

the arsenic-sulfur ring are comparable to other values available for ring and nonring compounds: 2.25 Å in the AsS_3^{3-} ion,¹¹ 2.23 and 2.21 Å for the gas-phase¹² and crystal¹³ values for As_4S_4 , and 2.25 Å for the As-S bonds in the gas phase of As_4S_6 .¹² The S-S distance of 2.036 (6) Å is equal to the 2.037 (5) Å value reported for the S_8 molecule.¹⁴ The SAsS and AsSAs angles in $\text{As}_2\text{S}_3(\text{C}_6\text{H}_5)_2$ are within several standard deviations of the values reported in the electron diffraction studies of As_4S_4 and As_4S_6 .⁷ The As-C distance of 1.95 (1) Å for this structure is within the range of values commonly found for this linkage.

The close comparisons of the $\text{As}_2\text{S}_3(\text{C}_6\text{H}_5)_2$ bond distances with a variety of As-S compounds, along with the S-S bond which is equal to the S_8 value, suggests that the As-S ring system does not have appreciable π bonding above that found in the average As-S and S-S bonds. The approximately tetrahedral angles of the ring atoms, giving a highly puckered ring, also support this conclusion. The arsenic atoms are 1.09 Å above and below the plane of the three sulfur atoms, the S(2) and S(2)' sulfur atoms are 0.61 Å above and below the plane of As(1)-S(1)-As(1)', and the As atom and its phenyl ring are coplanar within 0.03 Å.

The crystal packing is illustrated in Figure 2, which shows the contents of one unit cell projected on the xz plane. There are only two intermolecular distances less than Pauling's¹⁵ nonbonding radii values: there is an As-S distance (As(1) with S(2) in the position re-

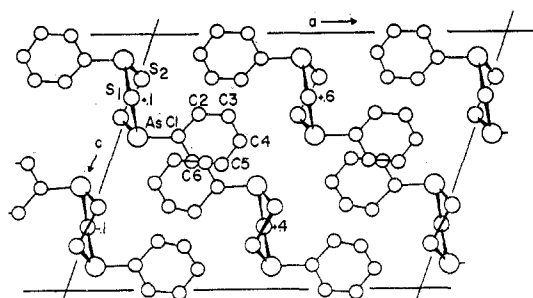


Figure 2.—The contents of the unit cell projected on the xz plane. The y values for the ring centers are given.

lated to the table value by $x, -y, 0.5 + z$) of 3.671 (5) Å compared to the sum of the van der Waals radii of 3.85 Å, and there is an As-As contact (As(1) with As(1) at $-x, -y, 1 - z$) of 3.901 (5) Å compared to the van der Waals sum of 4.0 Å. No special significance is attributed to these values.

The five-membered ring compound of known structure which is most closely related chemically to the present ring is $\text{S}_3\text{N}_2\text{Cl}_2$.¹⁶ The ring structures are quite different, however, in that the S_3N_2 ring is nearly planar and has S-N distances appreciably shorter than the value usually accepted for a single S-N bond. The planarity and shortened bonds apparently reflect $p\pi-d\pi$ bonding in the N-S system which is not present in the As-S ring of $\text{As}_2\text{S}_3(\text{C}_6\text{H}_5)_2$.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, IRVINE, CALIFORNIA 92664

The Crystal and Molecular Structure of the Tetranuclear Ruthenium Carbonyl Hydride $\alpha\text{-H}_2\text{Ru}_4(\text{CO})_{13}$

BY D. B. W. YAWNEY AND ROBERT J. DOEDENS*

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A single-crystal X-ray structural analysis has established the structure of one of two reported forms of the tetranuclear ruthenium carbonyl hydride $\text{H}_2\text{Ru}_4(\text{CO})_{13}$. This compound crystallizes in space group $P2_1/c$ of the monoclinic system, with eight molecules in a cell of dimensions $a = 9.534$ (10), $b = 9.032$ (9), $c = 47.44$ (4) Å, and $\beta = 90^\circ 29'$ (3'). The structural determination was based upon 1134 independent counter data; a blocked full-matrix, least-squares refinement converged to a conventional R factor of 0.059. The two crystallographically independent $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ molecules have similar configurations, with the metal atoms tetrahedrally disposed. Eleven of the thirteen carbonyl groups are terminally bound; the other two form asymmetric Ru-C \cdots Ru bridges with average Ru-C and Ru \cdots C distances of 1.94 (5) and 2.40 (6) Å, respectively. Two different metal-metal distances are observed; each molecule has two long Ru-Ru distances of mean value 2.93 (1) Å and four shorter distances averaging to 2.78 (2) Å. Indirect evidence implies that the hydrogen atoms are situated in bridging configurations on the two long Ru-Ru edges.

Introduction

The tetranuclear ruthenium carbonyl hydride $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ is obtained from $\text{Ru}_3(\text{CO})_{12}$ under a variety of conditions including reduction with NaBH_4 in THF,¹ treatment with OH^- in methanol followed by acidifi-

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cation,¹ reflux in various solvents,²⁻⁴ and reaction with alcohols, aldehydes, and ketones.⁵ Two distinct

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isomeric forms of this compound have been reported; one (designated as the α form) shows a singlet nmr peak at τ 28.6, while the other displays a singlet resonance at τ 19.1. The infrared spectra of the two forms exhibit only small differences.⁴ The tetrahydrido species H₄Ru₄(CO)₁₂ is sometimes produced along with the dihydride.^{1,2,4} When iron and ruthenium carbonyls react in organic solvents the mixed iron-ruthenium carbonyl species H₂FeRu₃(CO)₁₃, FeRu₂(CO)₁₂, and Fe₂Ru(CO)₁₂ may be obtained in addition to α -H₂Ru₄(CO)₁₃.³ The iron⁶ and osmium⁷ congeners of H₂Ru₄(CO)₁₃ are also known as is the mixed iron-osmium hydride H₂FeOs₃(CO)₁₃,⁸ in fact H₂Fe₄(CO)₁₃ was one of the first polynuclear metal carbonyl hydrides to be prepared and characterized.

