Crystal Structure and Molecular Geometry of Octadecacarbonylhexaruthenium Dihydride

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Abstract: Octadecacarbonylhexaruthenium dihydride, $H_2Ru_6(CO)_{18}$, crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5, no. 14), with a = 16.627 (23), b = 9.582 (5), c = 19.446 (19) Å, β = 120.58 (5)°, ρ_{obsd} = 2.80 (2), ρ_{calcd} = 2.771 g cm^{3-} for M = 1112.63 and Z = 4. X-Ray diffraction data to sin θ = 0.38 (Mo Kα radiation) were collected on a 0.01°-incrementing Supper-Pace Buerger automated diffractometer. The structure was solved by reiterative application of Sayre's relationships to the 283 reflections with $E \geq 1.6$ and was refined by difference-Fourier and least-squares refinement techniques. All nonhydrogen atoms were located accurately, the final discrepancy index being R_F = 5.72% for the 2780 independent nonzero reflections. The unit cell contains two sets of crystallographically distinct (but chemically identical) molecules which are centered on the special positions (0, 0, $^1/_2$; 0, $^1/_2$, 0) and ($^1/_2$, 0, 0; $^1/_2$, $^1/_2$, $^1/_2$). Each $H_2Ru_6(CO)_{18}$ molecule has precise C_i and approximate D_{3d} symmetry. The six ruthenium atoms define an octahedron, each ruthenium atom being associated with three terminal carbonyl ligands. A consideration of the symmetrical enlargement of (and distortion of carbonyl groups away from) two opposite faces of each octahedral Ru_6 cluster leads us to postulate the presence of triply bridging hydride ligands in mutually trans sites.

It is now firmly established[3] that a *terminal* hydride ligand occupies a regular stereochemical position and that a (transition metal)–hydrogen bond is of "normal" length (*i.e.*, may be predicted by the simple addition of the appropriate covalent radii). It should be noted, however, that structural data on both HRh[$P(C_6H_5)_3]_4$[4] and HRh[$P(C_6H_5)_3]_3[As(C_6H_5)_3]$[5] have provided equivocal information concerning the hydride ligand sites in these species.

Hydride ligands are also known to participate in two-electron, three-center bonds in which the M–H–M framework (M = transition metal) may be either linear (as in $[HCr_2(CO)_{10}^-]$[6,7] or $HRe_2Mn(CO)_{14}$[8,9]) or bent (as in $[(\pi\text{-}C_5H_5)_2Mo_2(CO)_4(H)\{P(CH_3)_2\}]$[10]).

Our previous X-ray diffraction studies on $[(C_6H_5)_4As^+][H_2Re_3(CO)_{12}^-]$ have suggested[11] that bridging hydride ligands cause irregularities in the disposition of carbonyl groups and that hydrogen-bridged rhenium–rhenium bonds are some 0.14 Å longer than nonbridged Re–Re linkages. Subsequent structural studies on $[(C_6H_5)_4As^+]_2[H_6Re_4(CO)_{12}^{2-}]$[12] and $H_2FeRu_3(CO)_{13}$[13] are consistent with these postulates. We now report the results of a crystallographic study on $H_2Ru_6(CO)_{18}$, a molecule believed to contain *triply* bridging hydride ligands. The preparation and characterization of this molecule have been described previously.[14]

Unit Cell and Space Group

A sample of $H_2Ru_6(CO)_{18}$ was provided by Dr. M. J. Mays of Cambridge University, England. Slow evaporation of a dichloromethane solution of the complex readily yielded beautiful, large, deep purple crystals which were air-stable and were not X-ray sensitive. Optical examination and the observed symmetry of the reciprocal lattice (C_{2h}, $2/m$) indicated a monoclinic system. Unit cell dimensions, determined by a least-squares analysis of reflection positions on 25° precession photographs taken with Mo Kα radiation ($\bar{\lambda}$ 0.7107 Å) at ambient temperatures (24 ± 2°) and calibrated with $Pb(NO_3)_2$ (a = 7.8566 Å), are: a = 16.627 (23), b = 9.582 (5), c = 19.446 (19) Å, β = 120.58 (5)°. The unit cell volume is V = 2667.1 Å^3.

A survey of photographs for levels 0–1kl, h0–1l, hk0–2 revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, compatible only with space group $P2_1/c$ (C_{2h}^5, no. 14).[15] The observed density (ρ_{obsd} = 2.80 (2) g cm^{-3} by flotation in bromoform–hexane) suggests four molecules per unit cell (ρ_{calcd} = 2.771 g cm^{-3} for M = 1112.63 and Z = 4).

Collection and Reduction of the X-Ray Diffraction Data

Two crystals were used during the crystallographic analysis. Both were well-developed parallelepipeds, prismatic in the 010 direction (well-developed 100, 101, $\bar{1}$01 faces) save for slanted (110 and 110) faces at the prism ends. Crystal B, of dimensions 0.20 × 0.62 × 0.44 mm, was mounted on its b axis; crystal C (0.30 × 0.50 × 0.46 mm) was aligned along its c axis. (In each case, dimensions refer sequentially to the 110, 010, and 001 directions.)

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Intensity data were collected with Mo Kα radiation ($\bar{\lambda}$ 0.7107 Å) on a 0.01°-incrementing Supper-Pace Buerger automated diffractometer using the stationary background–ω-scan–stationary background counting sequence described previously.[16] Details specific to the present investigation include the following: (a) generator output = 49 kV/19 mA; (b) scan angle (ω) = $[1.5 + (0.7/L)]°$, where $(1/L)$ is the Lorentz factor; (c) $d\omega/dt$ = 2°/min; (d) check reflections were monitored after each batch of 20 reflections; (e) initial and final backgrounds (B_1 and B_2) were measured for one-fourth the time of the main scan, the count associated with this scan being C.

The intensity (I) of a reflection was calculated by

$$I = C - 2(B_1 + B_2)$$

Deviations were assigned to reflections according to the following scheme, wherein $\delta = 3[C + 4(B_1 + B_2)]^{1/2}$ and is the maximum probable error (3σ level) in an intensity, *based solely on counting statistics.*

$$I \geqslant 4900, \sigma(I) = 0.1I$$

$$4900 > I \geqslant \delta, \sigma(I) = 7.0I^{1/2}$$

$$I < \delta, \sigma(I) = -1.0, \text{ and } I = \delta \text{ (reflection rejected)}$$

Data for the levels $h(0\text{–}10)l$ were collected from crystal B; these data are complete to sin θ = 0.38 (the useful limit on long-exposure Weissenberg photographs) save for reflections in the sphere $0 \leqslant \theta \leqslant 4°$ which are shielded from the counter by a Pb backstop. Correlation data from the levels $hk(0\text{–}5)$ were collected from crystal C. Of 3513 reflections from crystal B, 649 were rejected as being insignificantly above background; for crystal C the corresponding figures are 1419 collected, 279 rejected. All data were collected for Lorentz and polarization effects and absorption corrections were applied.[17] With μ = 33.15 cm^{-1}, transmission factors ranged from 0.362 to 0.692 for crystal B (volume 0.0232 mm^3) and from 0.233 to 0.462 for crystal C (volume 0.0381 mm^3). The two data sets were next merged to a common scale by a least-squares analysis of common reflections.[18] The resulting 2780 independent nonzero reflections were used in a Wilson plot,[19] which allowed all data to be placed on an (approximately) absolute scale. This and all subsequent computations were (unless stated otherwise) performed under the CRYRM system[20] on the Harvard University IBM 7094 computer.

