4\{P(OCH_3)_3\}_4]$ is rather shorter than those in $[FeRu_3(CO)_{13}H]^-$ and $[Ru_3(CO)_9(CCBu^t)H]$ [1.821(3) Å at 15 K and 1.792(5) Å at 298 K respectively]. This difference is attributable to variations in ruthenium co-ordination numbers and geometries and in the charges on these complexes. The dominant feature of the ruthenium co-ordination in $[Ru_4(CO)_8H_4\{P(OCH_3)_3\}_4]$ is the distorted octahedral configuration of ligating atoms. These distortions reflect the balance between electronic and steric factors, the former being primarily metal-ligand and the latter ligand-ligand interactions. In particular the distribution of the $P(OCH_3)_3$ groups is such as to minimize non-bonding interactions of the types Ru $\cdots$ P and P $\cdots$ P. This is consistent with the findings of a spectroscopic study of this complex,[6] namely that only one isomer is formed and that this isomer has one phosphite ligand attached to each ruthenium *cisoid* to the two hydrides bound to that atom. The P-Ru-C angles are, on average, larger than the C-Ru-C [and C-Ru-H (*cis*) and P-Ru-H] angles (see Table 1) reflecting the steric demands of the $P(OCH_3)_3$ moiety.

The geometry of the phosphite groups is in good agreement with that observed in comparable neutron studies.[18] The mean Ru-P bond length is ~0.08 Å shorter than that in the related $[Ru_4(CO)_{10}H_4(PPh_3)_2]$,[2,5] as might be expected in view of the strong π-acceptor function of the trimethyl phosphite ligand relative to aryl- and alkyl-phosphines.

The mean Ru-C distance as derived from *X*-ray and neutron data [1.859(3) *versus* 1.889(1) Å] shows a considerable shift, as does the mean $O-CH_3$ bond length [1.408(7) Å, *X*-ray constrained value, *versus* 1.440(1) Å]. Such a general trend is attributable both to librational shortening of bond lengths derived from room-temperature data, and to systematic differences from *X*-ray atomic positions determined as centroids of electron density.

The large number of independent, precise observations of

Table 2. Bond distances (Å) at 20 K (neutron values for molecules A and B) and at 293 K (*X*-ray values) [a]

	Neutron		
	A	B	*X*-ray
(*a*) Ru–Ru (unbridged)			
Ru(1)–Ru(2)	2.804(3)	2.796(3)	2.797(2)
Ru(3)–Ru(4)	2.775(3)	2.792(3)	2.792(2)
Average	⟨2.792(6)⟩		⟨2.795(3)⟩
(*b*) Ru–Ru (bridged)			
Ru(1)–Ru(3)	2.983(3)	2.991(3)	2.984(2)
Ru(1)–Ru(4)	2.982(3)	2.984(3)	2.973(3)
Ru(2)–Ru(3)	2.983(3)	2.978(3)	2.988(2)
Ru(2)–Ru(4)	2.968(3)	2.955(3)	2.961(2)
Average	⟨2.978(4)⟩		⟨2.977(6)⟩
(*c*) Ru–H			
Ru(1)–H(13)	1.760(6)	1.761(6)	1.52(7)
Ru(3)–H(13)	1.790(6)	1.783(6)	1.67(7)
Ru(1)–H(14)	1.773(5)	1.775(5)	1.72(6)
Ru(4)–H(14)	1.774(5)	1.775(5)	1.65(7)
Ru(2)–H(23)	1.759(5)	1.754(5)	1.64(7)
Ru(3)–H(23)	1.780(5)	1.773(5)	1.73(6)
Ru(2)–H(24)	1.784(5)	1.776(5)	1.75(6)
Ru(4)–H(24)	1.777(5)	1.777(5)	1.62(6)
Average	⟨1.773(2)⟩		⟨1.68(3)⟩
(*d*) Ru–P			
Ru(1)–P(1)	2.279(3)	2.286(3)	2.281(3)
Ru(2)–P(2)	2.281(3)	2.271(3)	2.270(3)
Ru(3)–P(3)	2.278(3)	2.287(3)	2.280(3)
Ru(4)–P(4)	2.283(3)	2.285(3)	2.274(3)
Average	⟨2.281(2)⟩		⟨2.276(3)⟩
(*e*) Ru–C			
Ru(1)–C(11)	1.896(3)	1.893(3)	1.861(8)
Ru(1)–C(12)	1.890(3)	1.884(3)	1.865(7)
Ru(2)–C(21)	1.896(3)	1.888(3)	1.858(8)
Ru(2)–C(22)	1.886(3)	1.891(3)	1.873(8)
Ru(3)–C(31)	1.886(3)	1.883(3)	1.875(8)
Ru(3)–C(32)	1.884(3)	1.884(3)	1.869(7)
Ru(4)–C(41)	1.885(3)	1.887(3)	1.883(8)
Ru(4)–C(42)	1.891(3)	1.897(3)	1.867(7)
Average	⟨1.889(1)⟩		⟨1.869(3)⟩
(*f*) C–H (methyl)			
Average	⟨1.084(6)⟩	⟨1.082(6)⟩	
Average	⟨1.083(1)⟩		
(*g*) C–O (carbonyl)			
C(11)–O(11)	1.150(4)	1.150(4)	1.16(1)
C(12)–O(12)	1.150(3)	1.157(3)	1.141(8)
C(21)–O(21)	1.149(3)	1.158(4)	1.152(9)
C(22)–O(22)	1.149(3)	1.146(3)	1.157(9)
C(31)–O(31)	1.148(4)	1.153(4)	1.130(9)
C(32)–O(32)	1.153(3)	1.151(3)	1.138(8)
C(41)–O(41)	1.153(4)	1.148(3)	1.132(9)
C(42)–O(42)	1.152(3)	1.151(3)	1.149(8)
Average	⟨1.151(1)⟩		⟨1.144(4)⟩
(*h*) P–O			
P(1)–O(13)	1.595(4)	1.596(3)	1.574(6)
P(1)–O(14)	1.610(4)	1.611(4)	1.601(5)
P(1)–O(15)	1.613(4)	1.608(4)	1.508(5)
P(2)–O(23)	1.610(4)	1.620(4)	1.549(6)
P(2)–O(24)	1.594(4)	1.595(4)	1.62(3) [b]
P(2)–O(25)	1.610(3)	1.610(3)	1.64(4) [b]
P(3)–O(33)	1.594(4)	1.586(4)	1.588(5)
P(3)–O(34)	1.606(4)	1.616(4)	1.602(7)
P(3)–O(35)	1.614(3)	1.606(3)	1.596(5)
P(4)–O(43)	1.614(4)	1.616(4)	1.60(1) [b]
P(4)–O(44)	1.591(4)	1.593(4)	1.570(6)
P(4)–O(45)	1.603(3)	1.594(3)	1.60(2) [b]
Average	⟨1.604(2)⟩		⟨1.600(8)⟩
(*i*) O–C (methoxy)			
O(13)–C(13)	1.442(3)	1.430(3)	1.44(1)
O(14)–C(14)	1.443(4)	1.442(4)	1.42(1)
O(15)–C(15)	1.436(3)	1.439(3)	1.43(1)
O(23)–C(23)	1.432(3)	1.435(3)	1.38(1)
O(24)–C(24)	1.450(3)	1.442(3)	1.43(3) [b]
O(25)–C(25)	1.431(3)	1.442(3)	1.38(4) [b]
O(33)–C(33)	1.443(3)	1.442(3)	1.405(9)
O(34)–C(34)	1.441(3)	1.442(4)	1.42(1)
O(35)–C(35)	1.443(3)	1.449(3)	1.440(8)
O(43)–C(43)	1.432(4)	1.436(3)	1.38(2)
O(35)–C(35)	1.443(3)	1.449(3)	1.440(8)
O(43)–C(43)	1.432(4)	1.436(3)	1.38(2) [b]
O(44)–C(44)	1.438(3)	1.442(4)	1.41(1) [b]
O(45)–C(45)	1.440(3)	1.438(3)	1.41(2) [b]
Average	⟨1.440(1)⟩		⟨1.408(7)⟩

[a] The e.s.d.s in parentheses are evaluated as in Table 1. [b] Average over two disordered sites.