The only definitive structural information for any of these H₂M₄(CO)₁₃ species stems from the crystal structure determination of H₂FeRu₃(CO)₁₃,⁹ in which the metal atoms were found to be arranged in a tetrahedral cluster as expected. Of the thirteen carbonyl groups, eleven are terminally bound and two are bound *via* asymmetric Fe-C-Ru bridges. Though the hydrogen atoms were not located, indirect evidence (involving metal-metal distances and metal-metal-carbon angles) was interpreted as favoring the presence of hydrogen atoms in bridging configurations on two of the Ru-Ru edges of the FeRu₃ tetrahedron.

As pointed out previously,³ spectroscopic data yielded no basis for concluding that the structures of α -H₂Ru₄(CO)₁₃ and H₂FeRu₃(CO)₁₃ were identical; in fact significant differences were observed in the infrared spectra of the two hydrides. In particular, two well-resolved bands (1884, 1845 cm⁻¹) were observed in the bridging carbonyl region for H₂FeRu₃(CO)₁₃, but only one broad, weak band (1880 cm⁻¹) was found for H₂Ru₄(CO)₁₃. In general, it has been difficult unambiguously to infer the structures of polynuclear metal carbonyl hydrides from spectral data alone. Complications include the possibility of asymmetrically bridging⁹ and triply bridging carbonyl groups in addition to the usual terminal and symmetrically bridging configurations and also the various possible modes of bonding of the hydrogen atom—terminal, doubly bridging (linear¹⁰ or bent¹¹⁻¹³), triply bridging,¹⁴ or perhaps enclosed within a polyhedron of metal atoms.^{15,16}

The relationship of the structures of the H₂M₄(CO)₁₃ molecules to those of the isoelectronic metal carbonylate anions [M₄(CO)₁₃]²⁻ (of which [Fe₄(CO)₁₃]²⁻^{6,17} and

[Ru₄(CO)₁₃]²⁻¹ are known) is also of interest. The structure of [Fe(C₅H₅N)₆]²⁺[Fe₄(CO)₁₃]²⁻ has been determined;¹⁸ the anion contains a tetrahedral cluster of iron atoms with nine terminal carbonyl groups, three highly asymmetric bridging carbonyls, and a single triply bridging CO group. This structure was used as a basis for one proposed structure of H₂Ru₄(CO)₁₃.¹

We now report the results of a determination of the crystal structure of α -H₂Ru₄(CO)₁₃ for which a structure much like that of H₂FeRu₃(CO)₁₃ has been found.

Collection and Reduction of the X-Ray Data

The sample of H₂Ru₄(CO)₁₃ employed in this work was prepared during the original synthetic studies of this system at the University of Bristol.³ Crystals were obtained by recrystallization from low-boiling (30–60°) petroleum ether or from cyclohexane. Examination under a polarizing microscope revealed that many of the well-formed dark red, rectangular, platelike crystals were twinned; this problem appeared to be less severe for crystals grown from cyclohexane. Even crystals which displayed no evidence of twinning under optical examination often gave split or poorly shaped spots on X-ray photographs. Weissenberg and precession photographs established the systematic absences $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, consistent with the space group C_{2h}⁵-P2₁/c. Lattice constants at 22°, obtained from a least-squares refinement of the settings of twelve carefully centered reflections (takeoff angle 1.3°, λ (Cu K α_1) 1.54051 Å), are $a = 9.534$ (10) Å, $b = 9.032$ (9) Å, $c = 47.44$ (4) Å, and $\beta = 90^\circ 29'$ (3').¹⁹ The observed (floatation in aqueous ZnBr₂) and calculated ($Z = 8$) densities are 2.2 (1) and 2.50 g/cm³, respectively. The limited number of very small crystals available precluded a more precise measurement of the density.

Intensity data were collected on a Picker four-angle diffractometer from a well-formed rectangular platelet of dimensions 0.16 × 0.18 × 0.04 mm along the crystallographic a , b , and c directions, respectively. The large flat faces were identified as {001}, while the small side faces belong to the {104} and {014} forms. The crystal was mounted about a^* in a thin-walled glass capillary. Narrow-source open-counter ω scans²⁰ of several strong reflections revealed a larger than usual peak width, as large as 0.4° full width at half-maximum for some reflections. Some of the broader peaks exhibited asymmetry or partially resolved satellite peaks. The occurrence of broad peaks could not be simply correlated with their location in reciprocal space or with any other parameter. The crystal used for data collection was the best one available, as judged by photographs which showed no trace of the anomalies observed for many other crystals. Because of our interest in this structural problem, we elected to proceed with the analysis in spite of the less than ideal quality of this crystal.

Data were collected by the θ - 2θ scan technique with Cu K α radiation.²¹ The diffracted beam was filtered through 0.0005-in. nickel foil and the pulse height analyzer was set to admit about 90% of the Cu K α peak. The peaks were scanned at 1.0°/min with a constant-scan range of -1.05 to +1.20° from the calculated 2θ value. This range was sufficient to accommodate even the broadest peaks. A 10-sec stationary-crystal, stationary-counter background count was taken at each end of the scan range. The takeoff angle was 2.4°. A receiving aperture 6.5

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(19) These values are very similar to the reported cell constants of H₂FeRu₃(CO)₁₃: $a = 47.00$, $b = 8.75$, $c = 9.56$ Å, $\beta = 90^\circ 50'$.