Elucidation and Refinement of Crystal Structure

Scattering factors for neutral carbon and oxygen[21] were used throughout. The Thomas–Fermi–Dirac values for neutral ruthenium[22] were corrected for the real, but not the imaginary, component of dispersion ($\Delta f' = -1.2, \Delta f'' = +1.1$e).[23]

The residual minimized during least-squares refinement was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w(hkl) = [\sigma\{F^2(hkl)\}]^{-2}$ and $\sigma\{F^2(hkl)\} = |F(hkl)|^2\sigma\{I(hkl)\}/I(hkl)$.

Discrepancy indices referred to below are defined thus: $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$.

A sharpened, three-dimensional Patterson map revealed interatomic vectors consistent with two different equilateral triangular arrangements of ruthenium atoms. As the relationship between these two sets was not readily interpretable, the structure was solved by direct methods.

Sayre's method[24] was applied using a locally modified version of the IBM 7094 program REL, by Long.[25] Normalized structure factors, $|E(hkl)|$, were calculated by the expression

$$|E(hkl)| = |F(hkl)|\left\{\epsilon^2 \sum_{i=1}^{i=N} f^2[i, \theta(hkl)]\right\}^{-1/2}$$

Here, $|F(hkl)|$ is the structure factor amplitude for the reflection hkl, the sum $i = 1 \rightarrow N$ is over *all atoms within the unit cell*, $f[i, \theta(hkl)]$ is the scattering factor for the ith atom at the Bragg angle $\theta(hkl)$, ϵ adjusts for the degeneracy in $F(hkl)$ for reflections at symmetry locations in reciprocal space (ϵ = 2 for $h0l$, $hk0$ reflections and ϵ = 1 for all others in space group $P2_1/c$), and $\langle|E^2(hkl)|\rangle$ is normalized by adjustment of a scale factor.

The origin of the unit cell was defined by assigning positive signs to three reflections of appropriate parity [*viz.*, -12,2,7 (E = 3.46), -14,5,4 (E = 3.36), -956 (E = 2.99)]. Possible signs for the 283 reflections with $E \geq 1.6$ were obtained using phase pyramids based on the 16 possible sign combinations for the reflections -14,5,12 (E = 3.22), 12,2,1 (E = 2.80), -14,5,6 (E = 2.77), and 11,1,0 (E = 2.76). The best solution converged in two cycles to a consistency index C (defined below) of 0.9928.

$$C = \left\langle \left| E_h \sum_{h=h_1+h_2} E_{h_1}E_{h_2} \right| \right\rangle \Big/ \left\langle |E_h| \sum_{h=h_1+h_2} |E_{h_1}||E_{h_2}| \right\rangle$$

(Sums are over all pairs of reflections h_1 and h_2 for which $h = h_1 + h_2$, and $\langle\ \rangle$ designates the average over all values of h.)

An F map based on the 283 phased reflections immediately revealed the positions of the four Ru_6 clusters within the unit cell.

Rather unexpectedly, the asymmetric unit consists of two half-molecules of $H_2Ru_6(CO)_{18}$, rather than one entire molecule. There are thus two unrelated sets of $H_2Ru_6(CO)_{18}$ molecules within the unit cell, one set centered on special positions 2(b) (*i.e.*, $^1/_2$, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$) and the other centered on special positions 2(c) (*i.e.*, 0, 0, $^1/_2$ and 0, $^1/_2$, 0).[15] In the absence of disorder, each molecule must possess precise C_i symmetry.

A difference-Fourier map, phased by the six ruthenium atoms (R_F = 23.85%), immediately revealed all 18 carbonyl groups. Three cycles of full-matrix least-squares refinement of positional and isotropic thermal

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[16] M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 1123 (1968).

[17] Using IMBIBE, a Fortran IV program for the IBM 360 written by J. Wormald, which uses a gaussian quadrature numerical integration technique applied to a crystal of essentially arbitrary shape. See C. W. Burnham, *Amer. Mineral.*, **51**, 159 (1966).

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[20] CRYRM is an integrated sequence of crystallographic routines for the IBM 7094 computer compiled under the direction of Dr. R. E. Marsh at the California Institute of Technology.

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[22] Reference 21, p 211.

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Table I. Final Atomic Coordinates (with esd's)[a,b] and Vibration Ellipsoids[c,d] for $H_2Ru_6(CO)_{18}$