Ru–H–Ru linkages available from the low-temperature neutron analysis provide the data required for detailed characterization of this class of bond. As is well known, the M–H–M bridge is typically bent with the angle at the hydride position varying through a wide range (85—155°).[19] The angles in the present complex fall in the middle of this range and represent archetypal M–H–M bonds. In contrast to the deformability of the angle at the hydrogen, metal–(μ-hydride) bond lengths vary relatively little and the bridging system is usually close to symmetrical even when the metals bridged are in different electronic environments [*e.g.* Os–(μ-H) range from 1.754 to 1.883 Å].[19] Qualitative inspection of the vibrational ellipsoids of the hydride hydrogen atoms (Figures 2 and 3) indicates that the principal motion of the nuclei is perpendicular to the Ru–H–Ru planes. The motion of the hydrogen atoms in M–H–M systems may be divided into three categories, two in-plane stretching modes (asymmetric and symmetric) and an out-of-plane deformation (see below, ν_{asym}, ν_{sym}, and ν_{def}). Infrared and Raman studies [20] of [Ru$_4$(CO)$_{12}$H$_4$], [Ru$_4$(CO)$_{12}$D$_2$H$_2$], and [Ru$_4$(CO)$_{12}$D$_4$] have shown the stretching vibrations to behave as essentially independent oscillators with typical isotope effects (ν_H/ν_D = 1.4). At the very low temperature of the neutron analysis, the motion of the hydride hydrogen atoms is almost exclusively due to zero-point vibrational effects. The contribution due to rigid body motion of the molecules is very small as indicated by the ruthenium atomic thermal parameters (mean square amplitude ~0.0028 Å^2). The r.m.s. amplitudes of vibration of the μ-H atoms are 0.188(4), 0.119(4), and 0.102(3) Å along the

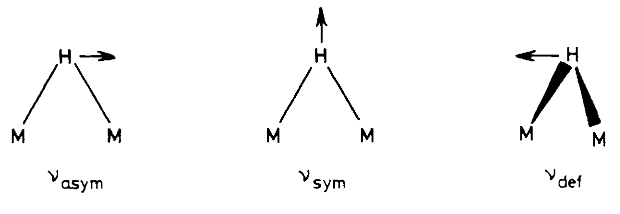

Table 3. Bond angles (°) at 20 K (neutron values for molecules A and B) and at 293 K (*X*-ray values) [a]

	Neutron		
	A	B	*X*-ray
(*a*) Ru–Ru–Ru			
Ru(2)–Ru(1)–Ru(3)	62.0(1)	61.8(1)	62.1(1)
Ru(2)–Ru(1)–Ru(4)	61.6(1)	61.4(1)	61.7(1)
Ru(3)–Ru(1)–Ru(4)	55.5(1)	55.7(1)	55.9(1)
Ru(1)–Ru(2)–Ru(3)	62.0(1)	62.3(1)	62.0(1)
Ru(1)–Ru(2)–Ru(4)	62.1(1)	62.4(1)	62.1(1)
Ru(3)–Ru(2)–Ru(4)	55.6(1)	56.1(1)	56.0(1)
Ru(1)–Ru(3)–Ru(2)	56.1(1)	55.9(1)	55.9(1)
Ru(1)–Ru(3)–Ru(4)	62.3(1)	62.0(1)	61.8(1)
Ru(2)–Ru(3)–Ru(4)	61.9(1)	61.5(1)	61.5(1)
Ru(1)–Ru(4)–Ru(2)	56.2(1)	56.2(1)	56.3(1)
Ru(1)–Ru(4)–Ru(3)	62.3(1)	62.3(1)	62.3(1)
Ru(2)–Ru(4)–Ru(3)	62.5(1)	62.3(1)	62.5(1)
(*b*) Ru–Ru–H			
Ru(2)–Ru(1)–H(13)	92.8(2)	91.2(2)	81(2)
Ru(2)–Ru(1)–H(14)	85.1(2)	86.5(2)	82(2)
Ru(3)–Ru(1)–H(13)	33.1(2)	32.7(2)	22(2)
Ru(3)–Ru(1)–H(14)	85.8(2)	85.1(2)	81(2)
Ru(4)–Ru(1)–H(13)	79.5(2)	81.0(2)	73(3)
Ru(4)–Ru(1)–H(14)	32.8(2)	32.8(2)	28(2)
Ru(1)–Ru(2)–H(23)	89.5(2)	90.7(2)	85(2)
Ru(1)–Ru(2)–H(24)	91.2(2)	90.3(2)	87(2)
Ru(3)–Ru(2)–H(23)	32.8(2)	32.6(2)	28(2)
Ru(3)–Ru(2)–H(24)	82.6(2)	84.7(2)	77(2)
Ru(4)–Ru(2)–H(23)	83.0(2)	82.1(2)	80(2)
Ru(4)–Ru(2)–H(24)	33.4(2)	33.7(2)	27(2)
Ru(1)–Ru(3)–H(13)	32.5(2)	32.2(2)	20(2)
Ru(1)–Ru(3)–H(23)	83.4(2)	84.2(2)	78(2)
Ru(2)–Ru(3)–H(13)	86.4(2)	85.0(2)	73(2)
Ru(2)–Ru(3)–H(23)	32.3(2)	32.2(2)	27(2)
Ru(4)–Ru(3)–H(13)	85.2(2)	86.5(2)	77(2)
Ru(4)–Ru(3)–H(23)	88.6(2)	86.8(2)	84(2)
Ru(1)–Ru(4)–H(14)	32.8(2)	32.8(2)	29(2)
Ru(1)–Ru(4)–H(24)	85.7(2)	84.4(2)	83(2)
Ru(2)–Ru(4)–H(14)	80.2(2)	81.7(2)	78(2)
Ru(2)–Ru(4)–H(24)	33.6(2)	33.7(2)	30(2)
Ru(3)–Ru(4)–H(14)	92.4(2)	91.4(2)	88(2)
Ru(3)–Ru(4)–H(24)	89.2(2)	90.6(2)	85(2)
(*c*) Ru–Ru–C			
Ru(2)–Ru(1)–C(11)	87.9(1)	90.1(1)	89.4(2)
Ru(2)–Ru(1)–C(12)	96.4(1)	94.9(1)	94.9(2)
Ru(3)–Ru(1)–C(11)	148.6(1)	149.8(1)	149.7(2)
Ru(3)–Ru(1)–C(12)	96.6(1)	98.3(1)	98.9(2)
Ru(4)–Ru(1)–C(11)	103.9(1)	102.6(1)	102.9(2)
Ru(4)–Ru(1)–C(12)	149.6(1)	150.2(1)	150.8(2)
Ru(1)–Ru(2)–C(21)	94.4(1)	93.3(1)	94.0(2)
Ru(1)–Ru(2)–C(22)	89.8(1)	93.5(1)	92.4(2)
Ru(3)–Ru(2)–C(21)	152.6(1)	153.2(1)	153.6(2)
Ru(3)–Ru(2)–C(22)	101.2(1)	100.4(1)	101.8(2)
Ru(4)–Ru(2)–C(21)	102.4(1)	104.2(1)	104.5(2)
Ru(4)–Ru(2)–C(22)	149.1(1)	151.6(1)	151.4(2)
Ru(1)–Ru(3)–C(31)	150.4(1)	150.3(1)	152.1(2)
Ru(1)–Ru(3)–C(32)	105.0(1)	103.5(1)	102.3(2)
Ru(2)–Ru(3)–C(31)	101.1(1)	101.5(1)	103.1(2)
Ru(2)–Ru(3)–C(32)	157.0(1)	155.7(1)	153.2(2)
Ru(4)–Ru(3)–C(31)	91.3(1)	91.1(1)	92.9(2)
Ru(4)–Ru(3)–C(32)	98.8(1)	98.7(1)	95.5(2)
Ru(1)–Ru(4)–C(41)	152.9(1)	152.8(1)	150.9(2)
Ru(1)–Ru(4)–C(42)	97.6(1)	99.1(1)	100.2(2)
Ru(2)–Ru(4)–C(41)	103.8(1)	103.4(1)	101.3(2)
Ru(2)–Ru(4)–C(42)	147.5(1)	148.0(1)	150.1(2)
Ru(3)–Ru(4)–C(41)	93.1(1)	93.2(1)	91.8(2)
Ru(3)–Ru(4)–C(42)	89.4(1)	89.1(1)	91.2(2)
(*d*) Ru–Ru–P			
Ru(2)–Ru(1)–P(1)	155.6(1)	165.4(1)	166.8(1)
Ru(3)–Ru(1)–P(1)	113.7(1)	110.9(1)	111.5(1)
Ru(4)–Ru(1)–P(1)	104.3(1)	104.0(1)	105.2(1)
Ru(1)–Ru(2)–P(2)	167.6(1)	169.6(1)	167.9(1)
Ru(3)–Ru(2)–P(2)	106.1(1)	109.1(1)	108.1(1)
Ru(4)–Ru(2)–P(2)	108.9(1)	108.3(1)	107.1(1)
Ru(1)–Ru(3)–P(3)	107.6(1)	107.0(1)	107.2(1)
Ru(2)–Ru(3)–P(3)	107.5(1)	107.4(1)	107.9(1)
Ru(4)–Ru(3)–P(3)	168.0(1)	167.1(1)	157.5(1)
Ru(1)–Ru(4)–P(4)	102.3(1)	102.5(1)	104.9(1)
Ru(2)–Ru(4)–P(4)	105.5(1)	105.5(1)	104.1(1)
Ru(3)–Ru(4)–P(4)	163.8(1)	163.8(1)	164.7(1)
(*e*) Ru–H–Ru			
Ru(1)–H(13)–Ru(3)	114.3(3)	115.1(3)	139(4)
Ru(1)–H(14)–Ru(4)	114.4(3)	114.4(3)	124(4)
Ru(2)–H(23)–Ru(3)	114.9(3)	115.2(3)	125(4)
Ru(2)–H(24)–Ru(4)	113.0(3)	112.6(3)	123(4)
(*f*) H–Ru–H			
H(13)–Ru(1)–H(14)	100.7(3)	101.3(2)	94(3)
H(23)–Ru(2)–H(24)	99.6(2)	100.4(3)	94(3)
H(13)–Ru(3)–H(23)	107.5(2)	106.8(2)	91(3)
H(14)–Ru(4)–H(24)	98.9(2)	99.0(2)	98(3)
(*g*) C–Ru–C			
C(11)–Ru(1)–C(12)	95.3(1)	94.7(1)	93.3(3)
C(21)–Ru(2)–C(22)	91.7(1)	91.4(1)	89.2(3)
C(31)–Ru(3)–C(32)	91.3(1)	92.3(1)	91.1(3)
C(41)–Ru(4)–C(42)	92.9(1)	91.6(1)	92.9(3)
(*h*) C–Ru–P			
C(11)–Ru(1)–P(1)	93.3(1)	93.7(1)	94.0(2)
C(12)–Ru(1)–P(1)	97.7(1)	98.7(1)	97.6(2)
C(21)–Ru(2)–P(2)	96.1(1)	93.7(1)	94.2(2)
C(22)–Ru(2)–P(2)	96.5(1)	94.0(1)	96.6(2)
C(31)–Ru(3)–P(3)	96.7(1)	97.9(1)	96.2(2)
C(32)–Ru(3)–P(3)	89.9(1)	90.2(1)	92.8(2)
C(41)–Ru(4)–P(4)	100.8(1)	100.4(1)	98.3(2)
C(42)–Ru(4)–P(4)	98.2(1)	99.1(1)	99.5(2)
(*i*) H–Ru–C (*trans*)			
H(13)–Ru(1)–C(11)	176.4(2)	176.4(2)	170(2)
H(14)–Ru(1)–C(12)	177.6(2)	176.5(2)	177(2)
H(23)–Ru(2)–C(21)	174.4(2)	173.6(2)	174(2)
H(24)–Ru(2)–C(22)	176.0(2)	174.6(2)	178(2)
H(13)–Ru(3)–C(31)	169.1(2)	170.9(2)	170(2)
H(23)–Ru(3)–C(32)	170.6(2)	172.0(2)	180(1)
H(14)–Ru(4)–C(41)	174.3(2)	174.3(2)	179(2)
H(24)–Ru(4)–C(42)	175.4(2)	175.8(2)	173(3)
(*j*) H–Ru–C (*cis*)			
H(13)–Ru(1)–C(12)	81.1(2)	81.8(2)	87(2)
H(14)–Ru(1)–C(11)	82.8(2)	82.2(2)	86(2)
H(23)–Ru(2)–C(22)	84.3(2)	83.3(2)	85(2)
H(24)–Ru(2)–C(21)	84.4(2)	84.6(2)	92(2)
H(13)–Ru(3)–C(32)	79.0(2)	79.4(2)	89(2)
H(23)–Ru(3)–C(31)	82.7(2)	81.7(2)	89(2)
H(14)–Ru(4)–C(42)	85.5(2)	85.2(2)	87(2)
H(24)–Ru(4)–C(41)	82.8(2)	84.3(2)	81(2)
(*k*) O–C–H			
Average	⟨109.5(4)⟩	⟨109.5(4)⟩	
Average	⟨109.5(3)⟩		

