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Crystallographic Studies on Ruthenium Carbonyl Hydrides. 3.¹⁻³ Molecular Geometry of $(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{10}(\text{diphos})$, Including the Direct Location and Refined Positions of All Four Bridging Hydride Ligands

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The molecular geometry of tetra- μ -hydrido-[bis-1,2-(diphenylphosphino)ethane]decacarbonyltetraruthenium, $(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{10}(\text{diphos})$, a species previously prepared by Shapley and Richter, has been determined by means of a full three-dimensional single-crystal X-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5 ; No. 14] with $a = 11.879$ (1) Å, $b = 33.565$ (4) Å, $c = 10.269$ (1) Å, $\beta = 108.37$ (1)°, and $V = 3886$ (1) Å³. Observed and calculated densities are 1.848 (10) and 1.857 g cm⁻³, respectively, for $Z = 4$ and mol wt 1086.85. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer using Mo $K\alpha$ radiation and a "wandering ω -scan" collection geometry. The structure was solved by a combination of Patterson, difference-Fourier, and least-squares refinement (485 varied parameters) techniques using the Syntex XTL system. The final discrepancy indices were $R_F = 3.8\%$ and $R_{wF} = 2.5\%$ for all 3630 independent reflections in the range $3^\circ \leq 2\theta \leq 40^\circ$ (not a single reflection rejected). All atoms were located. The positional and isotropic thermal parameters of the four μ -hydride ligands were optimized via least-squares refinement (as were positional and anisotropic thermal parameters for all nonhydrogen atoms). The four metal atoms define a tetrahedral cluster with the diphos ligand chelating to Ru(1). Three of the hydride ligands bridge the tetrahedral edges adjacent to Ru(1), while the fourth such ligand spans the Ru(2)–Ru(3) vector. The hydride-bridged ruthenium–ruthenium distances are Ru(1)–Ru(2) = 2.998 (1), Ru(1)–Ru(3) = 3.006 (1), Ru(1)–Ru(4) = 2.946 (1), and Ru(2)–Ru(3) = 2.931 (1) Å; the nonbridged ruthenium–ruthenium bonds, which are adjacent to one another, are Ru(2)–Ru(4) = 2.796 (1) and Ru(3)–Ru(4) = 2.785 (1) Å. The average hydride-bridged ruthenium–ruthenium distance of 2.970 ± 0.037 Å is some 0.18 Å greater than the average nonbridged ruthenium–ruthenium distance of 2.791 ± 0.007 Å. The individual Ru–H–Ru systems appear to be symmetric: ruthenium–hydrogen distances range from 1.64 (6) to 1.81 (4) Å, the average of the eight such vectors being 1.76 ± 0.06 Å. The angles subtended at the hydrogen atoms are as follows: Ru(1)–H(12)–Ru(2) = 116.5 (26), Ru(1)–H(13)–Ru(3) = 114.8 (23), Ru(1)–H(14)–Ru(4) = 119.8 (31), Ru(2)–H(23)–Ru(3) = 109.6 (23)°. The structure is completed by one terminal carbonyl ligand at Ru(1) and three terminal carbonyl ligands at each of the remaining three ruthenium atoms.

Introduction

Our interest in the structural characterization of transition-metal complexes containing bridging hydride ligands has now extended over rather more than a decade and we have examined species containing $\text{Re}(\mu\text{-H})\text{Re}$,⁴⁻⁷ $\text{Cu}(\mu\text{-H})\text{Cu}$,⁸ $\text{Rh}(\mu\text{-H})\text{Rh}$,⁹ $\text{Ir}(\mu\text{-H})\text{Ir}$,¹⁰ $\text{W}(\mu\text{-H})\text{W}$,¹¹ and $\text{Os}(\mu\text{-H})\text{Os}$ ¹²⁻¹⁷ systems. We have also surveyed the structural effects of hydride ligands in a variety of bridging modes³ and have reported previously on two other hydridoruthenium complexes, $(\mu_3\text{-H})_2\text{Ru}_6(\text{CO})_{18}$ ² and $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\text{C}=\text{NMe}_2)$.³

The present structural study of $(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{10}(\text{diphos})$ was undertaken for a variety of reasons including the following:

(1) The molecule is fluxional¹⁸ (i.e., undergoes continuous intramolecular rearrangement in solution), and it was deemed desirable to determine its solid-state structure, which is expected to be indicative of the ground-state structure in solution. It should be noted that there are three simple symmetrical geometries for the H_4M_4 core of molecules containing only bridging hydride ligands—I, having T_d symmetry and four μ_3 -bridging (or "facial") hydride ligands; II, having D_{2d} symmetry, with four μ_2 -hydride ligands and the two nonbridged M–M bonds opposite to one another; and III, having C_s symmetry, with four μ_2 -hydride ligands and the two nonbridged M–M bonds adjacent to each other.



Structure I has been found in $\text{H}_4\text{Re}_4(\text{CO})_{12}$ ^{19a} and $\text{H}_4\text{Co}_4(\eta^5\text{-C}_5\text{H}_5)_4$,^{19b} the D_{2d} core (II) is found in $\text{H}_4\text{-Ru}_4(\text{CO})_{12}$,²⁰ $\text{H}_4\text{Ru}_4(\text{CO})_{11}[\text{P}(\text{OMe})_3]$,²¹ and $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{PPh}_3)_2$.²⁰ Structure III has not, to our knowledge, been revealed previously. As shown below, this is, however, the structure of the core of $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{diphos})$.

(2) The complex is stable and crystals of ideal size and of pleasing appearance were available. In addition (and in

contrast to derivatives of third-row transition metals), absorption of Mo $K\alpha$ radiation by the sample is not a significant problem ($\mu \sim 16$ cm⁻¹ for the complex under consideration). These factors all augur well for directly determining the positions of the hydride ligands.

(3) We have recently reexamined the crystal structure of $\text{Ru}_3(\text{CO})_{12}$.²² It is thus possible to make precise comparisons of interatomic distances within the $(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{10}(\text{diphos})$ molecule with those in the archetypal binary metal carbonyl.

(4) The poly-hydride-bridged metal cluster cores provide a potential model for understanding the interaction of dihydrogen with transition-metal surfaces in heterogeneous catalysis.

A brief account of the structure of $(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{10}(\text{diphos})$ has appeared recently in conjunction with a report of the "edge-terminal-edge" mechanism for hydride scrambling within this species.¹⁸ We note here that, although Bau and co-workers^{20,21} have studied $\text{H}_4\text{Ru}_4(\text{CO})_{12}$, $\text{H}_4\text{Ru}_4(\text{CO})_{11}[\text{P}(\text{OMe})_3]$, and $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{PPh}_3)_2$, our present structural analysis is the first on a member of the $\text{H}_4\text{Ru}_4(\text{CO})_{12-n}\text{L}_n$ family in which the hydride ligands have been located directly and also optimized via least-squares refinement.

Experimental Section

Collection of Diffraction Data. Orange-red needle-shaped crystals of $(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{10}(\text{diphos})$ were provided by Professor J. R. Shapley of the University of Illinois at Urbana-Champaign. The crystal selected for data collection was a needle of length 0.4 mm and of square cross section (0.1 mm \times 0.1 mm). It was mounted along its extended direction (c) on a thin glass fiber, which was inserted into a brass pin with beeswax and placed on a eucentric goniometer.

Preliminary precession and cone-axis photographs yielded approximate axes lengths, indicated $2/m$ (C_{2h}) Laue symmetry, and revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5 ; No. 14] is thereby uniquely defined.

The goniometer was transferred to a Syntex $P2_1$ automated diffractometer which was controlled by a Data General Nova 1200 computer. The crystal was accurately centered by eye. Unit cell

Table I. Data for the X-ray Diffraction Study of $(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{10}$ (diphos)

(A) Crystal Data	
Cryst system: monoclinic	Temp 23 °C
Space group: $P2_1/c$ [C_2h^5 ; No. 14]	$Z = 4$
$a = 11.8790$ (14) Å	Mol wt 1086.85
$b = 33.5649$ (35) Å	$\rho(\text{obsd})^a = 1.848$ (10) g cm ⁻³
$c = 10.2689$ (12) Å	$\rho(\text{calcd}) = 1.857$ g cm ⁻³
$\beta = 108.372$ (8)°	
$V = 3885.7$ (7) Å ³	
(B) Intensity Data	
Radiation: Mo K α (λ 0.710 73 Å)	
Monochromator: highly oriented graphite	
Reflectns measd: $+h, +k, \pm l$	
Max 2θ : 40°	
Min 2θ : 3°	
Scan type: wandering ω scan	
Scan speed: 1.50°/min	
Scan range: 1.0° (0.7° offset for bgd)	
Reflectns collected: 4217 total, 3630 independent	
Abs coeff: 16.31 cm ⁻¹ ; no abs cor made (see text)	

^a Measured by flotation in aqueous BaI₂.

parameters and the orientation matrix were determined by a method described previously.²³

Both θ - 2θ and ω scans were recorded graphically for selected reflections along each of the principal reciprocal axes. As a result of the rather long b axis ($b = 33.565$ (4) Å—see Table I), there was a problem with resolution of adjacent reflections along b^* . We therefore decided to collect the set of intensity data via an ω -scan method, rather than the customary θ - 2θ routine.