Atom	x	y	z	B_{maj}, Å^2	B_{med}, A^2	B_{min}, A^2
Ru(1)	−0.03021 (9)	−0.13936 (11)	0.56415 (8)	2.81	2.03	1.90
Ru(2)	0.01932 (7)	0.15907 (12)	0.57755 (8)	2.81	1.93	1.83
Ru(3)	0.14002 (9)	−0.05160 (12)	0.56372 (8)	2.98	2.18	1.39
O(1)	0.0699 (9)	−0.4011 (11)	0.6626 (8)	5.40	4.45	1.37
O(2)	−0.1967 (8)	−0.3231 (12)	0.4661 (9)	7.89	3.29	0.68
O(3)	−0.0976 (13)	−0.0956 (16)	0.6831 (11)	11.71	5.47	2.10
O(4)	−0.0449 (11)	0.2030 (17)	0.6963 (9)	10.26	5.04	1.29
O(5)	−0.0774 (9)	0.4321 (11)	0.4991 (8)	6.78	4.65	0.21
O(6)	0.3968 (10)	0.3548 (14)	0.4375 (10)	10.51	4.52	2.27
O(7)	0.3117 (10)	0.0958 (14)	0.6912 (9)	9.20	6.68	1.16
O(8)	0.2285 (9)	−0.0923 (12)	0.4612 (9)	5.32	3.71	2.37
O(9)	0.2432 (11)	−0.3131 (14)	0.6535 (9)	9.59	5.54	1.47
C(1)	0.0382 (13)	−0.3012 (18)	0.6272 (12)	4.52	3.49	1.72
C(2)	−0.1369 (14)	−0.2501 (18)	0.4962 (11)	4.24	3.67	1.97
C(3)	−0.0664 (14)	−0.1089 (17)	0.6418 (15)	6.02	3.80	1.96
C(4)	−0.0228 (16)	0.1758 (17)	0.6523 (12)	8.27	2.72	1.17
C(5)	−0.0439 (12)	0.3278 (16)	0.5240 (11)	5.51	2.01	1.47
C(6)	0.1247 (13)	0.2620 (17)	0.6515 (13)	5.82	2.54	1.35
C(7)	0.2465 (14)	0.0487 (16)	0.6419 (13)	6.06	2.28	1.51
C(8)	0.1906 (12)	−0.0709 (16)	0.4955 (12)	6.17	1.74	1.19
C(9)	0.2008 (12)	−0.2175 (18)	0.6626 (12)	5.60	3.38	1.23
Ru(11)	0.60321 (9)	0.64517 (12)	0.56249 (8)	2.76	2.14	1.75
Ru(12)	0.57470 (9)	0.34712 (11)	0.58234 (8)	2.66	2.24	1.66
Ru(13)	0.43167 (9)	0.55515 (12)	0.55968 (8)	2.45	2.15	1.71
O(11)	0.6155 (9)	0.8977 (13)	0.6590 (8)	6.75	3.96	2.06
O(12)	0.6484 (11)	0.8250 (13)	0.4589 (9)	5.02	4.52	2.47
O(13)	0.8098 (10)	0.6139 (14)	0.6787 (10)	13.16	3.90	1.82
O(14)	0.7807 (9)	0.3112 (18)	0.7042 (10)	12.18	4.56	1.24
O(15)	0.5798 (8)	0.0743 (11)	0.5078 (8)	5.09	2.47	1.44
O(16)	0.5429 (10)	0.1881 (14)	0.7018 (9)	7.63	4.25	2.13
O(17)	0.4032 (11)	0.4069 (14)	0.6848 (9)	7.16	5.24	2.18
O(18)	0.2220 (10)	0.5889 (14)	0.4560 (8)	5.78	3.38	2.67
O(19)	0.4300 (11)	0.8173 (13)	0.6460 (9)	6.98	4.94	2.19
C(11)	0.6073 (14)	0.8023 (18)	0.6243 (10)	6.06	2.28	1.51
C(12)	0.6277 (12)	0.7538 (16)	0.4945 (11)	5.11	3.69	0.76
C(13)	0.7306 (14)	0.6201 (16)	0.6379 (12)	4.10	2.65	0.76
C(14)	0.7038 (14)	0.3329 (18)	0.6584 (12)	4.90	3.04	1.69
C(15)	0.5769 (11)	0.1825 (16)	0.5324 (11)	5.13	1.32	0.20
C(16)	0.5547 (13)	0.2495 (17)	0.6577 (12)	5.26	2.38	2.11
C(17)	0.4231 (12)	0.8175 (15)	0.4675 (11)	3.86	2.69	1.69
C(18)	0.3038 (12)	0.5721 (17)	0.4896 (10)	3.95	2.33	0.69
C(19)	0.4389 (13)	0.7222 (17)	0.6158 (12)	5.08	2.49	0.89

[a] Esd's are in parentheses after each parameter, right adjusted to the least significant digit. [b] Only the atoms of the asymmetric unit are listed; numbers 1–9 belong to the molecule at position 2(c) and numbers 11–19 to that at 2(b). [c] Major, median, and minor axes of the atomic vibration ellipsoids are defined in terms of the isotropic thermal parameter, B. The transformation to rms displacement is $(U^2)^{1/2} = [B/8\pi^2]^{1/2}$. [d] The atomic vibration ellipsoids are displayed for the full clusters in Figures 1 and 2.

parameters (along with the scale factor) led to convergence at $R_F = 9.40\%$, $R_{wF^2} = 6.29\%$. Three further cycles of refinement, now using anisotropic thermal parameters led to convergence, once more, at $R_F = 7.57\%$, $R_{wF^2} = 4.46\%$. (During anisotropic refinement, parameters were blocked into seven submatrices: matrix I contained the scale factor and parameters for all six ruthenium atoms; the parameters for the three carbonyl ligands on a given metal atom were each grouped into a separate submatrix.) A careful survey of observed and calculated structure factor amplitudes now suggested that the data were affected by secondary extinction. A single-parameter secondary extinction correction, based on the model of Zachariasen,[26] was therefore included in the computations. A further three cycles of refinement of positional and anisotropic thermal parameters led to final convergence at $R_F = 5.72\%$ and $R_{wF^2} = 2.93\%$. The resulting value of the secondary extinction correction was $\chi = 2.027 \times 10^{-6}$, where $F_{calcd}{}^2(\text{corr}) = F_{calcd}{}^2(\text{uncorr})/[1 + \chi\beta \cdot F_{calcd}{}^2(\text{uncorr})]$ and where $\beta = (1 + \cos^4 2\theta)/[\sin 2\theta \cdot (1 + \cos^2 2\theta)]$. The standard deviation of an observation of unit weight, defined by

$$\sum w(|F_o|^2 - |F_c|^2)^2/(m - n)$$

(m = number of observations, n = number of parameters refined) was 1.72, indicating that errors in our intensity data were slightly underestimated. Application of Hamilton R-factor ratio tests[27] confirms that both refinement of anisotropic thermal parameters and inclusion of a secondary extinction coefficient are highly meaningful procedures.

Searches made for the hydride ligands on difference-Fourier maps after the convergence of each type of refinement (*vide supra*) failed to produce conclusive results.

Final values for observed and calculated structure factors are listed elsewhere.[28]

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(26) W. H. Zachariassen, *Acta Crystallogr.*, **16**, 1139 (1963).

(27) W. C. Hamilton, *ibid.*, **18**, 502 (1965).