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TABLE I
 Atomic Positional and Thermal Parameters for $H_2Ru_4(CO)_{18}^a$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Molecule 1					Molecule 2				
Ru(1)	-0.1741 (5)	0.2430 (4)	0.0321 (1)	...	Ru(1)	-0.4544 (5)	0.2393 (4)	0.3066 (1)	...
Ru(2)	-0.2118 (5)	0.2121 (4)	0.0900 (1)	...	Ru(2)	-0.2434 (5)	0.4463 (4)	0.3149 (1)	...
Ru(3)	-0.4512 (5)	0.2520 (4)	0.0575 (1)	...	Ru(3)	-0.1701 (5)	0.1892 (4)	0.2860 (1)	...
Ru(4)	-0.2667 (5)	0.4898 (4)	0.0681 (1)	...	Ru(4)	-0.2151 (5)	0.1822 (5)	0.3444 (1)	...
C(1-1)	-0.197 (8)	0.286 (7)	-0.013 (2)	9.8 (22)	C(1-1)	-0.579 (6)	0.069 (6)	0.305 (1)	4.4 (15)
O(1-1)	-0.149 (6)	0.323 (5)	-0.029 (1)	10.7 (18)	O(1-1)	-0.655 (4)	-0.020 (4)	0.303 (1)	5.4 (10)
C(1-2)	0.014 (7)	0.250 (5)	0.041 (1)	5.9 (15)	C(1-2)	-0.587 (6)	0.351 (6)	0.330 (1)	3.8 (15)
O(1-2)	0.138 (5)	0.258 (4)	0.044 (1)	8.2 (12)	O(1-2)	-0.645 (5)	0.408 (5)	0.345 (1)	8.2 (14)
C(1-3)	-0.170 (6)	0.044 (7)	0.028 (1)	7.7 (18)	C(1-3)	-0.517 (8)	0.332 (7)	0.277 (2)	7.9 (21)
O(1-3)	-0.161 (4)	-0.084 (5)	0.024 (1)	9.7 (13)	O(1-3)	-0.559 (4)	0.405 (4)	0.256 (1)	6.9 (12)
C(2-1)	-0.285 (6)	0.226 (5)	0.128 (1)	5.7 (14)	C(2-1)	-0.081 (7)	0.547 (6)	0.325 (1)	5.4 (17)
O(2-1)	-0.313 (5)	0.247 (4)	0.152 (1)	8.8 (12)	O(2-1)	0.030 (5)	0.601 (4)	0.330 (1)	7.1 (12)
C(2-2)	-0.073 (8)	0.085 (7)	0.099 (2)	9.7 (22)	C(2-2)	-0.368 (7)	0.620 (6)	0.311 (1)	5.6 (18)
O(2-2)	0.028 (5)	0.013 (4)	0.102 (1)	9.1 (12)	O(2-2)	-0.425 (5)	0.714 (5)	0.306 (1)	7.8 (13)
C(2-3)	-0.327 (5)	0.046 (5)	0.081 (1)	3.8 (13)	C(2-3)	-0.189 (6)	0.448 (6)	0.274 (1)	4.1 (15)
O(2-3)	-0.355 (4)	-0.075 (4)	0.081 (1)	6.3 (10)	O(2-3)	-0.205 (4)	0.514 (4)	0.251 (1)	6.3 (11)
C(2-4)	-0.090 (6)	0.376 (5)	0.094 (1)	5.0 (14)	C(2-4)	-0.296 (5)	0.429 (5)	0.354 (1)	1.7 (12)
O(2-4)	0.024 (4)	0.427 (4)	0.102 (1)	8.1 (11)	O(2-4)	-0.345 (4)	0.479 (4)	0.376 (1)	7.0 (12)
C(3-1)	-0.560 (7)	0.291 (6)	0.092 (1)	6.8 (17)	C(3-1)	0.020 (8)	0.237 (6)	0.289 (1)	5.4 (16)
O(3-1)	-0.626 (5)	0.314 (4)	0.110 (1)	9.1 (13)	O(3-1)	0.135 (5)	0.270 (4)	0.290 (1)	7.8 (13)
C(3-2)	-0.565 (6)	0.377 (5)	0.032 (1)	4.2 (15)	C(3-2)	-0.137 (6)	-0.012 (7)	0.282 (1)	4.8 (16)
O(3-2)	-0.625 (5)	0.456 (5)	0.023 (1)	11.4 (16)	O(3-2)	-0.115 (4)	-0.134 (5)	0.281 (1)	6.2 (11)
C(3-3)	-0.553 (6)	0.097 (6)	0.045 (1)	7.1 (16)	C(3-3)	-0.167 (5)	0.194 (4)	0.248 (1)	0.9 (10)
O(3-3)	-0.622 (4)	-0.005 (4)	0.038 (1)	8.0 (11)	O(3-3)	-0.209 (5)	0.177 (4)	0.221 (1)	8.1 (13)
C(4-1)	-0.340 (5)	0.547 (5)	0.102 (1)	5.6 (15)	C(4-1)	-0.019 (8)	0.217 (6)	0.353 (1)	5.6 (19)
O(4-1)	-0.407 (4)	0.583 (4)	0.123 (1)	8.2 (12)	O(4-1)	0.094 (6)	0.238 (5)	0.358 (1)	9.3 (16)
C(4-2)	-0.374 (6)	0.618 (6)	0.047 (1)	5.9 (16)	C(4-2)	-0.184 (6)	-0.013 (7)	0.344 (1)	5.4 (17)
O(4-2)	-0.439 (5)	0.699 (5)	0.036 (1)	10.0 (14)	O(4-2)	-0.176 (4)	-0.140 (5)	0.344 (1)	6.9 (12)
C(4-3)	-0.138 (8)	0.644 (7)	0.069 (2)	8.8 (20)	C(4-3)	-0.271 (7)	0.181 (6)	0.383 (2)	5.4 (18)
O(4-3)	-0.053 (5)	0.729 (4)	0.074 (1)	7.5 (11)	O(4-3)	-0.295 (6)	0.166 (5)	0.407 (1)	10.1 (17)