Intensity data were collected via a "wandering ω -scan" method in 15 steps over a 1.0° range of ω . The peak profile was analyzed automatically and, if the peak maximum was offset from the center of the scan range, up to two additional steps were collected in the direction of offset. The number of extra steps necessary to center a reflection was stored in memory and used in determining the starting point for the next scan. Nevertheless, we still found it necessary to recenter and redetermine the orientation matrix after every 500 data.

Any step of the scan with a magnitude of 5000–50 000 counts/s was subjected to a linear coincidence correction. Several reflections were encountered in which a step had a magnitude > 50 000 counts/s. The intensities of these reflections (together with those of 16 standards) were later remeasured at a lower current setting on the X-ray generator (45 kV/5 mA, rather than the initial 45 kV/20 mA). The "strong" reflections were placed on the scale of the principal data set by using the scale factor between the two sets of standard reflections.

Backgrounds, offset from the center of the peak profile by 0.7°, were measured at each end of the ω scan, each for one-fourth the time of the ω scan. The stability of the entire system was monitored by measuring the intensity of three strong check reflections after every 47 data. No significant ($> 3\sigma$) fluctuations were observed from the average values.

Following data collection, several reflections close to $\chi = 90$ or 270° were measured at 10° intervals of rotation about their diffraction vector. Examination of these ψ scans showed that the worst variation in intensity [variation (%) = 100(maximum - minimum)/average] with ψ was less than 5%. No absorption corrections were made. ($\mu = 16.31$ cm⁻¹ and the probable systematic errors introduced by ignoring absorption effects are about 1.25% in $|F_o|$.)

Other details of data collection are listed in Table I. Systematically absent reflections were examined (all were within 3σ of $I = 0$) and rejected, as were all check reflections. Equivalent reflections were averaged, yielding 3630 independent data. These were reduced to net intensities (I) and their estimated standard deviations ($\sigma_c(I)$) were calculated based solely upon counting statistics. (See eq 1 and 2.)

$$I = CT - 2(B_1 + B_2) \quad (1)$$

$$\sigma_c(I) = [CT + 4(B_1 + B_2)]^{1/2} \quad (2)$$

Here, CT is the count associated with the 15 most representative contiguous steps of the ω scan, and B_1 and B_2 are the two background counts. Any reflection with $I < 0$ had its intensity reset to zero.

Solution and Refinement of the Structure. The structure was determined using a locally modified version of the Syntex XTL

Structure Determination system. The programs used include GECOR (Wilson plot and generation of $|E|$ values), FOUR (Fourier summations and Patterson functions), FMLS (full-matrix least-squares refinement), BLOCK (Gauss-Seidel blocked least-squares refinement), REVAL (computation of R factors and weighted statistics), HPOSN (calculation of idealized positions for hydrogen atoms), DISTAS (calculation of all distances and angles with esd's), PLANE (calculation of mean planes and χ^2 test), and ORTEP (modified thermal ellipsoid plotting program). All calculations were performed on our in-house Data General Nova 1200 computer (which has 24K of 16-bit words and is backed-up by a Diablo disk unit of 1.2 million 16-bit words).

The atomic scattering factors for neutral ruthenium, phosphorus, oxygen, carbon, and hydrogen were calculated from the analytical expressions of Cromer and Waber^{24a} and used throughout the structural analysis. Both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion^{24b} were included for all non-hydrogen atoms.

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. Here, $|F_o|$ is derived from I by correction for Lorentz and polarization factors, w is defined in eq 3, and $\sigma_c(F)$ is derived by finite differences (as shown in eq 4). The "ignorance factor" (P) was set at 0.01.

$$w = \{[\sigma_c(F)]^2 + \{PF\}^2\}^{-1} \quad (3)$$

$$\sigma_c(F) = [F^2 + \sigma_c(F^2)]^{1/2} - |F^2|^{1/2} \quad (4)$$

Discrepancy indices used in the text are defined by eq 5 and 6. The "goodness-of-fit" or "estimated standard deviation of an observation of unit weight" (GOF) is defined in eq 7, where NO is the number of observations and NV is the number of variables.

$$R_F = \left[\frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \right] \times 100\% \quad (5)$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2} \times 100\% \quad (6)$$

$$\text{GOF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\text{NO} - \text{NV}} \right]^{1/2} \quad (7)$$

The positions of the four ruthenium atoms were determined from an unsharpened, three-dimensional Patterson map. Full-matrix least-squares refinement of the scale factor, along with positional and isotropic thermal parameters of the four ruthenium atoms, led to $R_F = 29.5\%$.

The positions of all other nonhydrogen atoms were quickly and unambiguously determined from a difference-Fourier synthesis. Full-matrix least-squares refinement of positional and isotropic thermal parameters for all nonhydrogen atoms led to $R_F = 6.9\%$. Further refinement, now using *anisotropic* thermal parameters for atoms in the $\text{P}_2\text{Ru}_4(\text{CO})_{10}$ portion of the molecule, resulted in convergence with $R_F = 4.5\%$, $R_{wF} = 3.9\%$, and GOF = 1.92. At this juncture, a difference-Fourier synthesis (using all data) yielded the locations of the four hydride ligands (peak heights ranging from 0.76 to 0.50 e Å⁻³) and all 24 hydrogen atoms of the diphos ligand. The hydride ligands were included in our model and their positional and isotropic thermal parameters were refined. The hydrogen atoms of the diphos ligands were given idealized positions, based upon $d(\text{C-H}) = 0.95$ Å²⁵ and the appropriate sp^2 or sp^3 geometry. Their isotropic thermal parameters were fixed at values 1.0 Å² larger than that of the carbon atom to which they were bonded, i.e., $B(\text{H}_i) = B(\text{C}_i) + 1.0$; the parameters of these atoms were not refined.

Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms, and positional and isotropic thermal parameters for the four hydride ligands, led to final convergence [$(\Delta/\sigma)_{\text{max}} = 0.05$ for a nonhydrogen parameter, $(\Delta/\sigma)_{\text{max}} = 0.03$ for a hydrogen atom parameter] with $R_F = 3.8\%$, $R_{wF} = 2.5\%$, and GOF = 1.197 for NO = 3630 and NV = 485. (No reflections were rejected.) There was no evidence for secondary extinction. The function $\sum w(|F_o| - |F_c|)^2$ showed no significant systematic variations as a function of $|F_o|$, $(\sin \theta)/\lambda$, identity or parity of Miller indices, or sequence number. The weighting scheme was therefore declared satisfactory.

We now conducted two tests on the veracity of our hydride atom locations.

Table II. Final Positional Parameters, with Esd's,^a for $(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{10}(\text{diphos})$