(28) A compilation of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Office, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to authors, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Table II. Anisotropic Thermal Parameters ($\times 10^4$) for $H_2Ru_6(CO)_{18}$[a,b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru(1)	24.6 (0.8)	56.3 (1.4)	24.1 (0.6)	4.8 (1.6)	25.7 (1.1)	7.5 (1.4)
Ru(2)	22.7 (0.8)	55.1 (1.5)	21.7 (0.6)	−1.2 (1.5)	19.0 (1.1)	−8.7 (1.3)
Ru(3)	17.5 (0.7)	59.5 (1.4)	21.4 (0.6)	4.9 (1.6)	12.1 (1.1)	−0.8 (1.4)
O(1)	51 (9)	50 (14)	40 (7)	36 (18)	35 (13)	30 (16)
O(2)	17 (6)	91 (13)	65 (8)	−10 (16)	49 (13)	24 (17)
O(3)	102 (15)	182 (22)	74 (11)	104 (28)	149 (24)	57 (25)
O(4)	63 (11)	244 (27)	39 (7)	−37 (27)	79 (16)	−86 (22)
O(5)	47 (8)	29 (12)	55 (7)	64 (16)	44 (13)	34 (14)
O(6)	35 (9)	109 (17)	73 (10)	−35 (20)	23 (15)	−26 (20)
O(7)	36 (9)	163 (19)	40 (8)	−64 (20)	−15 (14)	−44 (20)
O(8)	31 (9)	107 (15)	42 (7)	10 (17)	36 (14)	−16 (16)
O(9)	68 (11)	87 (15)	46 (8)	83 (22)	15 (16)	41 (18)
C(1)	29 (10)	103 (21)	37 (10)	−22 (24)	43 (17)	−16 (23)
C(2)	43 (13)	89 (20)	25 (8)	−11 (28)	34 (18)	23 (21)
C(3)	41 (13)	79 (18)	51 (12)	41 (25)	49 (22)	30 (25)
C(4)	63 (14)	55 (20)	22 (8)	−53 (27)	1 (18)	−14 (22)
C(5)	31 (10)	106 (21)	29 (8)	−58 (24)	43 (16)	−52 (21)
C(6)	27 (10)	60 (19)	51 (11)	15 (24)	48 (18)	−4 (24)
C(7)	35 (12)	53 (18)	54 (11)	−13 (25)	63 (20)	−2 (23)
C(8)	15 (9)	67 (18)	37 (9)	9 (20)	9 (15)	−41 (20)
C(9)	17 (10)	10 (22)	37 (9)	−18 (25)	11 (16)	−28 (24)
Ru(11)	22.2 (0.7)	58.4 (1.5)	21.7 (0.6)	−5.4 (1.5)	18.7 (1.1)	−8.3 (1.3)
Ru(12)	23.7 (0.7)	58.7 (1.5)	20.7 (0.6)	12.2 (1.6)	20.5 (1.1)	12.4 (1.3)
Ru(13)	23.3 (0.7)	57.7 (1.4)	21.8 (0.6)	3.4 (1.5)	25.5 (1.1)	−0.9 (1.3)
O(11)	51 (9)	124 (17)	34 (6)	24 (20)	38 (12)	−49 (18)
O(12)	57 (10)	99 (16)	39 (7)	−24 (21)	59 (15)	13 (18)
O(13)	23 (8)	115 (19)	84 (10)	12 (19)	9 (15)	−41 (22)
O(14)	17 (7)	288 (28)	44 (8)	46 (23)	19 (13)	100 (25)
O(15)	22 (7)	68 (12)	41 (7)	−8 (15)	33 (12)	17 (14)
O(16)	67 (10)	132 (19)	46 (7)	42 (22)	79 (15)	73 (19)
O(17)	84 (12)	114 (18)	40 (7)	−30 (23)	75 (16)	29 (18)
O(18)	40 (9)	143 (20)	33 (6)	36 (20)	44 (13)	25 (17)
O(19)	82 (11)	78 (16)	39 (7)	−9 (21)	57 (15)	−35 (18)
C(11)	53 (13)	98 (21)	12 (7)	−38 (27)	26 (16)	−39 (20)
C(12)	33 (10)	56 (19)	26 (8)	−9 (23)	32 (15)	−47 (20)
C(13)	36 (13)	46 (7)	39 (9)	1 (24)	18 (19)	−3 (21)
C(14)	38 (14)	113 (21)	21 (8)	33 (26)	29 (19)	41 (21)
C(15)	16 (8)	45 (19)	42 (8)	33 (20)	48 (14)	39 (20)
C(16)	52 (12)	74 (19)	35 (9)	42 (24)	61 (18)	30 (23)
C(17)	32 (10)	61 (16)	33 (9)	9 (21)	40 (16)	−11 (20)
C(18)	29 (10)	98 (21)	15 (7)	8 (23)	31 (15)	28 (19)
C(19)	39 (11)	78 (20)	37 (9)	20 (23)	66 (18)	33 (22)

[a] The anisotropic thermal parameter (T) is defined as: $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Esd's are shown in parentheses.

The Molecular Structure

The two crystallographically independent $H_2Ru_6(CO)_{18}$ clusters are displayed,[29] together with their atomic vibration ellipsoids and the scheme used for numbering atoms, in Figures 1 and 2. Individual atomic coordinates, along with the axes dimensions for the atomic vibration ellipsoids, are listed in Table I; anisotropic thermal parameters are given in Table II.

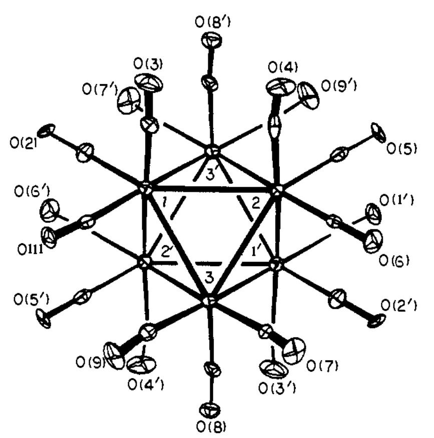

Figure 1. The $H_2Ru_6(CO)_{18}$ molecule centered on 0, 0, $^1/_2$. Carbon atoms are numbered similarly to their attached oxygen atoms. (OTLIPS diagram).[29]

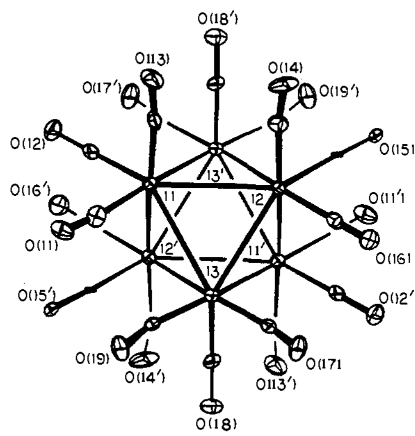

Figure 2. The $H_2Ru_6(CO)_{18}$ molecule centered at $^1/_2$, $^1/_2$, $^1/_2$. (OTLIPS diagram).[29]

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[29] These diagrams were drawn using OTLIPS, a program for an IBM 1620–CALCOMP plotter combination, written by Dr. P. H. Bird.

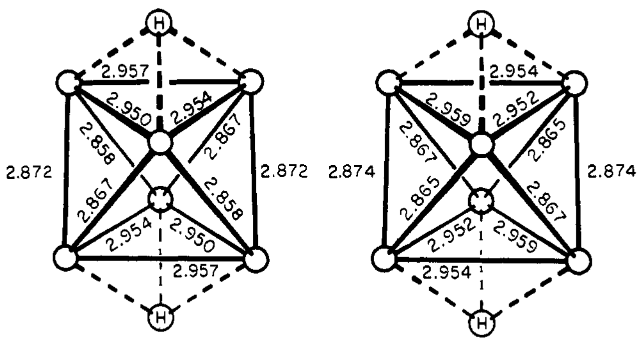

Figure 3. Ruthenium-ruthenium distances and probable hydride ligand positions within the two $H_2Ru_6(CO)_{18}$ molecules.

A survey of interatomic distances (Table III) and bond angles (Table IV) within the two independent clusters shows that (within the limits of experimental error) they are identical in every respect. Consequently, subsequent discussions [referring to the cluster centered on 0, 0, $^1/_2$ and defined by Ru(1)–(3), C(1)–(9), O(1)–(9), and the symmetry-related ($-x$, $-y$, $1 - z$) atoms Ru(1′)–(3′), C(1′)–(9′), O(1′)–(9′)] are pertinent to either cluster. Distances and angles referred to below are mean values from the two independent octahedral molecules.