Table 3 (*continued*)

	Neutron		
	A	B	*X*-ray
(*l*) H–Ru–P (*cis*)			
H(13)–Ru(1)–P(1)	86.9(2)	85.9(2)	95(2)
H(14)–Ru(1)–P(1)	80.8(2)	80.1(2)	85(2)
H(23)–Ru(2)–P(2)	80.5(3)	83.0(2)	88(2)
H(24)–Ru(2)–P(2)	83.3(2)	62.7(8)	84(2)
H(13)–Ru(3)–P(3)	88.5(2)	86.0(2)	94(2)
H(23)–Ru(3)–P(3)	83.6(2)	85.3(2)	87(2)
H(14)–Ru(4)–P(4)	74.0(2)	75.5(2)	82(2)
H(24)–Ru(4)–P(4)	84.3(2)	82.2(2)	86(2)
(*m*) Ru–C–O			
Ru(1)–C(11)–O(11)	176.7(2)	177.5(2)	176.8(6)
Ru(1)–C(12)–O(12)	176.7(2)	177.7(2)	178.9(6)
Ru(2)–C(21)–O(21)	177.3(2)	176.5(2)	177.0(6)
Ru(2)–C(22)–O(22)	177.8(2)	178.0(2)	178.6(6)
Ru(3)–C(31)–O(31)	176.9(2)	178.3(2)	178.6(6)
Ru(3)–C(32)–O(32)	176.3(2)	176.1(2)	176.6(6)
Ru(4)–C(41)–O(41)	179.3(2)	179.4(2)	178.1(6)
Ru(4)–C(42)–O(42)	179.4(2)	178.6(2)	177.7(6)
(*n*) Ru–P–O			
Ru(1)–P(1)–O(13)	112.5(2)	112.4(2)	114.3(2)
Ru(1)–P(1)–O(14)	121.3(2)	120.7(2)	121.4(2)
Ru(1)–P(1)–O(15)	118.9(2)	120.0(2)	118.2(2)
Ru(2)–P(2)–O(23)	119.9(2)	120.2(2)	121.9(2)
Ru(2)–P(2)–O(24)	112.1(2)	117.4(2)	115(3) [b]
Ru(2)–P(2)–O(25)	119.2(2)	109.9(2)	113(8) [b]
Ru(3)–P(3)–O(33)	114.1(2)	113.9(2)	113.4(2)
Ru(3)–P(3)–O(34)	109.9(2)	109.9(2)	111.3(2)
Ru(3)–P(3)–O(35)	122.1(2)	122.7(2)	121.7(2)
Ru(4)–P(4)–O(43)	124.3(2)	122.6(2)	121(4) [b]
Ru(4)–P(4)–O(44)	109.6(2)	110.3(2)	112.0(3)
Ru(4)–P(4)–O(45)	117.9(2)	118.6(2)	120(4) [b]
(*o*) O–P–O			
O(13)–P(1)–O(14)	104.8(2)	105.1(2)	105.1(3)
O(13)–P(1)–O(15)	99.4(2)	99.1(2)	97.5(1)
O(14)–P(1)–O(15)	96.7(2)	96.3(2)	93.4(3)
O(23)–P(2)–O(24)	105.2(2)	98.2(2)	98(8) [b]
O(23)–P(2)–O(25)	97.3(2)	103.5(2)	101(3) [b]
O(24)–P(2)–O(25)	100.3(2)	105.8(2)	101(2) [b]
O(33)–P(3)–O(34)	106.5(2)	106.2(2)	106.0(4)
O(33)–P(3)–O(35)	98.8(2)	98.8(2)	99.0(3)
O(34)–P(3)–O(35)	103.6(2)	103.7(2)	103.9(3)
O(43)–P(4)–O(44)	105.0(2)	104.7(2)	101(8) [b]
O(43)–P(4)–O(45)	96.5(2)	97.0(2)	96(2) [b]
O(44)–P(4)–O(45)	100.3(2)	100.8(2)	100(8) [b]
(*p*) P–O–C			
P(1)–O(13)–C(13)	122.5(2)	122.5(2)	125.0(6)
P(1)–O(14)–C(14)	120.0(2)	120.2(2)	120.2(5)
P(1)–O(15)–C(15)	119.2(2)	119.8(2)	120.5(5)
P(2)–O(23)–C(23)	120.7(2)	117.9(2)	132.4(6)
P(2)–O(24)–C(24)	122.5(2)	126.3(2)	121.3(8) [b]
P(2)–O(25)–C(25)	118.7(2)	122.0(2)	130(1) [b]
P(3)–O(33)–C(33)	126.1(2)	126.9(2)	129.4(6)
P(3)–O(34)–C(34)	123.6(2)	123.1(2)	129.3(6)
P(3)–O(35)–C(35)	118.9(2)	119.9(2)	120.1(4)
P(4)–O(43)–C(43)	121.2(2)	120.5(2)	130(1) [b]
P(4)–O(44)–C(44)	124.2(2)	123.2(2)	128.9(6)
P(4)–O(45)–C(45)	119.1(2)	119.3(2)	124(2) [b]
(*q*) H–C–H			
Average	⟨109.6(5)⟩	⟨109.5(5)⟩	
Average	⟨109.6(2)⟩		