Anisotropic Thermal Parameters^b ($\times 10^5$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Molecule 1						Molecule 2							
Ru(1)	1479 (86)	1366 (65)	36 (3)	296 (55)	77 (12)	-24 (13)	Ru(1)	927 (83)	1097 (68)	34 (3)	-109 (60)	27 (13)	6 (14)
Ru(2)	1613 (89)	1351 (70)	41 (3)	280 (57)	51 (13)	-11 (13)	Ru(2)	1141 (86)	877 (73)	38 (3)	-16 (58)	51 (14)	-9 (13)
Ru(3)	1635 (92)	1541 (68)	48 (3)	86 (61)	90 (14)	-74 (14)	Ru(3)	1079 (89)	1357 (82)	30 (3)	57 (63)	49 (14)	-22 (14)
Ru(4)	1850 (86)	981 (60)	38 (3)	65 (58)	100 (13)	-9 (12)	Ru(4)	1274 (92)	1157 (78)	29 (3)	-95 (62)	4 (14)	23 (14)

^a Numbers in parentheses in tables and in the text are estimated standard deviations in the least significant figures. ^b The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

mm wide by 4.5 mm high was positioned 20 cm from the crystal. Intensities of four standard reflections were monitored throughout the collection of data. During the course of data collection each of these reflections declined in intensity by about 10%; the observed intensities were corrected for this variation. Owing to the large value of *c* and the greater than usual breadth of many peaks, overlap of reflections was a potential problem. Hence all pairs of reflections whose centers were closer than 1.75° in the equatorial plane or 0.85° perpendicular to this plane were collected separately. These data were carefully examined for the effects of overlap—any which showed anomalous peak shapes or highly asymmetric backgrounds were omitted from further calculations. Data were collected to a limiting value of $2\theta = 80^\circ$, beyond which very few intensities were above background. Of the 2469 independent data within this limiting value of 2θ , 407 were identified as possibly subject to overlap; of these, only eight were actually rejected. No reflections were strong enough to require attenuation.

The data were processed according to previously described methods.²¹ The factor *p* in the expression for $\sigma(F)$ was taken as 0.06. A total of 1134 reflections had $F^2 > 3\sigma(F^2)$ and were employed in subsequent calculations. An absorption correction was carried out; based upon a linear absorption coefficient of 251 cm⁻¹, transmission factors ranged from 0.04 to 0.44. A Wilson plot was used to bring the data onto an approximate absolute scale and normalized structure factors (*E*'s) were calculated.

Solution and Refinement of the Structure

The eight ruthenium atoms in the crystallographic asymmetric unit were located by direct methods. Phasing of all 274 reflections with $E > 1.70$ was accomplished with a modified version of Long's program for the reiterative application of the Sayre

equation.²² Since most of the reflections with large *E* values had $l = 4n$, none of the program's algorithms for choice of a starting set of phases was suitable and a manual choice of starting set had to be made. The origin-defining reflections were chosen as 014 ($E = 3.44$), 314 ($E = 3.18$), and 041 ($E = 2.81$) and variable phases were assigned to 131 ($E = 2.86$), 3,2,12 ($E = 3.53$), and 1,6,18 ($E = 2.49$). Phases obtained from the solution which required the fewest cycles for convergence and had the highest consistency index were used to calculate an *E* map. On this map the eight ruthenium atoms showed up clearly in their expected configuration—two well-separated and approximately tetrahedral clusters. Two cycles of least-squares refinement of the ruthenium positional parameters, individual isotropic atomic temperature factors, and a scale factor led to discrepancy factors $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.207$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2} = 0.270$. Coordinates of the 52 carbon and oxygen atoms were found by conventional heavy-atom Fourier techniques.

Refinement of the structure was carried out by blocked full-matrix, least-squares methods. The blocking was necessitated by the limited storage capacity of our computer and was accomplished by varying the scale factor and the parameters of only one of the two independent molecules in each cycle. No more than two consecutive cycles were run on the same molecule. Refinement with isotropic temperature factors assigned to all atoms converged to $R_1 = 0.090$ and $R_2 = 0.101$. Further refinement with anisotropic thermal parameters for the ruthenium atoms yielded final discrepancy factors $R_1 = 0.059$ and $R_2 = 0.065$. In all refinements the individual structure amplitudes were given weights $w = 4F_o^2/\sigma^2(F_o^2)$ and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The scattering factors of

Cromer and Waber²³ were used for neutral Ru while those for C and O were taken from ref 24. The $\Delta f'$ and $\Delta f''$ values of Cromer²⁵ were employed in the correction of F_o for anomalous dispersion by the ruthenium atoms. The final standard deviation of an observation of unit weight was 1.34; calculation of mean $w(\Delta F)^2$ values for subsets of the data based upon F_o , intensity, and $(\sin \theta)/\lambda$ showed no significant trends.