Atom	x	y	z	Atom	x	y	z
Ru(1)	0.25750 (4)	0.13748 (1)	0.18215 (4)	C(109)	0.6987 (6)	0.1317 (2)	0.6476 (7)
Ru(2)	0.11744 (4)	0.07845 (1)	-0.02500 (5)	C(110)	0.6548 (7)	0.1025 (3)	0.7114 (7)
Ru(3)	0.32288 (4)	0.05068 (1)	0.19950 (5)	C(111)	0.5359 (7)	0.0937 (2)	0.6664 (7)
Ru(4)	0.34985 (4)	0.09601 (1)	-0.01587 (5)	C(112)	0.4605 (5)	0.1143 (2)	0.5565 (6)
C(11)	0.2286 (5)	0.1833 (2)	0.0752 (6)	C(201)	0.0252 (4)	0.1961 (2)	0.1947 (6)
O(11)	0.2140 (4)	0.2116 (1)	0.0096 (4)	C(202)	-0.0535 (5)	0.1842 (2)	0.0694 (6)
C(21)	0.0750 (6)	0.1155 (2)	-0.1684 (7)	C(203)	-0.1244 (6)	0.2119 (2)	-0.0172 (6)
O(21)	0.0437 (5)	0.1387 (2)	-0.2554 (5)	C(204)	-0.1166 (6)	0.2510 (2)	0.0160 (8)
C(22)	-0.0341 (6)	0.0708 (2)	0.0028 (7)	C(205)	-0.0413 (6)	0.2630 (2)	0.1393 (8)
O(22)	-0.1252 (4)	0.0664 (2)	0.0141 (6)	C(206)	0.0306 (5)	0.2357 (2)	0.2298 (6)
C(23)	0.0975 (6)	0.0340 (2)	-0.1462 (7)	C(207)	0.0352 (5)	0.1243 (2)	0.3533 (6)
O(23)	0.0796 (5)	0.0077 (2)	-0.2185 (5)	C(208)	0.0842 (6)	0.0889 (2)	0.4131 (7)
C(31)	0.4871 (7)	0.0570 (2)	0.2929 (7)	C(209)	0.0176 (7)	0.0624 (2)	0.4616 (7)
O(31)	0.5861 (4)	0.0604 (2)	0.3498 (5)	C(210)	-0.0980 (8)	0.0710 (3)	0.4510 (8)
C(32)	0.3559 (6)	0.0080 (2)	0.1000 (7)	C(211)	-0.1459 (6)	0.1054 (3)	0.3916 (9)
O(32)	0.3754 (5)	-0.0190 (2)	0.0424 (6)	C(212)	-0.0810 (6)	0.1327 (2)	0.3438 (7)
C(33)	0.2863 (6)	0.0205 (2)	0.3394 (8)	H(1a) ^b	0.3735	0.2128	0.5226
O(33)	0.2678 (6)	0.0007 (2)	0.4191 (6)	H(1b)	0.2944	0.2280	0.3805
C(41)	0.3291 (6)	0.1395 (2)	-0.1394 (7)	H(2a)	0.1650	0.2024	0.4815
O(41)	0.3234 (5)	0.1668 (2)	-0.2080 (5)	H(2b)	0.2410	0.1642	0.5266
C(42)	0.5174 (7)	0.0973 (2)	0.0357 (7)	H(102)	0.4538	0.2574	0.3597
O(42)	0.6183 (5)	0.1004 (2)	0.0608 (6)	H(103)	0.5751	0.2963	0.2687
C(43)	0.3325 (6)	0.0568 (2)	-0.1508 (8)	H(104)	0.6896	0.2666	0.1493
O(43)	0.3261 (5)	0.0340 (2)	-0.2372 (6)	H(105)	0.6860	0.1984	0.1231
H(12)	0.1197 (39)	0.1188 (13)	0.0912 (46)	H(106)	0.5622	0.1593	0.2042
H(13)	0.2931 (36)	0.0941 (12)	0.2854 (41)	H(108)	0.6537	0.1728	0.4936
H(14)	0.3679 (46)	0.1296 (16)	0.1207 (54)	H(109)	0.7812	0.1379	0.6784
H(23)	0.1678 (38)	0.0442 (13)	0.1172 (43)	H(110)	0.7065	0.0883	0.7867
P(1)	0.39930 (12)	0.17162 (4)	0.35051 (14)	H(111)	0.5048	0.0735	0.7104
P(2)	0.12814 (12)	0.15877 (4)	0.29650 (14)	H(112)	0.3783	0.1078	0.5247
C(1)	0.3208 (5)	0.2050 (2)	0.4358 (5)	H(202)	-0.0585	0.1569	0.0436
C(2)	0.2141 (5)	0.1835 (2)	0.4560 (5)	H(203)	-0.1795	0.2034	-0.1017
C(101)	0.4960 (5)	0.2043 (2)	0.2912 (5)	H(204)	-0.1638	0.2699	-0.0467
C(102)	0.5001 (5)	0.2452 (2)	0.3101 (6)	H(205)	-0.0378	0.2904	0.1639
C(103)	0.5728 (6)	0.2682 (2)	0.2566 (7)	H(206)	0.0832	0.2444	0.3154
C(104)	0.6408 (6)	0.2507 (2)	0.1862 (7)	H(208)	0.1642	0.0826	0.4210
C(105)	0.6373 (6)	0.2106 (2)	0.1696 (6)	H(209)	0.0522	0.0382	0.5024
C(106)	0.5650 (6)	0.1873 (2)	0.2192 (6)	H(210)	-0.1435	0.0530	0.4852
C(107)	0.5034 (5)	0.1441 (2)	0.4923 (6)	H(211)	-0.2267	0.1112	0.3817
C(108)	0.6230 (6)	0.1525 (2)	0.5378 (6)	H(212)	-0.1158	0.1571	0.3045

^a Esd's, shown in parentheses, are right adjusted to the least significant digit of the preceding number. They are derived from the inverse of the final least-squares matrix. ^b The hydrogens in the diphos ligand were included in the final model in their idealized calculated positions.

(1) The hydride atoms were removed from the model and the remaining parameters were refined to convergence once again. The resulting discrepancy indices were $R_F = 4.1\%$, $R_{wF} = 2.8\%$, and $\text{GOF} = 1.338$. Removal of the hydride ligands causes a significant increase in each of these indices.

(2) A difference-Fourier synthesis was carried out based on the model from (1) and using only those 874 reflections with $(\sin \theta)/\lambda < 0.3$. The four highest peaks, with heights 0.43, 0.43, 0.42, and 0.37 $e \text{ \AA}^{-3}$, appeared in the locations previously occupied by the bridging hydride ligands H(12), H(13), H(23), and H(14) (respectively). The appearance of these four peaks is illustrated in Figure 1. The next largest peak was of height 0.14 $e \text{ \AA}^{-3}$.

The positions of the hydride ligands are thus established unambiguously.

Final positional parameters with their estimated standard deviations (esd's) are collected in Table II; thermal parameters are listed in Table III.

Results and Discussion

Interatomic distances and their esd's are listed in Table IV; intramolecular angles (with esd's) are shown in Table V; selected least-squares planes are given in Table VI.

The crystal is composed of discrete ordered molecular units of $(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{10}(\text{diphos})$, which are mutually separated by normal van der Waals distances; there are no abnormally short intermolecular contacts. The geometry of the entire molecule is shown by the stereoscopic view of Figure 2. The scheme used for labeling atoms is shown in Figure 3, which is a view of the molecule (with the four phenyl groups of the diphos ligand omitted) projected onto the plane defined by

atoms Ru(2), Ru(3), and Ru(4). Carbon atoms of the phenyl groups are labeled cyclically, the first digit designating the phosphorus atom to which the phenyl group is attached. Thus, C(101) and C(107) are linked directly to P(1) while C(201) and C(207) are bonded to P(2). Hydrogen atoms are numbered identically with their attached carbon atoms.

The $(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{10}(\text{diphos})$ molecule is based upon a tetrahedral core of four ruthenium atoms. One of these ruthenium atoms [Ru(1)] is chelated by the diphos ligand and linked to a single terminal carbonyl ligand, while the remaining three ruthenium atoms [Ru(2), Ru(3), and Ru(4)] are each linked to three terminal carbonyl groups. The tetrahedral core approximates to C_3 symmetry, with the mirror plane containing the Ru(1)–Ru(4) vector and bisecting the Ru(2)–Ru(3) linkage.

The ruthenium–ruthenium distances fall into two clearly divided and distinct classes. The non-hydrido-bridged Ru–Ru linkages are "short" with bond lengths of 2.796 (1) \AA for Ru(2)–Ru(4) and 2.785 (1) \AA for Ru(3)–Ru(4), averaging 2.791 [7] \AA .²⁶ As such, these observed distances are in excellent agreement with nonbridged Ru–Ru vectors in other tetrahedral, tetranuclear ruthenium carbonyl hydride species—viz., 2.783 [13] \AA (average) in $\text{H}_2\text{Ru}_4(\text{CO})_{13}$,²⁷ 2.76 \AA (average) in $\text{H}_4\text{Ru}_4(\text{CO})_{11}[\text{P}(\text{OMe})_3]$,²¹ 2.786 [1] \AA (average) in (slightly disordered) $\text{H}_4\text{Ru}_4(\text{CO})_{12}$,²⁰ and 2.772 [2] \AA in $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{PPh}_3)_2$.²⁰ These "normal" ruthenium–ruthenium distances form a perfectly internally consistent set; they are, however, all substantially shorter than the average