[a] The e.s.d.s in parentheses are evaluated as in Table 1. [b] Averaged over two disordered sites.

principal axes of their thermal ellipsoids when averaged over the eight atoms. These principal axes lie close to directions of motion of the hydrogen atoms in the three modes of vibration described above, with the respective mean deviations between axes and directions of motion being 8, 25, and 26° for ν_{def}, ν_{sym}, and ν_{asym} respectively. Within the assumption that the hydrogens act as independent harmonic oscillators with their three modes uncoupled, the mean square amplitudes may be related [21] in a simple manner to the frequency of the appropriate mode, as given below; $\langle x^2 \rangle$ is the mean square amplitude, ν is the frequency in cm^{-1}, T is the temperature (K), c is the velocity of light, and m_H is the mass of the hydrogen atom, assuming the mass of the ruthenium atoms to be effectively infinite.

$$\langle x^2 \rangle = \frac{h}{8\pi^2 c\nu m_H}\left\{\coth\left(\frac{hc\nu}{2kT}\right)\right\}$$

This yields values of 477 (20), 1 190 (84), and 1 620 (91) cm^{-1}, where the estimated standard deviations in parentheses are based on the scatter of $\langle x^2 \rangle$ values, for ν_{def}, ν_{sym}, and ν_{asym} respectively. These values are in remarkably good agreement with the frequencies observed [21] for $[Ru_4(CO)_{12}H_4]$ for ν_{sym} and ν_{asym} (1 290 and 1 585 cm^{-1} in the Raman, and 1 272 and 1 605 cm^{-1} in the solid-state i.r. spectra). No assignment of the low-frequency region of these spectra has been made, although there are a number of bands in the region of 450 cm^{-1}. This analysis is therefore consistent with the Ru–H–Ru systems here present providing a single-minimum, symmetric, three-dimensional potential well in which the two-co-ordinate hydrogen atoms move. This picture of quintessential M–H–M bonds confirms that the observed symmetry of the Ru–H bond lengths is not an artefact of disorder between asymmetrically disposed sites but an inherent feature of such bonds. This is in contrast to the more complex potential wells observed for a variety of hydrogen-bonded X–H–X systems (X = F, O, N *etc.*). An approximate theoretical correlation of the M–H–M angle (θ) with the ratio ν_{asym}/ν_{sym} has been made,[22] with the result that $\nu_{asym}/\nu_{sym} \sim \tan(\theta/2)$. The value of θ observed here gives a predicted ratio $\nu_{asym}/\nu_{sym} = 1.55$. This may be compared with values of ν_{asym}/ν_{sym} observed for $[Ru_4(CO)_{12}H_4]$ of 1.26 and from the calculated frequencies here, 1.36.

The M–H–M systems have been classified as either 'open' or 'closed' depending on the degree of direct M–M interaction present.[23] According to currently used geometrical criteria the Ru–H–Ru bonds found here are closed; the mean Ru–H–Ru angle is 114.2(3)° and the corresponding angle between the Ru–C vectors *trans* to the μ-H atoms averages 122.9(11)°. The 'closedness' of these three-centre interactions is much less marked than for unsupported M–H–M bridges {*e.g.* in $[W_2(CO)_9H(NO)]$ the angles are 125° and 159°}.[23] We note that for this analysis of the three-centre bond to be meaningful the C–Ru–H–Ru–C system must be at least approximately planar. [In this case the largest r.m.s. deviations for any of the eight planes occur for those involving H(13A) and H(13B) and are *ca.* 0.05 Å.] Alternatively, the

Table 4. Summary of crystallographic measurements and refinements on $[Ru_4(CO)_8H_4\{P(OCH_3)_3\}_4]$ [a]

	X-Ray	Neutron
Temp./K	293(2)	20.0(5)
M	1 128.7	
Space group	$P2_1/c$ ($Z = 4$)	$P\bar{1}$ ($Z = 4$)
(*a*) Lattice parameters		
a/Å	15.700(4)	15.371(3)
b/Å	11.775(3)	11.508(2)
c/Å	21.331(5)	21.079(3)
α/°	90.0	90.07(1)
β/°	100.49(4)	100.09(1)
γ/°	90.0	92.09(2)
U/Å^3	3 877	3 668.5
D_c/g cm^{-3}	1.93	2.04
F(000)	2 224 e$^-$	591 fm
(*b*) Intensity measurements		
λ/Å	0.710 69	1.162 1(5)
$(\sin\theta/\lambda)_{max.}$/Å^{-1}	0.703	0.678
No. of reflections measured	8 945	9 835
Crystal faces	—	{100}, {001}, {110}, {$\bar{1}$10}, ($\bar{1}$02), ($\bar{1}$0$\bar{2}$)
Absorption coefficient [b]μ/cm^{-1}	16.9	1.786
Transmission range	0.637—0.546	0.862—0.727
(*c*) Refinement		
Least-squares	Full-matrix [c]	Block-diagonal [d]
Quantity minimized	$\Sigma w(F_o - \lvert F_c\rvert)^2$	$\Sigma w(F_o - \lvert F_c\rvert)^2$
w (weight)	$4F_o^2/\sigma^2(F_o^2)$	$4F_o^2/[\sigma^2(F_o^2) + (0.02\ F_o^2)]$
Scattering factor [e] (e$^-$)/ length [f] (fm)	Complex, neutral atoms	Ru, 7.21; P, 5.13; O, 5.803; C, 6.648; H, −3.74
NO (no. of observations)	6 647	8 601
NV (no. of variables)	448	1 306
(*d*) Constraints on parameters		
Positional	See text	None
Thermal: isotropic	H, O(disordered)	Ru, P, O(methoxy), C(carbonyl)
anisotropic	Ru, P, C, O	H, O(carbonyl), C(methyl)
Secondary extinction	None applied	Isotropic (Type I crystal), Lorentzian spread of mosaicity [d]
R.m.s. mosaic spread/s	—	9.6
Indices of fit [g]		
R(*F*)	0.043	0.048
R′(*F*)	0.038	0.038
S		1.52