Table III. Bond Lengths with Esd's (Å) for $H_2Ru_6(CO)_{18}$

Atoms	Length	Atoms	Length
(a) "Long" Ruthenium–Ruthenium Bonds			
Ru(1)–Ru(2)	2.950 (3)	Ru(11)–Ru(12)	2.952 (3)
Ru(2)–Ru(3)	2.954 (3)	Ru(12)–Ru(13)	2.959 (3)
Ru(3)–Ru(1)	2.957 (3)	Ru(13)–Ru(11)	2.954 (3)
		Mean	2.954 (3)[a]
(b) "Short" Ruthenium–Ruthenium Bonds			
Ru(1)–Ru(2′)	2.872 (3)	Ru(11)–Ru(12′)	2.874 (3)
Ru(2)–Ru(3′)	2.867 (3)	Ru(12)–Ru(13′)	2.867 (3)
Ru(3)–Ru(1′)	2.858 (3)	Ru(13)–Ru(11′)	2.865 (3)
		Mean	2.867 (5)[a]
(c) Ruthenium–Carbon Distances			
Ru(1)–C(1)	1.944 (20)	Ru(11)–C(11)	1.906 (20)
Ru(1)–C(2)	1.909 (23)	Ru(11)–C(12)	1.882 (18)
Ru(1)–C(3)	1.907 (21)	Ru(11)–C(13)	1.880 (21)
Ru(2)–C(4)	1.913 (22)	Ru(12)–C(14)	1.893 (21)
Ru(2)–C(5)	1.920 (19)	Ru(12)–C(15)	1.861 (18)
Ru(2)–C(6)	1.884 (21)	Ru(12)–C(16)	1.904 (20)
Ru(3)–C(7)	1.906 (21)	Ru(13)–C(17)	1.926 (19)
Ru(3)–C(8)	1.906 (19)	Ru(13)–C(18)	1.859 (18)
Ru(3)–C(9)	1.918 (20)	Ru(13)–C(19)	1.906 (20)
		Mean	1.901 (21)[a]
(d) Carbon–Oxygen Distances			
C(1)–O(1)	1.140 (24)	C(11)–O(11)	1.103 (25)
C(2)–O(2)	1.108 (25)	C(12)–O(12)	1.142 (24)
C(3)–O(3)	1.163 (30)	C(13)–O(13)	1.142 (27)
C(4)–O(4)	1.122 (28)	C(14)–O(14)	1.145 (27)
C(5)–O(5)	1.126 (23)	C(15)–O(15)	1.154 (22)
C(6)–O(6)	1.164 (27)	C(16)–O(16)	1.135 (25)
C(7)–O(7)	1.114 (27)	C(17)–O(17)	1.136 (25)
C(8)–O(8)	1.108 (24)	C(18)–O(18)	1.182 (23)
C(9)–O(9)	1.125 (26)	C(19)–O(19)	1.134 (25)
		Mean	1.135 (21)[a]

[a] Esd's on mean bond lengths are derived from the equation

$$\sigma = \left\{\left[\sum_{i=1}^{i=N}(\chi_i - \bar{\chi})^2\right]\Big/(N - 1)\right\}^{1/2}$$

where χ_i is the ith bond length and $\bar{\chi}$ is the mean of N equivalent bond lengths.

The Ru_6 Octahedron. The two metal skeletons are displayed, side-by-side, in Figure 3. Hydride ligands have been drawn in their presumed (*vide infra*) triply bridging positions. The hexanuclear metal cluster defines an octahedron in which two opposite faces are significantly larger than the remaining six. Ruthenium–ruthenium distances within the large faces range from 2.950 to 2.959, averaging 2.954 (3) Å, while the remaining metal–metal distances vary from 2.858 to 2.874, averaging 2.867 (5) Å. Bond angles within the enlarged (equilateral) faces (*i.e.*, Ru(1)–Ru(2)–Ru(3), etc.) are 59.9–60.1 (each ±0.05°), while angles for the remaining (isosceles) faces range from 58.7 to 59.2 and 61.9 to 62.2 (each ±0.05°). Clearly, the ruthenium–ruthenium bonds separate cleanly into two chemically distinct sets.

For the sake of comparison, it may be noted that Ru–Ru bonds in other organometallic species are 2.848 (6) Å for $Ru_3(CO)_{12}$,[30] 2.840–3.034 (σ = 0.006) Å for $Ru_6(CO)_{17}C$,[31] and 2.853–2.956 (σ = 0.007) Å for $Ru_6(CO)_{14}C$(mesitylene).[32]

Disposition of Carbonyl Ligands around the Ru_6 Cluster. As illustrated in Figures 1 and 2, each of the six ruthenium atoms bears three terminal carbonyl ligands. The six ruthenium atoms are chemically equivalent, thus explaining the simple pattern of the compound's infrared spectrum in the terminal carbonyl stretching region (found, three peaks at 2059 (s), 2053 (s), 2009 (m) cm^{-1}). Ruthenium–carbonyl linkages are quite normal, with ruthenium–carbon distances ranging from 1.859 to 1.944 Å (averaging 1.901 (21) Å) and carbon–oxygen distances varying from 1.103 to 1.182 Å, averaging 1.135 (21) Å. The Ru–C–O angles range from 169.2 (1.6) to 178.2 (1.8)°, the mean value being 172.9 (1.9)°. (The nonlinearity of M–C–O systems within terminal $M(CO)_3$ groups is, of course, expected and has been explained by Kettle.[33,34])

Examination of Figures 1 and 2 will show that the disposition of CO ligands around the Ru_6 cluster has systematic irregularities with ligands being distorted away from the enlarged equilateral ("open") faces. Consider, for example, the ligands attached to Ru(1): the angles C(1)–Ru(1)–Ru(2) = 132.0 (0.6) and C(3)–Ru(1)–Ru(3) = 130.2 (0.7)° show clearly that ligands C(1)–O(1) and C(3)–O(3) are not axial to the enlarged "open" face Ru(1)–Ru(2)–Ru(3); the angles C(1)–Ru(1)–Ru(3) = 88.6 (0.6) and C(1)–Ru(1)–Ru(2′) = 104.6 (0.6) show C(1)–O(1) to be nearly axial to the face Ru(1)–Ru(2′)–Ru(3), while the angles C(3)–Ru(1)–Ru(2) = 88.2 (0.7) and C(3)–Ru(1)–Ru(3′) = 105.7 (0.7)° show C(3)–O(3) to be approximately axial to the face Ru(1)–Ru(2)–Ru(3′). Similarly, the angles C(2)–Ru(1)–Ru(2′) = 77.8 (0.6) and C(2)–Ru(1)–Ru(3′) = 78.3 (0.6)° show that the ligand C(2)–O(2) positively leans in over the face Ru(1)–Ru(2′)–Ru(3′). A detailed study of Figure 1 and Table IV will reveal similar situations at Ru(2) and Ru(3).

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(30) R. Mason and W. R. Robinson, *J. Chem. Soc. A*, 778 (1968).

(31) A. Sirigu, M. Bianchi, and E. Benedetti, *Chem. Commun.*, 596 (1969).

(32) R. Mason and W. R. Robinson, *ibid.*, 468 (1968).

(33) S. F. A. Kettle, *Inorg. Chem.*, 4, 1661 (1965).

(34) S. F. A. Kettle, *J. Chem. Soc. A*, 420 (1966).