Table III. Anisotropic Thermal Parameters^{a-c} for $(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{10}$ (diphos)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ru(1)	2.17 (2)	1.85 (2)	2.02 (2)	0.01 (2)	0.59 (2)	0.02 (2)
Ru(2)	3.02 (2)	2.45 (2)	3.01 (2)	-0.30 (2)	0.32 (2)	-0.36 (2)
Ru(3)	2.92 (2)	2.13 (2)	3.82 (3)	0.24 (2)	0.80 (2)	0.29 (2)
Ru(4)	3.70 (3)	3.08 (3)	3.18 (3)	-0.26 (2)	1.66 (2)	-0.69 (2)
C(11)	2.7 (3)	3.3 (3)	2.7 (3)	0.4 (2)	1.1 (2)	-0.1 (3)
O(11)	6.0 (3)	3.6 (2)	5.3 (2)	0.9 (2)	1.6 (2)	2.3 (2)
C(21)	4.5 (4)	3.9 (4)	3.7 (4)	-0.9 (3)	-0.4 (3)	-0.6 (3)
O(21)	9.1 (4)	5.4 (3)	5.4 (3)	0.3 (3)	-0.3 (3)	1.8 (2)
C(22)	4.0 (4)	3.5 (4)	5.1 (4)	-1.0 (3)	0.1 (3)	-0.2 (3)
O(22)	3.4 (3)	9.8 (4)	9.4 (4)	-1.6 (3)	1.4 (3)	1.7 (3)
C(23)	5.9 (4)	3.8 (4)	3.5 (4)	-0.5 (3)	0.8 (3)	-0.7 (3)
O(23)	11.1 (4)	5.1 (3)	6.2 (3)	-1.8 (3)	1.7 (3)	-3.0 (2)
C(31)	4.9 (4)	2.7 (3)	4.9 (4)	0.9 (3)	1.1 (3)	0.1 (3)
O(31)	3.6 (2)	7.6 (3)	7.7 (3)	0.8 (2)	0.1 (2)	-0.2 (2)
C(32)	4.8 (4)	3.8 (4)	5.9 (4)	0.5 (3)	1.6 (3)	-1.0 (3)
O(32)	8.3 (4)	4.2 (3)	11.0 (4)	0.6 (2)	3.3 (3)	-2.9 (3)
C(33)	5.9 (4)	3.9 (4)	5.8 (4)	1.0 (3)	2.0 (3)	1.7 (3)
O(33)	11.5 (4)	7.2 (4)	9.6 (4)	1.4 (3)	5.1 (3)	4.9 (3)
C(41)	6.5 (4)	5.1 (4)	3.4 (4)	-0.6 (3)	2.5 (3)	-0.7 (3)
O(41)	12.3 (4)	6.7 (3)	4.7 (3)	-0.7 (3)	3.4 (3)	2.0 (3)
C(42)	5.3 (4)	3.1 (3)	5.4 (4)	-0.7 (3)	2.6 (4)	-2.0 (3)
O(42)	4.8 (3)	7.9 (4)	9.8 (4)	-0.6 (3)	3.4 (3)	-3.6 (3)
C(43)	6.5 (4)	5.2 (4)	6.2 (4)	-1.6 (3)	3.6 (4)	-2.4 (4)
O(43)	10.9 (4)	8.9 (4)	9.7 (4)	-3.4 (3)	6.3 (3)	-6.1 (3)
P(1)	2.24 (7)	2.57 (7)	2.55 (7)	-0.03 (6)	0.58 (6)	-0.19 (6)
P(2)	2.21 (7)	2.67 (7)	2.48 (7)	-0.03 (6)	0.72 (6)	-0.14 (6)
C(1)	2.4 (3)	3.6 (3)	2.9 (3)	0.1 (2)	0.2 (2)	-0.9 (2)
C(2)	2.6 (3)	4.1 (3)	3.0 (3)	0.6 (2)	0.9 (2)	-0.3 (2)
C(101)	2.4 (3)	2.5 (3)	2.8 (3)	-0.6 (2)	0.1 (2)	-0.3 (2)
C(102)	2.8 (3)	3.5 (4)	3.5 (3)	-0.2 (3)	0.4 (2)	0.3 (3)
C(103)	4.2 (4)	2.9 (3)	4.6 (4)	-1.0 (3)	-0.1 (3)	1.0 (3)
C(104)	3.6 (4)	6.3 (5)	4.2 (4)	-1.7 (4)	0.9 (3)	1.0 (3)
C(105)	3.7 (4)	5.9 (5)	4.7 (4)	-1.6 (3)	2.1 (3)	-1.0 (3)
C(106)	3.8 (3)	3.9 (3)	5.3 (4)	-1.0 (3)	2.4 (3)	-1.3 (3)
C(107)	2.2 (3)	3.4 (3)	2.6 (3)	0.2 (2)	0.6 (2)	-0.4 (2)
C(108)	3.1 (4)	3.5 (3)	3.8 (3)	0.2 (3)	0.6 (3)	-0.2 (3)
C(109)	3.0 (3)	6.2 (4)	4.9 (4)	1.3 (3)	-0.3 (3)	0.0 (4)
C(110)	5.4 (5)	8.1 (5)	4.0 (4)	2.9 (4)	-0.0 (4)	1.9 (4)
C(111)	5.9 (5)	6.6 (5)	4.4 (4)	1.3 (4)	1.8 (4)	2.6 (4)
C(112)	2.7 (3)	5.6 (4)	3.4 (3)	0.1 (3)	0.6 (3)	0.8 (3)
C(201)	1.8 (3)	2.8 (3)	2.9 (3)	0.1 (2)	0.9 (2)	-0.2 (2)
C(202)	3.4 (3)	3.1 (3)	3.8 (3)	1.0 (3)	0.4 (3)	-0.4 (3)
C(203)	4.6 (4)	5.7 (4)	4.1 (4)	1.7 (4)	0.7 (3)	-0.5 (4)
C(204)	4.7 (4)	4.8 (4)	5.2 (4)	1.9 (3)	0.9 (3)	1.4 (4)
C(205)	5.2 (4)	2.6 (3)	7.3 (5)	0.3 (3)	1.7 (4)	-0.5 (4)
C(206)	3.2 (3)	3.4 (4)	4.9 (4)	0.5 (3)	0.2 (3)	-0.9 (3)
C(207)	3.0 (3)	3.4 (3)	2.8 (3)	0.2 (2)	1.3 (2)	0.2 (2)
C(208)	4.0 (3)	4.2 (4)	5.3 (4)	-0.9 (3)	2.4 (3)	0.1 (3)
C(209)	6.6 (5)	5.2 (4)	6.5 (4)	-0.6 (4)	3.7 (4)	0.4 (3)
C(210)	6.4 (5)	6.3 (5)	6.7 (5)	-2.4 (4)	3.6 (4)	-0.0 (4)
C(211)	4.6 (4)	7.7 (6)	8.8 (6)	-1.0 (4)	3.8 (4)	1.1 (5)
C(212)	3.2 (4)	5.5 (4)	6.2 (4)	0.3 (3)	1.8 (3)	1.1 (3)

Atom	$B, \text{Å}^2$	Atom	$B, \text{Å}^2$	Atom	$B, \text{Å}^2$
H(12)	3.8 (12)	H(103)	5.1	H(203)	5.9
H(13)	2.7 (10)	H(104)	5.4	H(204)	5.9
H(14)	6.0 (14)	H(105)	5.5	H(205)	6.0
H(23)	3.4 (11)	H(106)	5.0	H(206)	5.1
H(1a)	4.0	H(108)	4.6	H(208)	5.4
H(1b)	4.0	H(109)	5.8	H(209)	6.6
H(2a)	4.2	H(110)	6.7	H(210)	6.9
H(2b)	4.2	H(111)	6.5	H(211)	7.2
H(102)	4.3	H(112)	4.8	H(212)	5.8
		H(202)	4.6		

^a The anisotropic thermal parameter is defined by $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^{*}b^{*} + 2B_{13}hla^{*}c^{*} + 2B_{23}klb^{*}c^{*})]$.

^b Isotropic thermal parameters are given for the hydrogen atoms. For those hydrogen atoms in the diphos ligand, B was fixed at a value 1.0 Å^2 greater than the isotropic factor of the corresponding carbon to which the hydrogen is bound. ^c Esd's, shown in parentheses, are right adjusted to the least significant digit of the preceding number.

Ru-Ru distance of 2.854 [5] Å in the *trinuclear* species $\text{Ru}_3(\text{CO})_{12}$.²²

The remaining four ruthenium-ruthenium distances are "long", individual values (in order of decreasing length) being Ru(1)-Ru(3) = 3.006 (1), Ru(1)-Ru(2) = 2.998 (1),

Ru(1)-Ru(4) = 2.946 (1), and Ru(2)-Ru(3) = 2.931 (1) Å . These metal-metal vectors are those shown to be spanned by μ_2 -bridging hydride ligands; the average distance of 2.970 [37] Å is 0.18 Å longer than the average nonbridged distance of 2.791 [7] Å . Our simplistic view of these data is that they

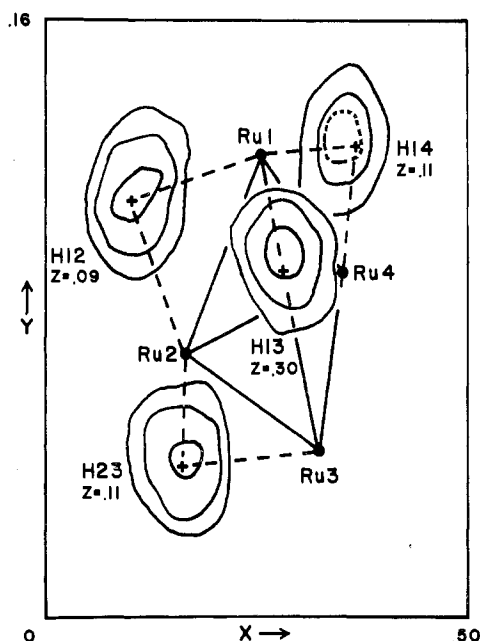


Figure 1. Difference-Fourier synthesis, based upon the model with hydride ligands omitted and using only those data with $(\sin \theta)/\lambda < 0.30 \text{ \AA}^{-1}$. Contours are at 0.1-electron intervals, the lowest such contour being at 0.2 e \AA^{-3} . (The highest contour for H(14) is, however, at 0.35 e \AA^{-3} .) Final (refined) ruthenium and hydride ligand positions are shown as filled circles and crosses, respectively.

are consistent with the $M(\mu\text{-H})M$ bond being represented as a closed two-electron, three-center bond (IV);³ an $M(\mu\text{-H})M$



system then, *by definition*, has less bonding electron density between the metal atoms than does a normal two-electron, two-center covalent $M\text{-}M$ σ bond; concomitantly, the metal-metal distance in a $M(\mu\text{-H})M$ system is expanded relative to a normal $M\text{-}M$ σ bond.