[a] Numbers in parentheses are estimated standard deviations in the least significant digits given, here and throughout this paper. [b] Ref. 16. [c] Ref. 14. [d] Computations carried out on the BNL CDC 7600 computer with programs of the CRYSNET system, and SFLS by R. Shiono as modified by the authors to refine a Type I extinction parameter (Lorentz mosaicity), see P. J. Becker and P. Coppens, *Acta Crystallogr., Sect. A*, 1974, **30**, 129. [e] Ref. 29. [f] L. Koester in ‘ Springer Tracts in Modern Physics,’ ed. G. Hohler, Springer, Berlin, 1977, vol. **80**, p. 36. [g] $R(F) = \Sigma\lvert F_o - F_c\rvert/\Sigma F_o$, $R'(F) = \lvert\Sigma w\lvert F_o - F_c\rvert^2/\Sigma w\lvert F_o\rvert^2\rvert^{\frac{1}{2}}$, and $S = [\Sigma w(F_o - \lvert F_c\rvert^2/(NO - NV)]^{\frac{1}{2}}$.

cis-ligand–Ru–H angles may be inspected in order to determine the ‘ closedness ’ of the Ru–H–Ru interactions, where an acute angle indicates that the system is closed. Here the *cis*-C–Ru–H and P–Ru–H angles average 82.8(5) and 82.7(10)° respectively. The large deviation of the H–Ru–H angle from the octahedral value [mean H–Ru–H 101.8(13)°] can likewise be rationalised as a consequence of the closed nature of the three-centre, two-electron bonds. The *X*-ray determined hydride positions show the expected systematic differences in Ru–H length [1.68(3) *versus* 1.773(2) Å] and Ru–H–Ru angle [128(4) *versus* 114.2(3)°] when compared to the internuclear values from the neutron analysis. As discussed by Petersen and Williams,[24] such distortions are to be expected for closed hydride bridges. In addition the parameters derived from room temperature *X*-ray data are likely to be affected by considerable librational effects in the same sense, with Ru–H bonds systematically shorter and Ru–H–Ru angles larger than the true internuclear values. It is possible however, that an ‘ open ’ M–H–M system, where the principal orbital overlap is outside the triangle defined by the M_2H nuclei, would result in distortion of the *X*-ray determined M–H bond lengths and M–H–M angles in the opposite sense.

Several possible orientations of the M_2H plane relative to the M_4 unit in tetrahedral clusters have been identified by Churchill and Hollander.[25] That observed here places the hydrides close to the C_2 axes of the D_{2d} tetrahedron. This orientation is close to that expected on simple steric grounds, as evidenced by the good agreement between the actual hydride positions and those predicted from the non-hydrogen framework using a potential energy technique[26] (r.m.s. deviation 0.036 Å).

Experimental

Structure Analyses.—X-Ray diffraction analysis. The diffraction data were obtained at room temperature from a crystal which was ground to a sphere of ~0.33 mm diameter. The space group $P2_1/c$ was assigned on the basis of Weissenberg

Table 5. *X*-Ray (293 K) atomic co-ordinates for monoclinic $[Ru_4(CO)_8H_4\{P(OCH_3)_3\}_4]$

Atom	*X/a*	*Y/b*	*Z/c*
Ru(1)	0.720 2(1)	0.481 2(1)	0.244 6(1)
Ru(2)	0.646 0(1)	0.342 0(1)	0.143 0(1)
Ru(3)	0.826 8(1)	0.424 7(1)	0.146 5(1)
Ru(4)	0.799 1(1)	0.254 9(1)	0.231 9(1)
H(13)	0.787 0(42)	0.496 6(55)	0.202 2(29)
H(14)	0.764 0(43)	0.354 6(53)	0.275 5(30)
H(23)	0.724 0(42)	0.390 9(54)	0.108 4(30)
H(24)	0.709 7(43)	0.232 7(52)	0.181 8(29)
P(1)	0.802 1(1)	0.560 8(1)	0.332 9(1)
P(2)	0.614 6(1)	0.214 0(2)	0.062 5(1)
P(3)	0.820 4(1)	0.576 9(2)	0.079 8(1)
P(4)	0.742 0(1)	0.140 0(2)	0.299 3(1)
C(11)	0.628 2(4)	0.447 4(6)	0.285 5(3)
C(12)	0.668 7(4)	0.614 4(6)	0.208 6(3)
C(21)	0.552 2(4)	0.301 5(7)	0.180 2(3)
C(22)	0.580 4(4)	0.461 6(6)	0.101 2(3)
C(31)	0.870 5(4)	0.321 9(6)	0.093 1(3)
C(32)	0.938 7(4)	0.461 0(6)	0.188 3(3)
C(41)	0.838 8(5)	0.141 5(5)	0.182 0(3)
C(42)	0.909 1(4)	0.278 0(6)	0.280 6(3)
O(11)	0.572 4(4)	0.430 2(5)	0.313 0(3)
O(12)	0.638 4(4)	0.696 7(4)	0.186 6(3)
O(21)	0.491 7(4)	0.277 1(6)	0.200 7(3)
O(22)	0.538 4(4)	0.534 2(5)	0.075 2(3)
O(31)	0.898 5(4)	0.261 2(5)	0.061 2(3)
O(32)	1.007 9(3)	0.482 9(5)	0.210 7(3)
O(41)	0.863 1(4)	0.071 5(5)	0.153 4(3)
O(42)	0.977 5(3)	0.288 6(5)	0.310 1(3)
C(13)	0.934 2(7)	0.510 4(9)	0.425 6(4)
C(14)	0.907 2(6)	0.698 1(9)	0.287 3(4)
C(15)	0.688 2(6)	0.673 7(8)	0.385 6(5)
C(23)	0.588 0(10)	0.027 1(8)	0.128 4(4)
C(24)	0.696 7(8)	0.123 9(10)	−0.024 3(5)
C(25)	0.461 0(5)	0.205 8(12)	−0.022 0(5)
C(33)	0.810 9(8)	0.804 6(6)	0.094 7(5)
C(34)	0.910 8(9)	0.545 3(11)	−0.011 6(6)
C(35)	0.697 1(6)	0.528 6(7)	−0.017 7(3)
C(43)	0.763 0(10)	−0.078 7(9)	0.267 8(6)
C(44)	0.589 4(6)	0.123 2(10)	0.338 8(5)
C(45)	0.854 2(6)	0.171 3(11)	0.407 2(5)
O(13)	0.874 6(4)	0.480 5(5)	0.369 6(3)
O(14)	0.848 4(4)	0.681 4(4)	0.329 8(3)
O(15)	0.755 8(3)	0.591 0(5)	0.392 2(2)
O(23)	0.603 6(6)	0.085 8(4)	0.075 5(3)
O(24A)	0.661 1(8)	0.223 6(8)	0.002 7(5)
O(24)	0.702 4(5)	0.183 7(9)	0.033 0(4)
O(25A)	0.510 9(5)	0.246 4(9)	0.031 2(4)
O(25)	0.549 3(6)	0.235 4(11)	−0.002 5(5)
O(33)	0.836 2(5)	0.694 9(4)	0.116 2(3)
O(34)	0.892 9(4)	0.568 7(6)	0.035 8(3)
O(35)	0.734 0(3)	0.608 3(4)	0.030 9(2)
O(43A)	0.761 2(12)	0.009 0(7)	0.310 3(6)
O(43)	0.713 1(6)	0.015 1(6)	0.273 0(5)
O(44)	0.645 1(4)	0.170 5(6)	0.301 0(3)
O(45A)	0.767 8(6)	0.170 4(15)	0.374 9(4)
O(45)	0.789 7(6)	0.107 3(8)	0.368 4(3)