Table IV. Bond Angles within the $H_2Ru_6(CO)_{18}$ Clusters[a]

Atoms	Angle, deg	Atoms	Angle, deg
	Within the CO Ligands		
Ru(1)-C(1)-O(1)	173.2 (1.8)	Ru(11)-C(11)-O(11)	173.9 (1.8)
Ru(1)-C(2)-O(2)	170.4 (1.9)	Ru(11)-C(12)-O(12)	174.3 (1.7)
Ru(1)-C(3)-O(3)	172.8 (2.1)	Ru(11)-C(13)-O(13)	172.8 (1.9)
Ru(2)-C(4)-O(4)	171.3 (2.0)	Ru(12)-C(14)-O(14)	173.6 (1.9)
Ru(2)-C(5)-O(5)	173.8 (1.7)	Ru(12)-C(15)-O(15)	173.8 (1.6)
Ru(2)-C(6)-O(6)	175.6 (1.9)	Ru(12)-C(16)-O(16)	178.2 (1.8)
Ru(3)-C(7)-O(7)	173.5 (1.9)	Ru(13)-C(17)-O(17)	172.2 (1.7)
Ru(3)-C(8)-O(8)	172.8 (1.7)	Ru(13)-C(18)-O(18)	169.2 (1.6)
Ru(3)-C(9)-O(9)	171.7 (1.9)	Ru(13)-C(19)-O(19)	169.9 (1.8)
			Av 172.9 (1.9)[b]
	Within the Ru_6 Octahedron		
Ru(2)-Ru(1)-Ru(3)	60.0 (0.05)	Ru(12)-Ru(11)-Ru(13)	60.1 (0.05)
Ru(3)-Ru(1)-Ru(2′)	59.1 (0.05)	Ru(13)-Ru(11)-Ru(12′)	59.0 (0.05)
Ru(2′)-Ru(1)-Ru(3′)	62.1 (0.05)	Ru(12′)-Ru(11)-Ru(13′)	62.0 (0.05)
Ru(3′)-Ru(1)-Ru(2)	59.0 (0.05)	Ru(13′)-Ru(11)-Ru(12)	58.9 (0.05)
Ru(3)-Ru(2)-Ru(1)	60.1 (0.05)	Ru(13)-Ru(12)-Ru(11)	60.0 (0.05)
Ru(1)-Ru(2)-Ru(3′)	59.1 (0.05)	Ru(11)-Ru(12)-Ru(13′)	59.2 (0.05)
Ru(3′)-Ru(2)-Ru(1′)	62.2 (0.05)	Ru(13′)-Ru(12)-Ru(11′)	62.0 (0.05)
Ru(1′)-Ru(2)-Ru(3)	59.2 (0.05)	Ru(11′)-Ru(12)-Ru(13)	59.1 (0.05)
Ru(1)-Ru(3)-Ru(2)	59.9 (0.05)	Ru(11)-Ru(13)-Ru(12)	59.9 (0.05)
Ru(2)-Ru(3)-Ru(1′)	58.8 (0.05)	Ru(12)-Ru(13)-Ru(11′)	58.8 (0.05)
Ru(1′)-Ru(3)-Ru(2′)	61.9 (0.05)	Ru(11′)-Ru(13)-Ru(12′)	61.9 (0.05)
Ru(2′)-Ru(3)-Ru(1)	58.7 (0.05)	Ru(12′)-Ru(13)-Ru(11)	59.0 (0.05)
	Between the CO Ligands		
C(1)-Ru(1)-C(2)	91.9 (0.9)	C(11)-Ru(11)-C(12)	93.2 (0.9)
C(2)-Ru(1)-C(3)	94.4 (0.9)	C(12)-Ru(11)-C(13)	93.3 (0.9)
C(3)-Ru(1)-C(1)	86.6 (0.9)	C(13)-Ru(11)-C(11)	86.8 (0.9)
C(4)-Ru(2)-C(5)	91.8 (0.9)	C(14)-Ru(12)-C(15)	91.8 (0.9)
C(5)-Ru(2)-C(6)	90.8 (0.9)	C(15)-Ru(12)-C(16)	92.4 (0.9)
C(6)-Ru(2)-C(4)	86.2 (0.9)	C(16)-Ru(12)-C(14)	86.3 (0.9)
C(7)-Ru(3)-C(8)	92.5 (0.9)	C(17)-Ru(13)-C(18)	93.7 (0.9)
C(8)-Ru(3)-C(9)	92.9 (0.9)	C(18)-Ru(13)-C(19)	93.6 (0.9)
C(9)-Ru(3)-C(7)	87.0 (0.9)	C(19)-Ru(13)-C(17)	88.2 (0.9)
	Between the CO Ligands and the Ru_6 Octahedron		
C(1)-Ru(1)-Ru(2)	132.0 (0.6)	C(11)-Ru(11)-Ru(12)	129.7 (0.6)
C(1)-Ru(1)-Ru(3)	88.6 (0.6)	C(11)-Ru(11)-Ru(13)	88.1 (0.6)
C(1)-Ru(1)-Ru(2′)	104.6 (0.6)	C(11)-Ru(11)-Ru(12′)	106.7 (0.6)
C(1)-Ru(1)-Ru(3′)	164.6 (0.6)	C(11)-Ru(11)-Ru(13′)	167.5 (0.6)
C(2)-Ru(1)-Ru(2)	136.1 (0.6)	C(12)-Ru(11)-Ru(12)	137.1 (0.6)
C(2)-Ru(1)-Ru(3)	135.3 (0.6)	C(12)-Ru(11)-Ru(13)	134.5 (0.6)
C(2)-Ru(1)-Ru(2′)	77.8 (0.6)	C(12)-Ru(11)-Ru(12′)	77.3 (0.6)
C(2)-Ru(1)-Ru(3′)	78.3 (0.6)	C(12)-Ru(11)-Ru(13′)	79.3 (0.6)
C(3)-Ru(1)-Ru(2)	88.2 (0.7)	C(13)-Ru(11)-Ru(12)	88.1 (0.7)
C(3)-Ru(1)-Ru(3)	130.2 (0.7)	C(13)-Ru(11)-Ru(13)	132.2 (0.7)
C(3)-Ru(1)-Ru(2′)	166.4 (0.7)	C(13)-Ru(11)-Ru(12′)	163.7 (0.7)
C(3)-Ru(1)-Ru(3′)	105.7 0.7)	C(13)-Ru(11)-Ru(13′)	103.5 (0.7)
C(4)-Ru(2)-Ru(1)	87.4 (0.7)	C(14)-Ru(12)-Ru(11)	88.7 (0.6)
C(4)-Ru(2)-Ru(3)	130.9 (0.7)	C(14)-Ru(12)-Ru(13)	132.1 (0.6)
C(4)-Ru(2)-Ru(1′)	164.7 (0.7)	C(14)-Ru(12)-Ru(11′)	164.4 (0.7)
C(4)-Ru(2)-Ru(3′)	103.9 (0.7)	C(14)-Ru(12)-Ru(13′)	104.4 (0.6)
C(5)-Ru(2)-Ru(1)	135.8 (0.6)	C(15)-Ru(12)-Ru(11)	134.8 (0.6)
C(5)-Ru(2)-Ru(3)	137.3 (0.6)	C(15)-Ru(12)-Ru(13)	136.1 (0.6)
C(5)-Ru(2)-Ru(1′)	79.5 (0.6)	C(15)-Ru(12)-Ru(11′)	78.1 (0.6)
C(5)-Ru(2)-Ru(3′)	78.4 (0.6)	C(15)-Ru(12)-Ru(13′)	77.0 (0.6)
C(6)-Ru(2)-Ru(1)	133.2 (0.7)	C(16)-Ru(12)-Ru(11)	132.7 (0.6)
C(6)-Ru(2)-Ru(3)	90.9 (0.7)	C(16)-Ru(12)-Ru(13)	90.2 (0.6)
C(6)-Ru(2)-Ru(1′)	106.3 (0.7)	C(16)-Ru(12)-Ru(11′)	105.8 (0.6)
C(6)-Ru(2)-Ru(3′)	165.3 (0.7)	C(16)-Ru(12)-Ru(13′)	165.1 (0.6)
C(7)-Ru(3)-Ru(1)	130.1 (0.7)	C(17)-Ru(13)-Ru(11)	130.1 (0.6)
C(7)-Ru(3)-Ru(2)	88.9 (0.6)	C(17)-Ru(13)-Ru(12)	87.6 (0.6)
C(7)-Ru(3)-Ru(1′)	107.0 (0.7)	C(17)-Ru(13)-Ru(11′)	105.2 (0.6)
C(7)-Ru(3)-Ru(2′)	167.5 (0.7)	C(17)-Ru(13)-Ru(12′)	165.9 (0.6)
C(8)-Ru(3)-Ru(1)	137.4 (0.6)	C(18)-Ru(13)-Ru(11)	136.2 (0.6)
C(8)-Ru(3)-Ru(2)	133.6 (0.6)	C(18)-Ru(13)-Ru(12)	134.5 (0.6)
C(8)-Ru(3)-Ru(1′)	76.7 (0.6)	C(18)-Ru(13)-Ru(11′)	77.2 (0.6)
C(8)-Ru(3)-Ru(2′)	79.5 (0.6)	C(18)-Ru(13)-Ru(12′)	78.3 (0.6)
C(9)-Ru(3)-Ru(1)	88.7 (0.6)	C(19)-Ru(13)-Ru(11)	88.0 (0.6)
C(9)-Ru(3)-Ru(2)	133.5 (0.6)	C(19)-Ru(13)-Ru(12)	131.9 (0.6)
C(9)-Ru(3)-Ru(1′)	162.6 (0.6)	C(19)-Ru(13)-Ru(11′)	164.0 (0.6)
C(9)-Ru(3)-Ru(2′)	102.9 (0.6)	C(19)-Ru(13)-Ru(12′)	103.8 (0.6)