We note here that μ_2 -hydrido-bridged ruthenium-ruthenium vectors in other tetrahedral carbonyl clusters are 2.930 [12] \AA (average) in $\text{H}_2\text{Ru}_4(\text{CO})_{13}$,²⁷ 2.93 \AA (average) in $\text{H}_4\text{Ru}_4(\text{CO})_{11}[\text{P}(\text{OMe})_3]$,²¹ 2.950 [1] \AA (average) in $\text{H}_4\text{Ru}_4(\text{CO})_{12}$,²⁰ and 2.966 [2] \AA (average) in $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{PPh}_3)_2$.²⁰ The μ_3 -hydrido-bridged $\text{Ru}\text{-Ru}$ vectors in the *octahedral* cluster $\text{H}_2\text{Ru}_6(\text{CO})_{18}$ have similar values, averaging 2.954 \AA .²

The present structural study of $(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{10}(\text{diphos})$ has two unique features.

(1) Unlike the arrangement of hydride ligands surmised for $\text{H}_4\text{Ru}_4(\text{CO})_{12}$, $\text{H}_4\text{Ru}_4(\text{CO})_{11}[\text{P}(\text{OMe})_3]$, and H_4Ru_4 -

Table IV. Interatomic Distances and Esd's (\AA) for $(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{10}(\text{diphos})$

(a) "Short" Ruthenium-Ruthenium Distances			
Ru(2)-Ru(4)	2.796 (1)	Ru(3)-Ru(4)	2.785 (1)
		Av	2.791 (7) ^a

(b) "Long" Ruthenium-Ruthenium Distances			
Ru(1)-Ru(2)	2.998 (1)	Ru(1)-Ru(4)	2.946 (1)
Ru(1)-Ru(3)	3.006 (1)	Ru(2)-Ru(3)	2.931 (1)
		Av	2.970 (37) ^a

(c) Ruthenium-Hydrogen Distances			
Ru(1)-H(12)	1.73 (5)	Ru(1)-H(14)	1.64 (6)
Ru(2)-H(12)	1.80 (4)	Ru(4)-H(14)	1.76 (5)
Ru(1)-H(13)	1.77 (4)	Ru(2)-H(23)	1.81 (4)
Ru(3)-H(13)	1.80 (4)	Ru(3)-H(23)	1.78 (5)
		Av	1.76 (6) ^a

(d) Ruthenium-Phosphorus Distances			
Ru(1)-P(1)	2.303 (2)	Ru(1)-P(2)	2.321 (2)

(e) Ruthenium-Carbonyl Carbon Distances			
Ru(1)-C(11)	1.857 (6)	Ru(3)-C(32)	1.873 (7)
Ru(2)-C(21)	1.872 (7)	Ru(3)-C(33)	1.917 (7)
Ru(2)-C(22)	1.927 (8)	Ru(4)-C(41)	1.898 (7)
Ru(2)-C(23)	1.910 (7)	Ru(4)-C(42)	1.892 (8)
Ru(3)-C(31)	1.895 (8)	Ru(4)-C(43)	1.874 (8)
		Av	1.892 (22) ^a

(f) Carbon-Oxygen Distances			
C(11)-O(11)	1.146 (7)	C(32)-O(32)	1.145 (9)
C(21)-O(21)	1.154 (8)	C(33)-O(33)	1.127 (10)
C(22)-O(22)	1.133 (10)	C(41)-O(41)	1.143 (9)
C(23)-O(23)	1.129 (8)	C(42)-O(42)	1.148 (10)
C(31)-O(31)	1.142 (9)	C(43)-O(43)	1.156 (10)
		Av	1.142 (10) ^a

(g) Phosphorus-Carbon and Carbon-Carbon Distances			
P(1)-C(1)	1.846 (6)	P(2)-C(2)	1.834 (6)
P(1)-C(101)	1.826 (6)	P(2)-C(201)	1.831 (6)
P(1)-C(107)	1.836 (6)	P(2)-C(207)	1.818 (6)
C(1)-C(2)	1.529 (8)		

(h) Carbon-Carbon (Phenyl) Distances			
C(101)-C(102)	1.383 (8)	C(104)-C(105)	1.354 (12)
C(102)-C(103)	1.395 (9)	C(105)-C(106)	1.373 (10)
C(103)-C(104)	1.375 (10)	C(106)-C(101)	1.388 (9)
C(107)-C(108)	1.378 (9)	C(110)-C(111)	1.373 (12)
C(108)-C(109)	1.388 (10)	C(111)-C(112)	1.384 (10)
C(109)-C(110)	1.370 (11)	C(112)-C(107)	1.381 (9)
C(201)-C(202)	1.389 (8)	C(204)-C(205)	1.361 (11)
C(202)-C(203)	1.376 (9)	C(205)-C(206)	1.390 (10)
C(203)-C(204)	1.350 (11)	C(206)-C(201)	1.373 (9)
C(207)-C(208)	1.378 (9)	C(210)-C(211)	1.342 (13)
C(208)-C(209)	1.383 (11)	C(211)-C(212)	1.384 (11)
C(209)-C(210)	1.373 (13)	C(212)-C(207)	1.382 (9)
		Av	1.376 (13) ^a

^a Esd's on average distances are calculated via the "scatter equation", i.e., $\sigma(\text{av}) = [\sum(d_i - \bar{d})^2 / (N - 1)]^{1/2}$, where \bar{d} is the average distance, d_i is the i th such distance, and the sum is over N equivalent distances. The resulting value is an *external* estimate of the esd of any one individual measurement.

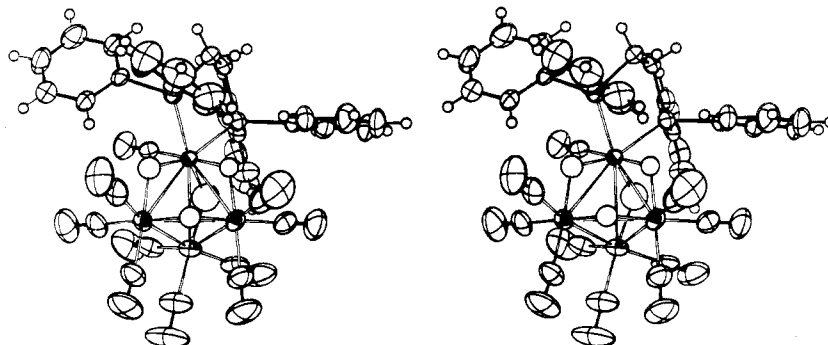


Figure 2. Stereoscopic diagram of $(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{10}(\text{diphos})$.