During the course of the refinement it became clear that the standard deviations of the structural parameters were larger, by a factor of at least 2, than might normally be expected in a crystal structure analysis of a compound of this sort. The small size and marginal quality of the crystal employed as well as the rather limited number of nonzero data undoubtedly play a part in this problem. Other possibilities which could not be overlooked included an orientational disorder of all or part of the molecule or twinning on a microscopic scale. Such phenomena are known for a number of other polynuclear metal carbonyl species.^{14, 26, 27} With this in mind, a final difference Fourier map was examined carefully for effects attributable to the presence of alternative atomic positions. On this map, the greatest peak height was 1.1 e/Å³, as compared to peak heights of 1.5–2.9 e/Å³ observed for carbon and oxygen atoms on previous difference Fourier maps. Of the ten highest peaks (≥ 0.8 e/Å³), five were in positions which were chemically reasonable alternatives to refined atoms; three of these peaks represented possible alternative positions for the asymmetrically bridging carbon atoms C(2-3) and C(2-4). These results suggested that other molecular orientations were present, but no convincing detailed picture of a disorder could be extracted from them. Peaks clearly attributable to hydrogen atoms were not found on this map.

A final attempt to define the nature of the problem involved carbonyl group (1-1) of molecule 1, the group most severely departing from its expected configuration. A structure factor calculation based on all atoms except for those in this carbonyl group was carried out and a partial difference map was calculated in the vicinity of Ru(1). The CO group appeared on this map as a single elongated peak whose maximum (2.7 e/Å³) coincided with the refined oxygen atom position. This atom was included in a second structure factor calculation; the carbon atom appeared on the subsequent difference map as a peak of height 1.4 e/Å³ at its refined position. This peak was somewhat elongated in the c direction. No other discrete peaks greater in height than 0.6 e/Å³ appeared within bonding distance of Ru(1).

Based upon the results of the structure refinement, the final difference maps, and the occurrences of some broad and anomalously shaped reflections, we conclude that alternative orientations of the H₂Ru₄(CO)₁₃ molecule are probably present in the crystal. The varying quality of the crystals observed indicates that the extent of this problem differs from crystal to crystal. We take the refined atomic coordinates to represent the principal contribution to the overall structure, possibly perturbed by other contributions of lesser importance. The tabulated esd's appear to be only slightly underestimated, as measured by the agreement between equivalent distances in the two independent molecules and by the variations in presumably equivalent distances within each molecule. Thus the 22 terminal C–O bond distances, which should be nearly identical, have a mean value of 1.14 Å, with a root-mean-square deviation of 0.082 Å from the mean. This compares with the mean least-squares standard deviation of 0.082 Å for these distances.

The final atomic positional and thermal parameters and their estimated standard deviations are listed in Table I. Intramolecular distances are tabulated in Table II and bond angles are given in Table III. Table IV presents information relating to the anisotropic thermal parameters of the ruthenium atoms and intermolecular contacts less than 3.10 Å are listed in Table V. A table of observed and calculated structure factors is available.²⁸

(23) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(24) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

(25) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(26) C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, **88**, 1821 (1966); **91**, 1351 (1969).

(27) C. H. Wei, G. R. Wilkes, and L. F. Dahl, *ibid.*, **89**, 4792 (1967).

(28) A listing of 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 Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

TABLE II
INTRAMOLECULAR DISTANCES (Å)

Distance	Molecule 1	Molecule 2
Ru(1)–Ru(2)	2.785 (7)	2.771 (7)
Ru(1)–Ru(3)	2.915 (7)	2.924 (7)
Ru(1)–Ru(4)	2.947 (6)	2.935 (8)
Ru(2)–Ru(3)	2.764 (7)	2.786 (7)
Ru(2)–Ru(4)	2.762 (6)	2.778 (7)
Ru(3)–Ru(4)	2.818 (7)	2.805 (8)
Ru(1)–C(1-1)	2.20 (8)	1.95 (6)
Ru(1)–C(1-2)	1.84 (7)	1.97 (6)
Ru(1)–C(1-3)	1.81 (6)	1.75 (8)
Ru(2)–C(2-1)	1.93 (6)	1.86 (7)
Ru(2)–C(2-2)	1.80 (8)	1.98 (6)
Ru(2)–C(2-3)	1.90 (5)	2.01 (7)
Ru(2)–C(2-4)	1.89 (5)	1.94 (5)
Ru(3)–C(3-1)	1.97 (7)	1.86 (7)
Ru(3)–C(3-2)	1.97 (6)	1.85 (6)
Ru(3)–C(3-3)	1.81 (6)	1.81 (5)
Ru(3)–C(2-3)	2.47 (5)	2.42 (5)
Ru(4)–C(4-1)	1.85 (6)	1.94 (8)
Ru(4)–C(4-2)	1.84 (6)	1.79 (6)
Ru(4)–C(4-3)	1.85 (7)	1.93 (8)
Ru(4)–C(2-4)	2.31 (5)	2.40 (4)
C(1-1)–O(1-1)	0.94 (8)	1.09 (5)
C(1-2)–O(1-2)	1.19 (6)	1.04 (6)
C(1-3)–O(1-3)	1.18 (5)	1.23 (8)
C(2-1)–O(2-1)	1.20 (6)	1.19 (6)
C(2-2)–O(2-2)	1.16 (7)	1.03 (6)
C(2-3)–O(2-3)	1.13 (4)	1.23 (6)
C(2-4)–O(2-4)	1.25 (5)	1.22 (6)
C(3-1)–O(3-1)	1.10 (7)	1.14 (7)
C(3-2)–O(3-2)	1.01 (6)	1.13 (5)
C(3-3)–O(3-3)	1.17 (6)	1.33 (6)
C(4-1)–O(4-1)	1.21 (6)	1.11 (8)
C(4-2)–O(4-2)	1.09 (6)	1.15 (5)
C(4-3)–O(4-3)	1.14 (7)	1.14 (8)

Description of the Structure

The crystal structure of H₂Ru₄(CO)₁₃ is made up of tetranuclear molecules. The two crystallographically independent molecules have similar configurations²⁹ and are situated such that pairs of ruthenium atoms are separated by a translation of approximately $1/4c$; however these two molecules are differently oriented. Figure 1 is a perspective view of the molecular structure, while Figure 2 schematically depicts the packing of the Ru₄ tetrahedra in the unit cell.