[a] Esd's in parentheses. [b] See Table III, footnote *a*.

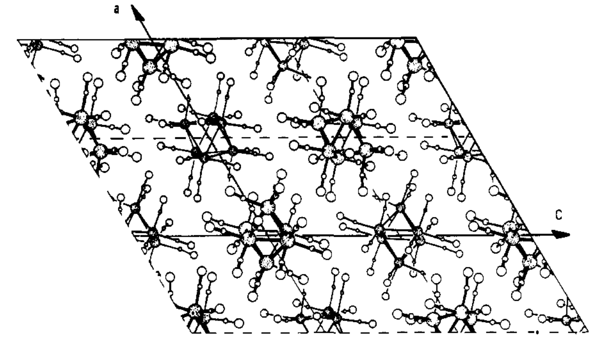

Figure 4. Packing of $H_2Ru_6(CO)_{18}$ molecules within the unit cell, viewed down *b*.

Thus, there are three carbonyl ligands in an axial conformation relative to each of the six small isosceles faces of the Ru_6 octahedron, while no carbonyl ligands are in a truly axial conformation relative to the two large "open" faces Ru(1)–Ru(2)–Ru(3) and Ru(1′)–Ru(2′)–Ru(3′). (Similar arguments apply to the other cluster molecule which completes the asymmetric unit.)

The Hydride Ligands. Previous mass spectrometric measurements on the complex (and on its dideuterio analog)[14] had confirmed the material's identity as $H_2Ru_6(CO)_{18}$. There is also no *a priori* reason for which the metal core of a cluster $Ru_6(CO)_{18}$ (with the bonding described above) should distort from regular O_h symmetry. The enlargement of faces in the octahedron and the distortion of ligands away from these enlarged faces is therefore strong circumstantial evidence for the presence of two hydride ligands (which were not directly located by the present diffraction study). The trigonal symmetry of the facial enlargement and distortion is especially noteworthy; from it, we conclude that each of the hydride ligands is symmetrically bonded to *three* ruthenium atoms. We thus have the first crystallographic evidence for *triply bridging* ligands. (The only other complex containing triply bridging hydride ligands which has previously been subjected to crystallographic examination is the highly delocalized species $(\pi-C_5H_5)_4Rh_3H$.[35,36])

The Crystal Structure. The $H_2Ru_6(CO)_{18}$ units within the crystal are separated by normal van der Waal's distances. Packing in the crystal is illustrated in Figure 4. A list of intramolecular contacts (complete to 3.1 Å) appears as Table V. The shortest intermolecular contact is O···O = 2.87 Å.

Discussion

$H_2Ru_6(CO)_{18}$ is the first non-carbide-containing octahedral metal carbonyl cluster discovered which is outside the cobalt triad. (Known species include $Co_6(CO)_{16}$,[37] $[Co_6(CO)_{15}{}^{2-}]$,[38] $[Co_6(CO)_{14}{}^{4-}]$,[39] $[Ni_2Co_4(CO)_{14}{}^{2-}]$,[40] $Rh_6(CO)_{16}$,[41] $[Rh_6(CO)_{15}{}^{2-}]$,[42,43] $[Rh_6(CO)_{14}{}^{4-}]$,[44] $Ir_6(CO)_{16}$,[43] $[Ir_6(CO)_{15}{}^{2-}]$,[43] $[Rh_{12}(CO)_{30}{}^{2-}]$,[45] and $Co_2Rh_4(CO)_{16}$.[46])

Table V. Intermolecular Contacts (to 3.1 Å) for $H_2Ru_6(CO)_{18}$

Atom	Atom, translation[a]	Distance, Å	Atom	Atom, translation[a]	Distance, Å
O(5)···	O(5′), I	2.87	O(15′)···	O(12′), I	3.00
O(2′)···	O(12′)	2.88	O(16)···	O(19′), IV	3.02
O(2)···	O(12), II	2.88	O(4)···	O(3′), IV	3.03
O(15′)···	O(15), I	2.89	O(4′)···	O(3), V	3.03
O(5)···	O(2), I	2.92	O(8′)···	O(18′), III	3.06
O(2′)···	O(5′), I	2.92	O(18)···	O(8), I	3.06
O(5)···	O(18′), III	2.95	O(1′)···	O(6′), I	3.09
O(18)···	O(5′), I	2.95	O(6)···	O(1), I	3.09
O(8′)···	O(15), III	2.97	O(2)···	O(18′), II	3.10
O(15′)···	O(8), I	2.97	O(2′)···	O(18)	3.10
O(12)···	O(15), I	3.00			

[a] Translations: I = $x, 1 + y, z$; II = $-1 + x, -1 + y, z$; III = $-1 + x, y, z$; IV = $x, \frac{1}{2} - y, \frac{1}{2} + z$; V = $x, -\frac{1}{2} - y, -\frac{1}{2} + z$.