Table V. Angles (in deg, with Esd's) within the (μ -H) $_2$ Ru $_4$ (CO) $_{10}$ (diphos) Molecule

Ru(2)-Ru(1)-Ru(3)	58.45 (2)	Ru(1)-Ru(2)-Ru(3)	60.91 (2)	Ru(1)-Ru(4)-Ru(2)	62.88 (2)
Ru(2)-Ru(1)-Ru(4)	56.10 (2)	Ru(1)-Ru(3)-Ru(4)	61.03 (2)	Ru(1)-Ru(4)-Ru(3)	63.19 (2)
Ru(3)-Ru(1)-Ru(4)	55.78 (2)	Ru(2)-Ru(3)-Ru(4)	58.49 (2)	Ru(2)-Ru(4)-Ru(3)	63.37 (2)
Ru(1)-H(12)-Ru(2)	116.5 (26)	H(12)-Ru(1)-P(1)	114.8 (23)	H(13)-Ru(1)-P(1)	88.8 (14)
H(12)-Ru(1)-Ru(2)	32.5 (15)	H(12)-Ru(1)-P(2)	81.8 (14)	H(13)-Ru(1)-P(2)	91.2 (14)
H(12)-Ru(1)-Ru(3)	82.2 (15)	H(13)-Ru(1)-Ru(2)	32.8 (14)	H(13)-Ru(1)-C(11)	177.0 (14)
H(12)-Ru(1)-Ru(4)	87.2 (15)	H(13)-Ru(1)-C(11)	87.4 (14)	H(13)-Ru(3)-C(31)	89.5 (14)
H(12)-Ru(2)-Ru(1)	31.0 (15)	H(13)-Ru(1)-Ru(4)	32.3 (13)	H(13)-Ru(3)-C(32)	175.7 (14)
H(12)-Ru(2)-Ru(3)	83.3 (15)	H(13)-Ru(3)-Ru(2)	83.4 (13)	H(13)-Ru(3)-C(33)	86.3 (14)
H(12)-Ru(2)-Ru(4)	90.6 (15)	H(13)-Ru(3)-Ru(4)	92.1 (13)	H(23)-Ru(2)-C(21)	176.2 (14)
Ru(1)-H(14)-Ru(4)	119.8 (31)	Ru(2)-H(23)-Ru(3)	109.6 (23)	H(23)-Ru(2)-C(22)	83.3 (14)
H(14)-Ru(1)-Ru(2)	87.3 (19)	H(23)-Ru(2)-Ru(1)	83.0 (14)	H(23)-Ru(2)-C(23)	88.3 (14)
H(14)-Ru(1)-Ru(3)	69.2 (19)	H(23)-Ru(2)-Ru(3)	34.9 (14)	H(23)-Ru(3)-C(31)	178.0 (14)
H(14)-Ru(1)-Ru(4)	31.2 (19)	H(23)-Ru(2)-C(21)	92.0 (14)	H(23)-Ru(3)-C(32)	90.6 (14)
H(14)-Ru(4)-Ru(1)	29.0 (18)	H(23)-Ru(3)-Ru(1)	83.2 (14)	H(23)-Ru(3)-C(33)	81.2 (14)
H(14)-Ru(4)-Ru(2)	91.9 (18)	H(23)-Ru(3)-Ru(2)	35.5 (14)	H(13)-Ru(3)-H(23)	90.0 (20)
H(14)-Ru(4)-Ru(3)	74.5 (18)	H(23)-Ru(3)-Ru(4)	92.9 (14)		
H(12)-Ru(1)-H(13)	91.9 (20)	H(12)-Ru(2)-H(23)	90.6 (20)		
H(12)-Ru(1)-H(14)	118.0 (24)				
Ru(2)-Ru(1)-C(11)	99.76 (18)	Ru(1)-Ru(2)-C(21)	97.28 (21)	Ru(1)-Ru(4)-C(41)	95.72 (22)
Ru(3)-Ru(1)-C(11)	146.46 (18)	Ru(3)-Ru(2)-C(21)	146.24 (21)	Ru(2)-Ru(4)-C(41)	102.77 (22)
Ru(4)-Ru(1)-C(11)	91.30 (18)	Ru(4)-Ru(2)-C(21)	89.02 (21)	Ru(3)-Ru(4)-C(41)	158.06 (22)
Ru(2)-Ru(1)-P(1)	166.55 (4)	Ru(1)-Ru(2)-C(22)	143.58 (22)	Ru(1)-Ru(4)-C(42)	112.56 (22)
Ru(3)-Ru(1)-P(1)	108.88 (4)	Ru(3)-Ru(2)-C(22)	94.61 (22)	Ru(2)-Ru(4)-C(42)	162.73 (22)
Ru(4)-Ru(1)-P(1)	114.20 (4)	Ru(4)-Ru(2)-C(22)	83.63 (22)	Ru(3)-Ru(4)-C(42)	99.46 (22)
Ru(2)-Ru(1)-P(2)	104.75 (4)	Ru(1)-Ru(2)-C(23)	116.21 (22)	Ru(1)-Ru(4)-C(43)	149.73 (23)
Ru(3)-Ru(1)-P(2)	117.93 (4)	Ru(3)-Ru(2)-C(23)	115.36 (22)	Ru(2)-Ru(4)-C(43)	87.13 (23)
Ru(4)-Ru(1)-P(2)	160.80 (4)	Ru(4)-Ru(2)-C(23)	173.81 (22)	Ru(3)-Ru(4)-C(43)	100.97 (23)
C(11)-Ru(1)-P(1)	89.27 (19)	C(21)-Ru(2)-C(22)	90.15 (30)	C(41)-Ru(4)-C(42)	94.18 (31)
C(11)-Ru(1)-P(2)	90.89 (19)	C(21)-Ru(2)-C(23)	96.92 (31)	C(41)-Ru(4)-C(43)	94.88 (32)
P(1)-Ru(1)-P(2)	84.90 (5)	C(22)-Ru(2)-C(23)	98.03 (31)	C(42)-Ru(4)-C(43)	94.81 (32)
Ru(1)-C(11)-O(11)	178.1 (5)	Ru(2)-C(23)-O(23)	175.7 (7)	Ru(4)-C(42)-O(42)	175.1 (6)
Ru(2)-C(21)-O(21)	176.6 (6)	Ru(3)-C(31)-O(31)	175.5 (6)	Ru(4)-C(43)-O(42)	175.9 (7)
Ru(2)-C(22)-O(22)	177.5 (6)	Ru(3)-C(32)-O(33)	176.4 (6)		
Ru(1)-P(1)-C(1)	107.41 (18)	Ru(1)-P(1)-C(101)	108.70 (19)	C(2)-P(2)-C(201)	106.47 (26)
Ru(1)-P(1)-C(101)	115.89 (19)	C(1)-P(1)-C(107)	110.58 (18)	C(2)-P(2)-C(207)	103.03 (27)
Ru(1)-P(1)-C(107)	119.71 (19)	C(101)-P(1)-C(107)	122.13 (20)	C(201)-P(2)-C(207)	104.78 (26)
P(1)-C(1)-C(2)	110.0 (4)	P(2)-C(201)-C(202)	122.1 (4)	P(2)-C(207)-C(208)	118.5 (5)
P(1)-C(101)-C(102)	123.2 (4)	P(2)-C(201)-C(206)	119.0 (4)	P(2)-C(207)-C(212)	122.8 (5)
P(1)-C(101)-C(106)	118.0 (4)	P(2)-C(2)-C(1)	110.1 (4)		
C(106)-C(101)-C(102)	118.9 (5)	C(103)-C(104)-C(105)	119.4 (7)	C(203)-C(204)-C(205)	119.7 (7)
C(101)-C(102)-C(103)	119.6 (6)	C(104)-C(105)-C(106)	121.2 (7)	C(204)-C(205)-C(206)	120.8 (7)
C(102)-C(103)-C(104)	120.6 (6)	C(105)-C(106)-C(101)	120.4 (6)	C(205)-C(206)-C(201)	119.6 (6)
C(112)-C(107)-C(108)	118.9 (6)	C(109)-C(110)-C(111)	119.9 (8)	C(209)-C(210)-C(211)	119.1 (8)
C(107)-C(108)-C(109)	120.5 (6)	C(110)-C(111)-C(112)	120.0 (7)	C(210)-C(211)-C(212)	121.7 (8)
C(108)-C(109)-C(110)	120.1 (7)	C(111)-C(112)-C(107)	120.6 (6)	C(211)-C(212)-C(207)	119.7 (7)

(a) Angles within Ru $_4$ Tetrahedron

Ru(1)-Ru(3)-Ru(2)
 Ru(1)-Ru(3)-Ru(4)
 Ru(2)-Ru(3)-Ru(4)

(b) Angles Involving Hydrides

Ru(1)-H(13)-Ru(3)
 H(13)-Ru(1)-Ru(2)
 H(13)-Ru(1)-Ru(3)
 H(13)-Ru(1)-Ru(4)
 H(13)-Ru(3)-Ru(1)
 H(13)-Ru(3)-Ru(2)
 H(13)-Ru(3)-Ru(4)
 Ru(2)-H(23)-Ru(3)
 H(23)-Ru(2)-Ru(1)
 H(23)-Ru(2)-Ru(3)
 H(23)-Ru(2)-Ru(4)
 H(23)-Ru(3)-Ru(1)
 H(23)-Ru(3)-Ru(2)
 H(23)-Ru(3)-Ru(4)
 H(12)-Ru(2)-H(23)

(c) Ru-Ru-CO and Ru-Ru-P Angles

Ru(1)-Ru(3)-C(31)
 Ru(2)-Ru(3)-C(31)
 Ru(4)-Ru(3)-C(31)
 Ru(1)-Ru(3)-C(32)
 Ru(2)-Ru(3)-C(32)
 Ru(4)-Ru(3)-C(32)
 Ru(1)-Ru(3)-C(33)
 Ru(2)-Ru(3)-C(33)
 Ru(4)-Ru(3)-C(33)