Within the tetrahedron of metal atoms, the Ru–Ru distances fall distinctly into two groups—the Ru(1)–Ru(3) and Ru(1)–Ru(4) distances range from 2.915 (7) to 2.947 (6) Å with a mean value of 2.930 (12) Å; the remaining Ru–Ru distances lie between 2.762 (6) and 2.818 (7) Å and average to 2.783 (18) Å. These distances may be compared with the mean values of 2.801 and 2.908 Å for the "short" and "long" Ru–Ru distances in H₂FeRu₃(CO)₁₃⁹ and with the slightly longer average values of 2.954 and 2.866 Å for the two types of Ru–Ru separation in H₂Ru₆(CO)₁₈.¹⁴ Previously reported Ru–Ru bond lengths have ranged from 2.698 (3)³⁰ to 3.034 (5) Å.³¹

Eleven of the thirteen carbonyl groups are terminally

(29) In view of the enforced limitations of this structural analysis, we feel that no significance can be attached to the few apparent (based on the tabulated esd's) differences between the two independent molecules. We prefer to use the presence of two crystallographically independent molecules in the asymmetric unit as a check and to concentrate on their common features. All structural parameters quoted are the same for both molecules and averages are taken over both molecules. Numbers in parentheses following mean values are root-mean-square deviations from the mean.

(30) M. R. Churchill, K. Gold, and P. H. Bird, *Inorg. Chem.*, **8**, 1956 (1969).

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

TABLE III
BOND ANGLES (DEG)