and oscillation photographic data. The diffractometric measurements were made with graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å) on a Syntex $P2_1$ instrument. Accurate lattice parameters were derived by an unconstrained least-squares fit to the difference in the ω-centroids of 1 124 Friedel pairs with $40 < 2\theta < 60°$ scanned at $\pm(\omega, 2\theta)$.[27] The refined values of α and γ were equal to 90.00(4)° within 0.2σ. The reflection intensity data were measured in one quadrant of reciprocal space by the $\omega/2\theta$ scan method. The scans with widths $\Delta 2\theta = (2° + \alpha_1\alpha_2$ splitting) were centred on the calculated peak positions. Scan times were determined on the basis of 2 s prescans through the Bragg positions. Reflections with prescan intensities below a low threshold were not recorded. Background intensities were estimated by stationary counts at the scan extremes. Integrated intensities were obtained by subtraction of background from scan extremes, and the variance in each value was computed from counting statistics. The intensities of two reflections which were monitored after every 28 as a check on instrument and crystal stability showed no systematic variation during the measurements. The data were corrected for Lorentz and polarisation effects and for absorption by an empirical method [27] based on 480 azimuthal scan intensities from 12 independent reflections. Observations were averaged according to $2/m$ symmetry, and all independent reflections were used in the structure analysis.

The four independent Ru atoms were located by direct methods. Positions of the remaining 44 non-hydrogen atoms were obtained from difference-Fourier maps. Four methoxy oxygen atoms, a pair on each of two $P(OCH_3)_3$ groups, were located at positions of two-fold disorder, but the alternative carbon positions in these disordered conformations were not resolved by the data. The four hydride atoms were located at prominent peaks on a difference map weighted to emphasize low angle data.* The 36 methyl hydrogen atoms were omitted from the model since there was no evidence of them on the difference maps. For the disordered oxygen atoms, occupancy factors were varied in the final refinement under constraints that required equal weighting for any two oxygens at acceptable contact distance within a $P(OCH_3)_3$ group and full occupancy for the two alternative sets of sites taken together. Constraints were also imposed on their positional parameters to force these P–O and O–CH_3 bond lengths to common values, which refined to 1.599(3) and 1.409(3) Å, respectively. The independent occupancy factors at convergence were 0.48(1) for atoms O(24A) and O(25A), and 0.61(1) for atoms O(43A) and O(45A). Extinction effects in the data were negligible and were not accounted for in the refinement. Additional details of the refinement are given in Table 4. The weighted error $w(F_o - |F_c|)^2$ in the final cycle was independent of F_o but tended to larger values for low angle data to which the methyl hydrogen atoms would be expected to make significant contributions.

Neutron diffraction analysis. The diffraction data were measured with an automated four-circle diffractometer at the Brookhaven High Flux Beam Reactor. The wavelength of the neutron beam [1.1621(5) Å] was selected by diffraction from the (220) planes of a germanium monochromating crystal and was calibrated against a KBr crystal [$a_o = 6.600\,00(13)$ Å at 298 K]. The sample crystals were grown by slow evaporation of a saturated methylene chloride–hexane solution of the hydride. Prior to the diffraction studies, the stability of crystals at low temperatures was tested by cooling specimens under vacuum to liquid nitrogen temperature. A marked reversible colour change from deep orange at 298 K to yellow below ~200 K was noted, but no damage to the crystals was observed. The diffraction data were collected on a tablet-shaped crystal of approximate dimensions 0.8 × 0.9 × 4.1 mm, mounted with rubber glue on a vanadium pin, and placed

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* Computations carried out on the University of Cambridge IBM 370/165 computer with programs written by G. M. Sheldrick.

Table 6. Neutron (20 K) atomic co-ordinates for triclinic $[Ru_4(CO)_8H_4\{P(OCH_3)_3\}_4]$