(d) CO-Ru-CO and CO-Ru-P Angles

C(31)-Ru(3)-C(32)
 C(31)-Ru(3)-C(33)
 C(32)-Ru(3)-C(33)
 (e) Ru-C-O Angles
 Ru(3)-C(33)-O(33)
 Ru(4)-C(41)-O(41)
 Ru(4)-C(41)-O(41)

(f) Ru-P-C and C-P-C Angles

C(1)-P(1)-C(101)
 C(1)-P(1)-C(107)
 C(101)-P(1)-C(107)

(g) P-C-C Angles

P(2)-C(201)-C(202)
 P(2)-C(201)-C(206)
 (h) Phenyl C-C-C Angles
 C(206)-C(201)-C(202)
 C(201)-C(202)-C(203)
 C(202)-C(203)-C(204)
 C(212)-C(207)-C(208)
 C(207)-C(208)-C(209)
 C(208)-C(209)-C(210)

Table VI. Least-Squares Planes^{a, b} and Deviations of Atoms Therefrom^c

Atom	Dev, Å	Atom	Dev, Å
Plane I: $0.5051X - 0.1084Y + 0.8562Z = 4.1858$			
C(101)*	-0.0002	C(105)*	-0.0096
C(102)*	-0.0039	C(106)*	0.0064
C(103)*	0.0036	P(1)	0.0627
C(104)*	0.0040	Ru(1)	1.9188
Plane II: $-0.3761X + 0.6766Y + 0.6331Z = 4.6550$			
C(107)*	-0.0050	C(111)*	-0.0027
C(108)*	0.0024	C(112)*	0.0059
C(109)*	0.0019	P(1)	-0.0477
C(110)*	-0.0031	Ru(1)	1.3378
Plane III: $-0.8930X - 0.1359Y + 0.4290Z = 0.2195$			
C(201)*	0.0042	C(205)*	-0.0039
C(202)*	0.0014	C(206)*	-0.0051
C(203)*	-0.0120	P(2)	0.2065
C(204)*	0.0144	Ru(1)	2.2903
Plane IV: $0.0256X + 0.4462Y + 0.8946Z = 4.9249$			
C(207)*	0.0020	C(211)*	0.0095
C(208)*	0.0007	C(212)*	-0.0060
C(209)*	-0.0015	P(2)	-0.0524
C(210)*	-0.0035	Ru(1)	1.2146
Plane V: $-0.0196X + 0.8260Y - 0.5633Z = 2.7632$			
P(1)*	0.0000	C(2)	-0.1989
Ru(1)*	0.0000	H(13)	-1.7702
P(2)*	0.0000	C(11)	1.8562
C(1)	0.4819		

^a Equations to planes are expressed in orthonormal coordinates (X, Y, Z) which are related to the fractional coordinates (x, y, z) via the transformation

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & 0 & c \cos \beta \\ 0 & b & 0 \\ 0 & 0 & c \sin \beta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

^b Only atoms marked with an asterisk were included in calculation of the plane. ^c Important interplanar angles: plane I-plane II = 73.81°; plane III-plane IV = 72.53°.

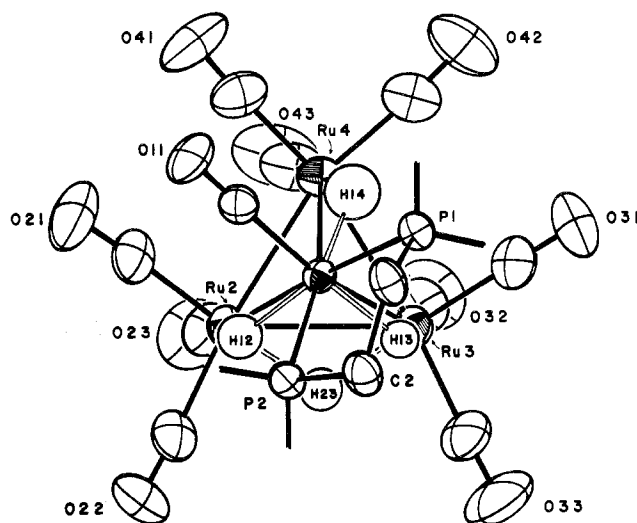


Figure 3. Labeling of atoms in the $(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{10}(\text{diphos})$ molecule. (Phenyl rings and hydrogen atoms on C(1) and C(2) are omitted for clarity.) Ru(1) is unlabeled and occupies the apex of the tetrahedron in the center of the figure.

$(\text{CO})_{10}(\text{PPh}_3)_2$ —see structure II—the present molecule has a $(\mu\text{-H})_4\text{Ru}_4$ core of only C_s symmetry, with three μ_2 -bridging hydride ligands bound to Ru(1) and only one to Ru(4) (i.e., structure III).

(2) This is the first structural study of a tetranuclear ruthenium carbonyl hydride derivative in which the hydride ligands have been located directly. All four hydride ligands

were well-behaved upon refinement, and their positional and isotropic thermal parameters converged satisfactorily. [Final thermal parameters were 3.8 (12) Å² for H(12), 2.7 (10) Å² for H(13), 6.0 (14) Å² for H(14), and 3.4 (11) Å² for H(23).] The four Ru-H-Ru systems appear to be symmetrical. Interatomic distances and angles are as follows: Ru(1)-H(12) = 1.73 (5) Å, Ru(2)-H(12) = 1.80 (4) Å, Ru(1)-H(12)-Ru(2) = 116.5 (26)°; Ru(1)-H(13) = 1.77 (4) Å, Ru(3)-H(13) = 1.80 (4) Å, Ru(1)-H(13)-Ru(3) = 114.8 (23)°; Ru(1)-H(14) = 1.64 (6) Å, Ru(4)-H(14) = 1.76 (5) Å, Ru(1)-H(14)-Ru(4) = 119.8 (31)°; Ru(2)-H(23) = 1.81 (4) Å, Ru(3)-H(23) = 1.78 (5) Å, Ru(2)-H(23)-Ru(3) = 109.6 (23)°. The average Ru-H distance is 1.76 [6] Å and the average Ru-H-Ru angle is 115 [4]°.

The ten carbonyl ligands are all in terminal locations and the associated Ru(CO)₃ or Ru(CO)₂P₂ moieties are staggered relative to the appropriate opposite triangular Ru₃ face; the Ru-C-O systems are each close to linear, individual values ranging from 175.1 (6) to 179.2 (6)° (average = 176.8 [13]°). The average ruthenium-carbonyl and carbon-oxygen bond distances are 1.892 [22] and 1.142 [10] Å, respectively. The larger esd associated with the average ruthenium-carbonyl (vis-a-vis carbon-oxygen) distance suggests that the Ru-CO linkages may be nonequivalent. This appears to be the case. The shortest, Ru(1)-C(11) = 1.857 (6) Å, is that associated with the tri- μ -hydrido-bridged atom, Ru(1). Ru-CO distances trans to bridging hydride ligands range from 1.872 (7) to 1.910 (7) Å, averaging 1.885 [16] Å; those trans to Ru-Ru linkages vary from 1.892 (8) to 1.927 (8) Å (average = 1.909 [16] Å).

The six carbonyl ligands that are trans to bridging hydride ligands are associated with H-Ru-CO (trans) angles ranging from 173.3 (15) to 178.0 (14)° (average = 175.9 (16)°). The two phosphorus atoms are also trans to bridging hydride ligands; here the H-Ru-P angles are 158.6 (15) and 167.9 (19)° (average = 163.7 [66]°). The distortion from linearity results directly from the chelation of the diphos ligand (P(1)-Ru(1)-P(2) = 84.90 (5)°).

The diphos ligand is bonded to the cluster with ruthenium-phosphorus distances of Ru(1)-P(1) = 2.303 (2) Å and Ru(1)-P(2) = 2.321 (2) Å. The five-membered Ru-P-C-C-P ring has the usual puckered geometry. The absolute configuration of the diphos ligand shown in Figure 3 is that described as "λ". Thus, C(1) lies +0.482 Å and C(2) lies -0.199 Å from the P(1)-Ru(1)-P(2) plane. (For reference purposes, C(11) lies +1.856 Å and H(13) lies -1.77 Å from the P(1)-Ru(1)-P(2) plane—see Table VI.)

Phosphorus-phenyl bond lengths range from 1.818 (6) to 1.836 (6) Å, the average value being 1.828 [8] Å. Phosphorus-C(sp³) distances are P(1)-C(1) = 1.846 (6) Å and P(2)-C(2) = 1.834 (6) Å (average = 1.840 [8] Å).