While sophisticated numerical molecular orbital calculations on octahedral transition metal clusters are presently not feasible, two papers have appeared in which symmetry considerations have been used to predict the nature of the molecular orbitals in $Ru_6(CO)_{16}$; such a discussion is immediately applicable to the present case of $H_2Ru_6(CO)_{18}$.

Dahl and coworkers[41] treat each metal atom in the octahedral cluster as having local D_{4d} symmetry. Of the $18\frac{1}{3}$ electrons per metal atom, 16 are thus involved in σ bonds in a square-antiprismatic coordination sphere about the metal (d^4sp^3 hybridization, d_{z^2} not being used). The remaining $2\frac{1}{3}$ electrons per metal atom (7 electron pairs in all) are then accommodated in nonbonding molecular orbitals of A_{1g}, E_g, T_{1u} symmetry (derived from the six metal d_{z^2} orbitals), with the highest occupied molecular orbital being an antibonding orbital of A_{2u} symmetry (the sets of metal d_{xy} and $d_{x^2-y^2}$ orbitals reduce as $A_{2u} + E_u + T_{2g}$ and $A_{2g} + E_g + T_{2u}$, respectively). This treatment therefore suggests that octahedral metal–carbonyl cluster complexes (in each of which the (metal)$_6$ core possesses 86 outer valence electrons—*i.e.*, two more than the number predicted by the "noble gas rule") should readily oxidize to a dication. (It may be noted that Chini and Albano[38] have presented a similar treatment for $Rh_6(CO)_{16}$, but have assumed sp^3 hybridization of each rhodium atom (to the four bonded carbonyl groups), with the $d_{x^2-y^2}$ and d_{xy} orbitals *nonbonding* and with metal–metal bonding accommodated by linear combinations of the individual d_{xz}, d_{yz}, and d_{z^2} orbitals on the rhodium atoms.)

However, Kettle's[47] topological equivalent-orbital treatment of $Rh_6(CO)_{16}$ (in which both σ and π metal–ligand interactions are considered) indicates that there is a *deficit* of electrons and that a dianion, $Rh_6(CO)_{16}{}^{2-}$, should be capable of isolation.

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At a purely empirical level, it is found that *all* octahedral metal–carbonyl clusters have an 86-outer-electron configuration, and that no electron-rich or electron-deficient redox products have yet been encountered. Thus, the $H_2Ru_6(CO)_{18}$ molecule is very stable and can be recovered quantitatively after boiling a CH_2Cl_2 solution in air for a prolonged period.

Finally, it should be noted that iron forms a hexanuclear octahedral anion of identity $[Fe_6(CO)_{16}C^{2-}]$, rather than $[Fe_6(CO)_{18}{}^{2-}]$.[48]

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A Rearrangement of Tetramethyldiarsine Disulfide

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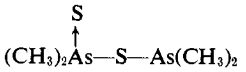
Abstract: The proton nmr spectra of solutions of tetramethyldiarsine disulfide in various solvents are inconsistent with both the solid-state structure, $R_2As(S)SAsR_2$, and the formulation $R_2As\text{–}S\text{–}S\text{–}AsR_2$. The intensities of the observed resonance peaks are dependent upon the solvent, concentration, time, and temperature. The spectral behavior in tetrachloroethane has been interpreted in terms of the equilibrium $R_2As\text{–}S\text{–}S\text{–}AsR_2 \leftrightarrows R_2As(S)SAsR_2$. The interpretation is supported by infrared data. Equilibrium constants, enthalpy changes, entropy changes, and free energy changes for the reaction have been calculated at several temperatures.

In our attempts to prepare dimethyldithioarsinic acid by the reaction of dimethylarsinic acid with H_2S, the disulfide II was isolated. This compound was first reported by Bunsen[1] in 1843. It was assumed to possess a disulfide link and two trivalent arsenic atoms, as is shown in I. However, current evidence is consistent with structure II. Synthesis of the compound from bis(dimethylarsine) sulfide and an excess of sulfur[1] suggests the presence of pentavalent arsenic, since trivalent arsines usually react with sulfur to produce pentavalent derivatives.[2] Furthermore, it has been found that the compound undergoes reaction with metal ions to produce salts of dimethyldithioarsinic acid, $(CH_3)_2As(S)SH$.[1] Also, the action of trifluoromethyl iodide on $(CH_3)_4As_2S_2$ has been reported to yield dimethyl(trifluoromethyl)arsine sulfide, $(CH_3)_2As(S)CF_3$, and dimethyl(trifluoromethyl)arsine, $(CH_3)_2AsCF_3$.[3] Finally, in 1964, Camerman and Trotter[4] determined the structure of $(CH_3)_4As_2S_2$ by single-crystal X-ray analysis and found that the compound contains trivalent and pentavalent arsenic atoms, as shown in II.

$(CH_3)_2As{-}S{-}S{-}As(CH_3)_2$

I


$(CH_3)_2\overset{\overset{S}{\uparrow}}{As}{-}S{-}As(CH_3)_2$

II

Consideration of structure II suggests that the proton nmr spectrum should display two peaks of equal intensity. However, in the present study, three methyl resonances were observed whose intensity ratios (determined on equilibrated solutions) were dependent on the solvent employed. In order to explain the apparent discrepancy between the predicted and observed proton nmr spectra of II, the work herein reported was undertaken.

Results and Discussion

Proton Nmr Spectra. The peak intensities observed in the nmr spectra of $(CH_3)_4As_2S_2$ were found to be dependent upon the solvent, concentration, temperature, and the time elapsed between the preparation of the solution and the nmr measurement.

The spectrum of a freshly prepared CCl_4 solution of $(CH_3)_4As_2S_2$ at 37° showed three sharp singlets at 2.14, 1.55, and 1.40 ppm having an intensity ratio of 1.0:1.0:0.50. After 20 min the peaks became equal in intensity and did not change thereafter. Fresh solutions in methanol displayed two resonances of equal intensity at 2.14 and 1.50 ppm. On standing, however, a new peak at 1.37 ppm was observed. At equilibrium, an intensity ratio of 1.0:0.95:0.17 was reached. The time required to reach equilibrium varied with the solvents. The location and relative intensities of the proton nmr signals at equilibrium in various solvents at 37° are given in Table I.

In most cases the spectra display three sharp peaks. The peaks at about 2.10 and 1.50 ppm were of approximately equal intensity in most solvents. However, the relative intensity of a peak at about 1.36 ppm was found to vary widely, depending on the solvent used.

Comparison of the spectra of $(CH_3)_4As_2S_2$ with those of similar compounds aided in the assignment of the peaks. The methyl proton resonances of $(CH_3)_2As{-}As(CH_3)_2$ [1.02 ppm;[5] 1.02 ppm (this work)], $(CH_3)_3As$

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