	Molecule A				Molecule B		
Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ru(1A)	0.719 5(1)	0.474 4(2)	0.243 77(9)	Ru(1B)	−0.720 9(1)	1.001 5(2)	0.256 06(9)
Ru(2A)	0.647 4(1)	0.322 7(2)	0.142 42(9)	Ru(2B)	−0.644 3(1)	0.859 4(2)	0.356 51(9)
Ru(3A)	0.831 7(1)	0.417 1(2)	0.146 82(9)	Ru(3B)	−0.829 2(1)	0.929 5(2)	0.355 17(6)
Ru(4A)	0.803 2(1)	0.246 7(2)	0.234 71(9)	Ru(4B)	−0.798 9(1)	0.762 4(2)	0.266 19(9)
H(13A)	0.809 3(3)	0.517 3(4)	0.206 4(2)	H(13B)	−0.806 4(3)	1.035 2(4)	0.297 9(2)
H(14A)	0.760 5(3)	0.347 2(4)	0.284 1(2)	H(14B)	−0.764 3(3)	0.871 3(4)	0.215 4(2)
H(23A)	0.728 6(3)	0.373 3(4)	0.098 8(2)	H(23B)	−0.726 0(3)	0.893 5(5)	0.401 3(2)
H(24A)	0.703 2(3)	0.203 4(4)	0.183 0(2)	H(24B)	−0.694 6(3)	0.734 3(4)	0.313 8(2)
P(1A)	0.796 9(2)	0.557 7(2)	0.335 7(1)	P(1B)	−0.807 6(2)	1.077 8(2)	0.167 9(1)
P(2A)	0.619 9(2)	0.195 4(2)	0.057 6(1)	P(2B)	−0.607 1(2)	0.728 9(2)	0.436 5(1)
P(3A)	0.825 7(2)	0.567 4(2)	0.076 2(1)	P(3B)	−0.823 2(2)	1.082 1(2)	0.425 6(1)
P(4A)	0.747 0(2)	0.138 2(2)	0.309 7(1)	P(4B)	−0.741 9(2)	0.661 5(2)	0.190 5(1)
C(11A)	0.619 5(1)	0.436 9(2)	0.282 1(1)	C(11B)	−0.626 1(1)	0.975 2(2)	0.212 0(1)
C(12A)	0.673 9(1)	0.611 8(2)	0.204 0(1)	C(12B)	−0.670 7(1)	1.141 3(2)	0.295 3(1)
C(21A)	0.551 7(1)	0.269 7(2)	0.181 9(1)	C(21B)	−0.546 9(1)	0.827 4(2)	0.316 6(1)
C(22A)	0.581 2(1)	0.444 6(2)	0.101 2(1)	C(22B)	−0.580 8(1)	0.984 8(2)	0.403 7(1)
C(31A)	0.875 7(1)	0.307 6(2)	0.095 0(1)	C(31B)	−0.870 5(1)	0.813 8(2)	0.406 8(1)
C(32A)	0.947 2(1)	0.467 2(2)	0.184 7(1)	C(32B)	−0.945 0(1)	0.966 7(2)	0.317 0(1)
C(41A)	0.849 9(1)	0.129 7(2)	0.189 3(1)	C(41B)	−0.840 6(1)	0.638 6(2)	0.312 7(1)
C(42A)	0.914 7(1)	0.287 3(2)	0.284 8(1)	C(42B)	−0.914 0(1)	0.784 5(2)	0.219 1(1)
O(11A)	0.560 0(2)	0.418 4(2)	0.307 5(1)	O(11B)	−0.570 1(2)	0.961 5(2)	0.183 3(1)
O(12A)	0.650 3(2)	0.697 2(2)	0.179 6(1)	O(12B)	−0.642 6(2)	1.228 1(2)	0.319 7(1)
O(21A)	0.491 5(2)	0.237 9(2)	0.203 5(1)	O(21B)	−0.484 5(2)	0.808 2(2)	0.295 2(1)
O(22A)	0.538 7(2)	0.516 3(2)	0.075 2(1)	O(22B)	−0.541 0(2)	1.058 4(2)	0.433 5(1)
O(31A)	0.906 2(2)	0.243 5(2)	0.064 2(1)	O(31B)	−0.897 8(2)	0.744 3(2)	0.438 2(1)
O(32A)	1.017 8(2)	0.502 1(2)	0.205 2(1)	O(32B)	−1.015 6(2)	0.994 0(2)	0.296 5(1)
O(41A)	0.878 0(2)	0.057 2(2)	0.161 8(1)	O(41B)	−0.866 5(2)	0.562 9(2)	0.340 5(1)
O(42A)	0.983 0(2)	0.311 6(2)	0.315 0(1)	O(42B)	−0.984 4(2)	0.796 0(2)	0.191 1(1)
O(13A)	0.868 4(2)	0.473 9(2)	0.373 5(1)	O(13B)	−0.886 4(2)	0.989 9(2)	0.136 7(1)
O(14A)	0.848 9(2)	0.681 4(2)	0.334 4(1)	O(14B)	−0.853 1(2)	1.200 8(2)	0.172 5(1)
O(15A)	0.744 9(2)	0.588 9(2)	0.393 3(1)	O(15B)	−0.766 6(2)	1.107 4(2)	0.104 4(1)
O(23A)	0.575 6(2)	0.068 8(2)	0.066 4(1)	O(23B)	−0.616 4(2)	0.590 7(2)	0.420 8(1)
O(24A)	0.706 7(2)	0.171 4(2)	0.028 6(1)	O(24B)	−0.660 5(2)	0.729 9(2)	0.494 9(1)
O(25A)	0.553 8(2)	0.230 9(2)	−0.006 8(1)	O(25B)	−0.504 5(2)	0.748 7(2)	0.468 5(1)
O(33A)	0.843 9(2)	0.692 4(2)	0.109 6(1)	O(33B)	−0.844 1(2)	1.203 3(2)	0.391 7(1)
O(34A)	0.899 0(2)	0.553 7(2)	0.031 2(1)	O(34B)	−0.895 5(2)	1.060 8(2)	0.471 9(1)
O(35A)	0.737 0(2)	0.594 2(2)	0.025 9(1)	O(35B)	−0.734 8(2)	1.121 0(2)	0.474 6(1)
O(43A)	0.758 2(2)	−0.000 0(2)	0.318 7(1)	O(43B)	−0.753 1(2)	0.521 7(2)	0.182 9(1)
O(44A)	0.643 6(2)	0.156 0(2)	0.302 2(1)	O(44B)	−0.638 1(2)	0.688 2(2)	0.198 2(1)
O(45A)	0.778 0(2)	0.172 8(2)	0.384 2(1)	O(45B)	−0.773 0(2)	0.691 5(2)	0.116 4(1)
C(13A)	0.926 8(1)	0.508 9(2)	0.432 2(1)	C(13B)	−0.947 0(1)	1.016 4(2)	0.079 4(1)
C(14A)	0.908 0(2)	0.701 3(2)	0.289 0(1)	C(14B)	−0.903 4(1)	1.221 5(2)	0.222 8(1)
C(15A)	0.679 8(1)	0.676 5(2)	0.383 3(1)	C(15B)	−0.696 9(1)	1.195 2(2)	0.107 3(1)
C(23A)	0.606 8(1)	−0.000 3(2)	0.121 6(1)	C(23B)	−0.569 1(1)	0.546 7(2)	0.373 4(1)
C(24A)	0.707 2(1)	0.088 6(2)	−0.023 2(1)	C(24B)	−0.690 2(2)	0.629 4(2)	0.527 2(1)
C(25A)	0.461 5(1)	0.236 2(2)	−0.005 0(1)	C(25B)	−0.464 7(1)	0.685 0(2)	0.524 3(1)
C(33A)	0.811 3(2)	0.800 8(2)	0.082 5(1)	C(33B)	−0.814 2(2)	1.317 0(2)	0.417 1(1)
C(34A)	0.915 2(1)	0.637 6(2)	−0.016 5(1)	C(34B)	−0.912 8(1)	1.145 9(2)	0.517 9(1)
C(35A)	0.701 3(1)	0.507 6(2)	−0.022 2(1)	C(35B)	−0.695 4(1)	1.041 3(2)	0.523 6(1)
C(43A)	0.734 9(2)	−0.078 7(2)	0.265 2(1)	C(43B)	−0.723 1(1)	0.447 7(2)	0.236 5(1)
C(44A)	0.589 2(1)	0.111 3(2)	0.346 3(1)	C(44B)	−0.584 6(1)	0.643 3(2)	0.154 7(1)
C(45A)	0.869 3(1)	0.161 5(2)	0.413 3(1)	C(45B)	−0.864 9(1)	0.676 0(2)	0.088 2(1)
H(131A)	0.892 3(5)	0.506 9(8)	0.471 6(3)	H(131B)	−0.917 7(4)	1.000 4(6)	0.037 5(2)
H(132A)	0.955 8(5)	0.593 8(6)	0.427 4(3)	H(132B)	−1.004 9(4)	0.960 0(6)	0.078 7(3)
H(133A)	0.979 0(5)	0.449 0(7)	0.438 9(4)	H(133B)	−0.967 8(4)	1.105 2(5)	0.080 0(3)
H(141A)	0.874 0(4)	0.688 7(5)	0.240 0(2)	H(141B)	−0.918 4(4)	1.312 4(5)	0.220 1(3)
H(142A)	0.931 4(4)	0.790 3(5)	0.295 6(3)	H(142B)	−0.865 5(4)	1.204 3(5)	0.269 9(2)
H(143A)	0.962 8(4)	0.644 4(6)	0.298 9(3)	H(143B)	−0.964 2(4)	1.166 8(6)	0.215 1(3)
H(151A)	0.647 0(4)	0.675 0(5)	0.424 5(3)	H(151B)	−0.695 6(5)	1.223 9(7)	0.059 6(3)
H(152A)	0.711 0(4)	0.761 4(5)	0.379 3(3)	H(152B)	−0.635 8(4)	1.161 8(8)	0.126 5(5)
H(153A)	0.631 8(4)	0.658 7(5)	0.339 1(3)	H(153B)	−0.708 1(7)	1.267 7(7)	0.134 3(5)
H(231A)	0.601 0(4)	0.045 9(5)	0.165 7(2)	H(231B)	−0.583 6(4)	0.595 0(5)	0.328 6(2)
H(232A)	0.564 7(4)	−0.079 1(5)	0.118 0(3)	H(232B)	−0.497 7(3)	0.552 3(5)	0.391 1(2)
H(233A)	0.675 6(3)	−0.021 7(5)	0.122 8(3)	H(233B)	−0.590 3(4)	0.456 4(4)	0.364 5(2)
H(241A)	0.755 3(9)	0.111 1(9)	−0.046 4(5)	H(241B)	−0.635 9(4)	0.575 6(5)	0.547 0(3)
H(242A)	0.716(1)	0.009 5(7)	−0.006 5(4)	H(242B)	−0.721 1(4)	0.662 2(5)	0.565 4(3)
H(243A)	0.650 0(6)	0.084(1)	−0.054 3(5)	H(243B)	−0.737 0(4)	0.576 6(5)	0.493 9(3)
H(251A)	0.430 4(3)	0.272 8(5)	−0.050 5(2)	H(251B)	−0.499 7(4)	0.697 5(5)	0.564 1(2)
H(252A)	0.450 8(3)	0.293 6(5)	0.034 3(3)	H(252B)	−0.397 3(3)	0.720 5(5)	0.537 5(2)

Table 6 (*continued*)