Distances and angles within the phenyl groups are all normal. The six-membered carbocyclic rings are each planar within the limits of experimental error (see Table VI). As expected, internal angles at the P-bonded carbon atoms are each reduced from the regular trigonal angle:²⁸ C(106)-C(101)-C(102) = 118.9 (5), C(112)-C(107)-C(108) = 118.9 (6), C(206)-C(201)-C(202) = 118.9 (5), C(212)-C(207)-C(208) = 118.7 (6)°.

Finally, it should be noted that, while the $\text{H}_4\text{Ru}_4(\text{CO})_{10}$ -(diphos) molecule overall obeys the EAN rule (60 outer valence electrons for a tetrahedral cluster²⁹), individual ruthenium atoms do not.

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Registry No. $(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{10}(\text{diphos})$, 66322-95-0.

Supplementary Material Available: Listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) For our previous contributions in this area, see ref 2 and 3.
- (2) $(\mu_3\text{-H})_2\text{Ru}_6(\text{CO})_{18}$: M. R. Churchill and J. Wormald, *J. Am. Chem. Soc.*, **93**, 5670 (1971).
- (3) $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\text{C}=\text{NMe}_2)$: M. R. Churchill, B. G. DeBoer, and F. J. Rotella, *Inorg. Chem.*, **15**, 1843 (1976).
- (4) $\text{HR}_2\text{Mn}(\text{CO})_{14}$: M. R. Churchill and R. Bau, *Inorg. Chem.*, **6**, 2086 (1967).
- (5) $[\text{H}_2\text{Re}_3(\text{CO})_{12}]^-$: M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Am. Chem. Soc.*, **90**, 7135 (1968).
- (6) $[\text{HRe}_3(\text{CO})_{12}]^{2-}$: S. W. Kirtley, H. D. Kaesz, M. R. Churchill, and C. Knobler, in preparation; S. W. Kirtley, Ph.D. Dissertation, UCLA, 1972.
- (7) $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$: H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley, and M. R. Churchill, *J. Am. Chem. Soc.*, **91**, 1021 (1969).
- (8) $\text{H}_6\text{Cu}_6(\text{PPh}_3)_6$: M. R. Churchill, S. A. Bezman, J. A. Osborn, and J. Wormald, *Inorg. Chem.*, **11**, 1818 (1972).
- (9) $[(\text{C}_5\text{Me}_5)\text{RhCl}]_2(\mu\text{-H})(\mu\text{-Cl})$: M. R. Churchill and S. W. Ni, *J. Am. Chem. Soc.*, **95**, 2150 (1973).
- (10) $[(\text{C}_5\text{Me}_5)\text{IrCl}]_2(\mu\text{-H})(\mu\text{-Cl})$: M. R. Churchill and S. A. Julis, *Inorg. Chem.*, **16**, 1488 (1977).
- (11) $[\text{H}_2\text{W}_2(\text{CO})_2]^{2-}$: M. R. Churchill and S. W. Chang, *Inorg. Chem.*, **13**, 2413 (1974).
- (12) $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{11}$: M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **16**, 878 (1977).
- (13) $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CHCH}_2\text{PMe}_2\text{Ph})$: M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **16**, 1141 (1977).
- (14) $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$: M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **16**, 2397 (1977).
- (15) $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$: M. R. Churchill, F. J. Hollander, and J. P. Hutchinson, *Inorg. Chem.*, **16**, 2697 (1977).
- (16) $(\mu\text{-H})\text{Os}_3(\text{CO})_8[\text{C}(\text{O}-)\text{C}(\text{CHMe}-)\text{CHCHCtEt}]$: M. R. Churchill, R. A. Lashewycz, M. Tachikawa, and J. R. Shapley, *J. Chem. Soc., Chem. Commun.*, 699 (1977).
- (17) $(\mu\text{-H})_2\text{Os}_3\text{Re}_2(\text{CO})_{26}$: J. R. Shapley, G. A. Pearson, M. Tachikawa, G. D. Schmidt, M. R. Churchill, and F. J. Hollander, *J. Am. Chem. Soc.*, **99**, 8064 (1977).
- (18) J. R. Shapley, S. I. Richter, M. R. Churchill, and R. A. Lashewycz, *J. Am. Chem. Soc.*, **99**, 7384 (1977).
- (19) (a) R. D. Wilson and R. Bau, *J. Am. Chem. Soc.*, **98**, 4687 (1976); (b) G. Huttner and H. Lorenz, *Chem. Ber.*, **108**, 973 (1975).
- (20) R. D. Wilson, S. M. Wu, R. A. Love, and R. Bau, submitted for publication in *Inorg. Chem.* (We thank Professor R. Bau for providing a copy of this manuscript prior to publication.)
- (21) Reported in footnote 24 of ref 19.
- (22) M. R. Churchill, F. J. Hollander, and J. P. Hutchinson, *Inorg. Chem.*, **16**, 2655 (1977).
- (23) M. R. Churchill, R. A. Lashewycz, and F. J. Rotella, *Inorg. Chem.*, **16**, 265 (1977).
- (24) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974: (a) pp 99-101; (b) pp 149-150.
- (25) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).
- (26) Esd's on average values are shown in square brackets.
- (27) D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.*, **11**, 828 (1972).
- (28) A. Domenicano, A. Vacigo, and C. A. Coulson, *Acta Crystallogr., Sect. B*, **31**, 1630 (1975).
- (29) H. D. Kaesz, *Chem. Br.*, **9**, 344 (1973).

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Crystal and Molecular Structure of a Tantalum-Alkylidene Complex, $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$

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Bis(η^5 -cyclopentadienyl)chloro(neopentylidene)tantalum, $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$, previously prepared by Schrock, has been subjected to a full three-dimensional single-crystal X-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^2 ; No. 14] with $a = 6.5957$ (8) Å, $b = 15.4418$ (19) Å, $c = 14.3363$ (19) Å, $\beta = 103.023$ (10)°, $V = 1422.6$ (3) Å³, and $\rho(\text{calcd}) = 1.946$ g cm⁻³ for $Z = 4$ and mol wt 416.73. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer using Mo $K\alpha$ radiation. The structure was solved via a combination of Patterson, Fourier, and least-squares refinement techniques. Final discrepancy indices are $R_F = 2.7\%$ and $R_{wF} = 2.3\%$ for the 1870 reflections with $4^\circ < 2\theta < 45^\circ$ (no reflections rejected). All atoms, including all hydrogen atoms, were located and refined. The two $\eta^5\text{-C}_5\text{H}_5$ rings subtend an angle of 130.9° at the metal atom; the chloride and neopentylidene ligand occupy equatorial coordination sites, with $d(\text{Ta}-\text{Cl}) = 2.479$ (2) Å and $\text{Cl}-\text{Ta}-\text{C}(1) = 97.63$ (18)°. The tantalum-neopentylidene linkage is 2.030 (6) Å, consistent with its formulation as $\text{Ta}=\text{CHCMe}_3$. A surprising feature of the analysis is the $\text{Ta}=\text{C}(1)-\text{C}(2)$ angle of 150.4 (5)°—some 30° greater than the normal sp^2 -hybridized (trigonal-planar) angle of 120° .

Introduction

Alkylidene and alkylidyne complexes of tantalum have recently been synthesized by Schrock and co-workers;¹⁻⁶ X-ray diffraction studies have previously been reported for the methylene complex $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_2)(\text{CH}_3)$ ⁴ and for the neopentylidyne complex $[(\text{Me}_3\text{CCH}_2)_3\text{Ta}=\text{CCMe}_3]\text{Li}(\text{dmp})$.²

We now report the results of a single-crystal X-ray diffraction study of the neopentylidene complex $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$.³ A preliminary account of this work has appeared previously.⁷

Experimental Section

A. Data Collection. Crystals of $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$ were kindly supplied by Professor R. R. Schrock of the Massachusetts Institute of Technology. The clear yellow columnar crystals are extended along their a axes. The complex is air sensitive, decomposing totally in approximately 24-36 h following initial exposure.

Using a small (ca. 6-L capacity) specially designed drybox, which permitted examination of the crystals with an externally mounted high-magnification microscope, several samples were cleaved from larger columns and sealed into thin-walled capillaries. All manipulations were carried out in an atmosphere of carefully purified argon. After 24 h, the samples were examined for signs of decomposition. The best crystal was then selected for data collection; it was 0.37 mm \times 0.22 mm \times 0.20 mm and had been mechanically wedged into a 0.2 mm diameter thin-walled capillary. The capillary was inserted into a brass pin with beeswax and mounted in a eucentric goniometer. Preliminary precession and cone-axis photographs provided approximate unit cell parameters, indicated $2/m$ Laue symmetry, and revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^2 ; No. 14] is strongly indicated. The crystal was transferred to a Syntex $P2_1$ automated diffractometer, its extended (real) a axis being close to coincidence with the spindle axis (ϕ) of the diffractometer. Crystal alignment, determination of orientation matrix and accurate cell