Angle	Molecule 1	Molecule 2	Angle	Molecule 1	Molecule 2
Ru(2)-Ru(1)-Ru(3)	57.97 (17)	58.50 (17)	Ru(1)-Ru(4)-C(2-4)	75.2 (13)	72.9 (12)
Ru(2)-Ru(1)-Ru(4)	57.54 (15)	58.18 (17)	Ru(2)-Ru(4)-C(4-1)	89.6 (15)	93.3 (17)
Ru(3)-Ru(1)-Ru(4)	57.47 (15)	57.22 (18)	Ru(2)-Ru(4)-C(4-2)	151.6 (17)	148.4 (21)
Ru(1)-Ru(2)-Ru(3)	63.36 (18)	63.49 (18)	Ru(2)-Ru(4)-C(4-3)	123.3 (21)	117.5 (18)
Ru(1)-Ru(2)-Ru(4)	64.18 (15)	63.85 (18)	Ru(2)-Ru(4)-C(2-4)	42.5 (13)	43.2 (13)
Ru(3)-Ru(2)-Ru(4)	61.32 (16)	60.55 (18)	Ru(3)-Ru(4)-C(4-1) ^b	97.4 (15)	93.0 (20)
Ru(1)-Ru(3)-Ru(2)	58.66 (17)	58.01 (16)	Ru(3)-Ru(4)-C(4-2) ^b	92.3 (17)	88.6 (21)
Ru(1)-Ru(3)-Ru(4)	61.84 (16)	61.58 (18)	Ru(3)-Ru(4)-C(4-3)	170.6 (22)	172.7 (20)
Ru(2)-Ru(3)-Ru(4)	59.30 (16)	59.58 (17)	Ru(3)-Ru(4)-C(2-4)	101.8 (13)	102.8 (13)
Ru(1)-Ru(4)-Ru(2)	58.29 (16)	57.96 (16)	C(1-1)-Ru(1)-C(1-2)	107.6 (28)	91.8 (24)
Ru(1)-Ru(4)-Ru(3)	60.69 (16)	61.20 (19)	C(1-1)-Ru(1)-C(1-3)	94.5 (27)	98.2 (29)
Ru(2)-Ru(4)-Ru(3)	59.38 (17)	59.87 (17)	C(1-2)-Ru(1)-C(1-3)	92.2 (23)	89.7 (28)
Ru(2)-Ru(1)-C(1-1)	166.2 (19)	169.0 (16)	C(2-1)-Ru(2)-C(2-2)	95.7 (29)	97.9 (24)
Ru(2)-Ru(1)-C(1-2) ^b	85.1 (19)	92.5 (16)	C(2-1)-Ru(2)-C(2-3)	92.7 (22)	92.0 (25)
Ru(2)-Ru(1)-C(1-3) ^b	90.2 (22)	92.0 (23)	C(2-1)-Ru(2)-C(2-4)	95.3 (22)	90.1 (24)
Ru(3)-Ru(1)-C(1-1) ^a	108.6 (19)	115.7 (16)	C(2-2)-Ru(2)-C(2-3)	88.3 (25)	93.1 (25)
Ru(3)-Ru(1)-C(1-2)	142.3 (19)	150.4 (16)	C(2-2)-Ru(2)-C(2-4)	91.4 (27)	90.1 (24)
Ru(3)-Ru(1)-C(1-3) ^a	95.0 (19)	96.7 (23)	C(2-3)-Ru(2)-C(2-4)	172.0 (23)	175.9 (19)
Ru(4)-Ru(1)-C(1-1) ^a	114.0 (17)	110.9 (17)	C(3-1)-Ru(3)-C(3-2)	96.4 (23)	93.8 (23)
Ru(4)-Ru(1)-C(1-2) ^a	98.0 (16)	104.1 (18)	C(3-1)-Ru(3)-C(3-3)	97.8 (26)	92.2 (25)
Ru(4)-Ru(1)-C(1-3)	144.8 (21)	147.0 (23)	C(3-1)-Ru(3)-C(2-3)	90.8 (20)	82.2 (21)
Ru(1)-Ru(2)-C(2-1)	163.3 (16)	165.8 (17)	C(3-2)-Ru(3)-C(3-3)	86.8 (24)	85.4 (23)
Ru(1)-Ru(2)-C(2-2)	101.0 (24)	94.8 (17)	C(3-2)-Ru(3)-C(2-3)	165.5 (18)	159.6 (25)
Ru(1)-Ru(2)-C(2-3)	86.4 (16)	93.5 (15)	C(3-3)-Ru(3)-C(2-3)	79.8 (21)	74.9 (19)
Ru(1)-Ru(2)-C(2-4)	85.8 (17)	83.6 (13)	C(4-1)-Ru(4)-C(4-2)	95.5 (24)	90.2 (24)
Ru(3)-Ru(2)-C(2-1)	101.8 (17)	109.2 (18)	C(4-1)-Ru(4)-C(4-3)	91.7 (27)	94.0 (29)
Ru(3)-Ru(2)-C(2-2)	144.6 (22)	139.8 (19)	C(4-1)-Ru(4)-C(2-4)	86.7 (21)	96.7 (20)
Ru(3)-Ru(2)-C(2-3)	60.5 (14)	57.8 (15)	C(4-2)-Ru(4)-C(4-3)	84.5 (27)	93.5 (26)
Ru(3)-Ru(2)-C(2-4)	117.0 (16)	118.1 (13)	C(4-2)-Ru(4)-C(2-4)	165.4 (21)	166.3 (22)
Ru(4)-Ru(2)-C(2-1)	102.8 (14)	102.1 (18)	C(4-3)-Ru(4)-C(2-4)	81.1 (24)	74.3 (22)
Ru(4)-Ru(2)-C(2-2)	143.3 (22)	141.9 (19)	Ru(1)-C(1-1)-O(1-1)	143 (8)	174 (5)
Ru(4)-Ru(2)-C(2-3)	121.7 (14)	118.0 (15)	Ru(1)-C(1-2)-O(1-2)	173 (6)	171 (6)
Ru(4)-Ru(2)-C(2-4)	55.8 (16)	58.0 (13)	Ru(1)-C(1-3)-O(1-3)	174 (6)	176 (6)
Ru(1)-Ru(3)-C(3-1)	146.2 (18)	147.6 (18)	Ru(2)-C(2-1)-O(2-1)	170 (5)	173 (5)
Ru(1)-Ru(3)-C(3-2) ^a	105.2 (15)	110.2 (17)	Ru(2)-C(2-2)-O(2-2)	171 (7)	171 (7)
Ru(1)-Ru(3)-C(3-3) ^a	108.9 (19)	110.6 (15)	Ru(2)-C(2-3)-O(2-3)	154 (5)	144 (5)
Ru(1)-Ru(3)-C(2-3)	74.4 (11)	82.0 (14)	Ru(2)-C(2-4)-O(2-4)	149 (4)	152 (4)
Ru(2)-Ru(3)-C(3-1)	89.9 (18)	91.3 (17)	Ru(3)-C(3-1)-O(3-1)	176 (6)	178 (6)
Ru(2)-Ru(3)-C(3-2)	149.7 (15)	155.6 (19)	Ru(3)-C(3-2)-O(3-2)	168 (6)	176 (6)
Ru(2)-Ru(3)-C(3-3)	121.7 (18)	118.3 (12)	Ru(3)-C(3-3)-O(3-3)	176 (6)	160 (4)
Ru(2)-Ru(3)-C(2-3)	42.2 (11)	44.8 (15)	Ru(3)-C(2-3)-O(2-3)	129 (4)	133 (5)
Ru(4)-Ru(3)-C(3-1) ^b	92.7 (16)	95.5 (20)	Ru(4)-C(4-1)-O(4-1)	170 (5)	178 (7)
Ru(4)-Ru(3)-C(3-2) ^b	90.8 (14)	96.1 (19)	Ru(4)-C(4-2)-O(4-2)	176 (6)	173 (5)
Ru(4)-Ru(3)-C(3-3)	169.5 (20)	172.1 (15)	Ru(4)-C(4-3)-O(4-3)	168 (7)	172 (6)
Ru(4)-Ru(3)-C(2-3)	101.4 (11)	104.2 (16)	Ru(4)-C(2-4)-O(2-4)	130 (4)	129 (4)
Ru(1)-Ru(4)-C(4-1)	146.9 (15)	147.8 (19)	Ru(2)-C(2-3)-Ru(3)	77 (2)	77 (2)
Ru(1)-Ru(4)-C(4-2) ^a	109.0 (18)	106.9 (20)	Ru(2)-C(2-4)-Ru(4)	82 (2)	79 (2)
Ru(1)-Ru(4)-C(4-3) ^a	112.1 (21)	111.5 (20)			

^a Denotes an equatorial Ru-Ru-C angle for a Ru-Ru edge proposed to be hydrogen bridged. ^b Denotes a corresponding angle for a nonbridged edge (see text).