	Molecule A				Molecule B		
Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
H(253A)	0.433 6(3)	0.150 0(5)	0.000 9(3)	H(253B)	−0.464 3(4)	0.592 1(4)	0.512 9(2)
H(331A)	0.845 3(4)	0.867 9(5)	0.114 7(3)	H(331B)	−0.753 6(4)	1.342 8(5)	0.400 9(3)
H(332A)	0.824 6(4)	0.814 5(5)	0.034 1(3)	H(332B)	−0.865 8(4)	1.375 9(5)	0.397 9(3)
H(333A)	0.740 4(4)	0.802 8(5)	0.081 3(3)	H(333B)	−0.802 1(5)	1.319 7(5)	0.469 4(2)
H(341A)	0.949 1(4)	0.715 3(5)	0.006 5(3)	H(341B)	−0.944 6(4)	1.219 9(5)	0.493 2(3)
H(342A)	0.958 3(4)	0.597 7(5)	−0.045 3(3)	H(342B)	−0.852 6(4)	1.175 5(5)	0.549 6(3)
H(343A)	0.853 6(4)	0.661 2(6)	−0.047 8(3)	H(343B)	−0.956 6(4)	1.103 7(5)	0.546 5(3)
H(351A)	0.713 1(4)	0.420 6(5)	−0.003 9(3)	H(351B)	−0.695 8(4)	0.953 1(4)	0.504 0(3)
H(352A)	0.729 6(4)	0.519 4(5)	−0.065 3(2)	H(352B)	−0.731 3(4)	1.039 7(5)	0.563 5(2)
H(353A)	0.629 9(3)	0.518 4(5)	−0.033 0(3)	H(353B)	−0.628 2(3)	1.072 8(5)	0.539 3(3)
H(431A)	0.758 7(5)	−0.162 0(5)	0.281 0(3)	H(431B)	−0.755 0(4)	0.362 3(5)	0.225 4(3)
H(432A)	0.764 5(4)	−0.050 5(5)	0.224 7(2)	H(432B)	−0.740 1(4)	0.480 6(5)	0.280 9(2)
H(433A)	0.661 9(3)	−0.085 6(5)	0.250 2(3)	H(433B)	−0.651 5(3)	0.438 0(5)	0.242 8(3)
H(441A)	0.522 7(3)	0.135 3(6)	0.327 6(3)	H(441B)	−0.517 7(3)	0.673 3(6)	0.173 1(3)
H(442A)	0.610 2(4)	0.147 5(5)	0.393 9(2)	H(442B)	−0.604 7(4)	0.678 0(5)	0.106 9(2)
H(443A)	0.591 9(4)	0.017 0(5)	0.348 9(3)	H(443B)	−0.588 7(4)	0.549 1(5)	0.152 9(3)
H(451A)	0.906 3(3)	0.118 9(5)	0.381 1(2)	H(451B)	−0.895 3(4)	0.759 9(5)	0.081 8(3)
H(452A)	0.898 1(4)	0.247 4(5)	0.425 4(3)	H(452B)	−0.901 1(4)	0.622 9(6)	0.117 6(3)
H(453A)	0.871 3(4)	0.110 9(6)	0.456 9(3)	H(453B)	−0.868 6(4)	0.633 5(6)	0.042 2(3)

Table 7. Important thermal parameters * for triclinic $[Ru_4(CO)_8H_4\{P(OCH_3)_3\}_4]$ at 20 K

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru(1A)	0.002 5(4)					
Ru(2A)	0.002 8(4)					
Ru(3A)	0.002 6(3)					
Ru(4A)	0.003 1(4)					
H(13A)	0.018(2)	0.023(3)	0.028(3)	−0.004(2)	0.012(2)	−0.005(2)
H(14A)	0.031(3)	0.015(2)	0.015(2)	0.007(2)	0.009(2)	0.002(2)
H(23A)	0.012(2)	0.030(3)	0.013(2)	−0.004(2)	0.003(2)	0.001(2)
H(24A)	0.019(2)	0.014(2)	0.024(2)	0.001(2)	−0.009(2)	0.005(2)
Ru(1B)	0.002 5(3)					
Ru(2B)	0.002 6(3)					
Ru(3B)	0.003 0(4)					
Ru(4B)	0.002 5(3)					
H(13B)	0.025(2)	0.017(2)	0.030(3)	0.008(2)	0.018(2)	0.009(2)
H(14B)	0.027(3)	0.013(2)	0.015(2)	−0.005(2)	0.004(2)	−0.000(2)
H(23B)	0.012(2)	0.037(3)	0.013(2)	0.010(2)	0.002(2)	0.004(2)
H(24B)	0.016(2)	0.012(2)	0.030(3)	0.002(2)	−0.002(2)	−0.005(2)

* The thermal parameters are of the form: isotropic = $\exp[-8\pi^2U\left(\frac{\sin\theta}{\lambda}\right)^2]$ and anisotropic = $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$.

in a helium-filled aluminium can inside a closed-cycle refrigerator [Air Products and Chemicals Inc. Displex(R) model CS-202]. The crystal was shown to have 2/*m* diffraction symmetry at room temperature and to undergo a lattice transformation that reduced its symmetry to $\bar{1}$ at 20 K. The temperature of the crystal was lowered at the rate of ~1° min^{-1} and held at 20.0(5) K during the three week period of the diffraction measurements. The lattice parameters at 20 K were determined by a least-squares fit to $\sin^2\theta$ values for 32 strong reflections with $39 < 2\theta < 59°$. These values as well as integrated reflection intensities were reproducible within their error limits after warming the crystal to 298 K and re-cooling to 20 K, confirming the reversibility of the monoclinic ⟷ triclinic transformation. Scans along the lattice rows (*h*0*h*), ($\bar{h}$0*h*), (*hh*0), (0*k*0), and (00*l*) verified the periodicity of the triclinic lattice given in Table 4. The reflection intensity data were measured by a θ/2θ step-scan method. Counts were accumulated at each step until a monitor count of the direct beam reached a present value requiring about 2 s. Between 55 and 75 points were sampled on the reflection profiles. Scan widths varying between 2.6 and 5.0° with increasing 2θ were chosen so that of the total number of points sampled about 20% represented background values. All reflections (±*h*, *k*, ±*l*) were measured below $\sin\theta/\lambda = 0.46$ Å^{-1}. Beyond this value to $(\sin\theta/\lambda)_{max.} = 0.68$ Å^{-1}, the hemisphere was divided into six shells of approximately equal volumes, and the 500 strongest reflections were measured in each shell. The reflections measured at high scattering angles were those having the largest intensities predicted from the nuclear model with $P\bar{1}$ symmetry which had been reliably fitted to the low angle data. The crystal and instrumental stabilities were monitored by remeasuring two reflections at ~3 h intervals; variations in their intensities were random within ~2%. The integrated intensity (*I*) and variance [$\sigma^2(I)$] for each reflection were evaluated from $I = C - kB$, and $\sigma^2(I) = C + k^2B$ taking the counts *C* in the central 80% of the scan and the background *B* estimated from the two extreme 10% parts (*i.e.* $k = 4$). Lorentz and absorption corrections [28, *] were applied,

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* Values of the absorption coefficients $(\mu/\rho)_{X\text{-ray}}$ for all elements, and $(\mu/\rho)_{neutron}$ for all except H are taken from ref. 29, and $(\mu/\rho)_{neutron}$ for H from ref. 30.

and symmetry-related observations were averaged to give the 8 601 independent observations used in the analysis. The agreement index * $R(\bar{F}^2)$ was 0.022% for Friedel pairs in the *h*0*l* zone.

The structure determination was initiated with co-ordinates derived from the *X*-ray analysis and thermal factors *B* of 0.5 Å^2, assuming $P\bar{1}$ symmetry and two independent molecules per cell. New positions for the hydride and disordered oxygen atoms were obtained from difference maps evaluated with the low resolution data ($\sin\theta/\lambda < 0.46$ Å^{-1}; 5 901 reflections). Those positions related by pseudo-monoclinic 2_1 symmetry were refined by differential Fourier synthesis; the two independent molecules were thus selected and their uniqueness confirmed by large shifts (~0.7 Å) in peripheral OCH_3 groups. Further refinement against the entire data set was continued by Fourier methods until the complete model of 176 atoms was obtained. The final refinement was by block-diagonal least squares under the conditions and constraints specified in Table 4. Convergence was achieved at an agreement index $R'(F)$ of 0.038 with maximum shift in the 1 306 parameters of 0.16σ in the final cycle. In the final difference map, there was no residual nuclear density to indicate the disorder observed at room temperature. The largest features were small negative residuals near methyl hydrogen atoms which were attributed to departures from harmonic thermal vibrations.

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* $R(F^2) = \Sigma|F^2 - \langle F^2\rangle|/\Sigma\langle F^2\rangle$ summed for observations on equivalent reflections.

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