TABLE IV
ROOT-MEAN-SQUARE AMPLITUDES OF THERMAL MOTION (Å)

	Molecule 1			Molecule 2		
	Maximum	Inter-mediate	Minimum	Maximum	Inter-mediate	Minimum
Ru(1)	0.284 (7)	0.238 (7)	0.170 (9)	0.233 (8)	0.209 (9)	0.182 (10)
Ru(2)	0.287 (7)	0.233 (7)	0.198 (8)	0.246 (9)	0.193 (9)	0.186 (9)
Ru(3)	0.298 (8)	0.266 (6)	0.185 (9)	0.239 (7)	0.235 (9)	0.167 (11)
Ru(4)	0.308 (7)	0.204 (7)	0.180 (9)	0.245 (8)	0.219 (8)	0.177 (11)

bound with mean Ru-C and C-O distances of 1.89 (10) and 1.14 (6) Å, respectively. The remaining two carbonyl groups form highly asymmetric bridges from Ru(2) to Ru(3) and to Ru(4). Each of the asymmetrically bridging groups is bound to Ru(2) at a distance (range 1.89 (5)-2.01 (7) Å; mean 1.94 (5) Å) indistinguishable from that found for the terminal carbonyl groups and interacts with a second ruthenium atom at a significantly greater distance (range 2.31 (5)-2.47 (5) Å; mean 2.40 (6) Å). The Ru(2)-C-O angles for these carbonyl groups depart significantly

TABLE V
INTERMOLECULAR CONTACTS LESS THAN 3.10 Å

Atoms ^a	Transformation ^b	Distance, Å
C1(1-1)-O1(3-2)	-1 - x, 1 - y, -z	2.88 (6)
O1(1-1)-O1(3-2)	-1 - x, 1 - y, -z	3.00 (6)
O1(1-1)-O1(4-3)	-x, 1 - y, -z	2.87 (6)
O1(2-1)-O2(1-1)	-1 - x, 1/2 + y, 1/2 - z	3.04 (6)
O1(1-2)-C1(3-2)	1 + x, y, z	3.07 (8)
O1(1-2)-O1(3-2)	1 + x, y, z	3.07 (6)
O1(1-3)-O1(4-3)	x, -1 + y, z	3.07 (6)
O1(2-2)-O1(4-3)	x, -1 + y, z	3.00 (5)
O1(2-3)-O1(4-2)	x, 1/2 - y, -1/2 + z	3.08 (6)
O1(2-4)-C2(4-2)	-x, 1/2 + y, 1/2 - z	3.04 (7)
O1(2-4)-O2(4-2)	-x, 1/2 + y, 1/2 - z	2.98 (7)
O1(3-1)-O2(4-2)	-1 - x, 1/2 + y, 1/2 - z	2.91 (7)
O2(1-1)-O2(2-3)	-1 - x, -1/2 + y, 1/2 - z	2.90 (7)
O2(1-2)-O2(4-1)	-1 + x, y, z	2.98 (5)
O2(2-1)-O2(3-3)	-x, 1/2 + y, 1/2 - z	3.07 (7)

^a In references to intermolecular contacts the number of the molecule to which an atom belongs is written immediately after its chemical symbol. Thus C1(3-2) refers to carbon atom 3-2 of molecule 1. ^b In all cases the transformation applies to the second atom of the pair listed.

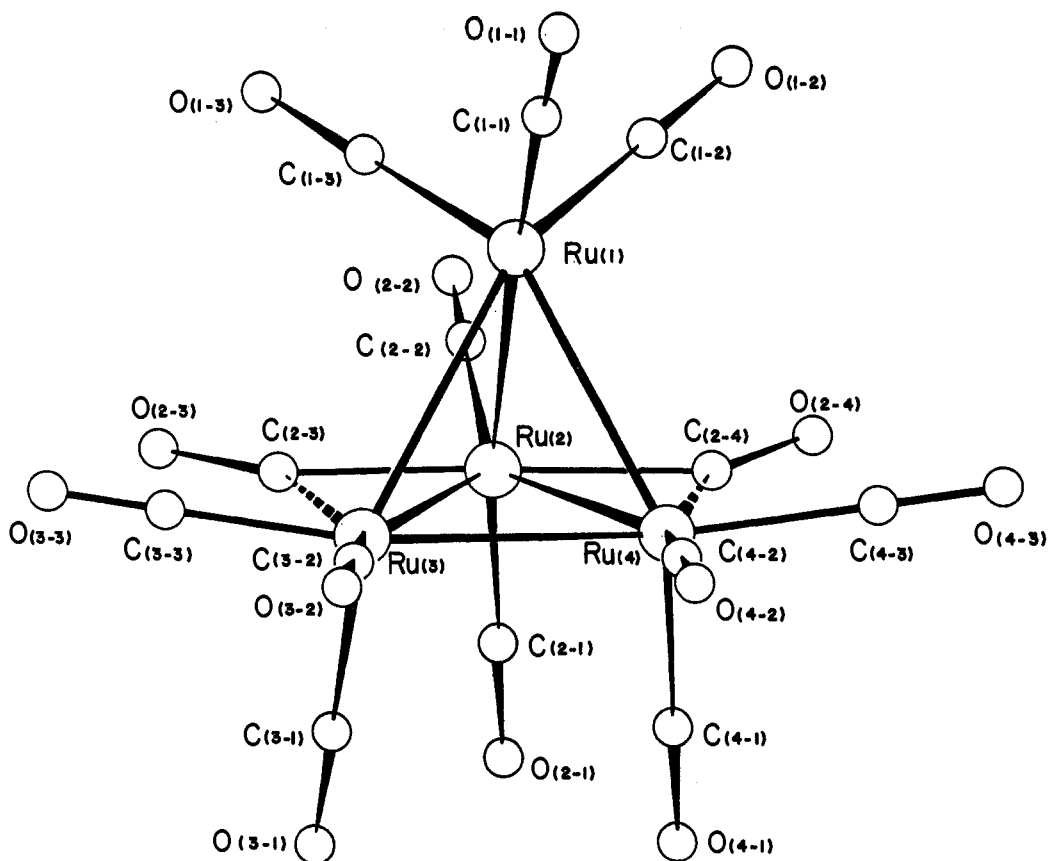


Figure 1.—A perspective view of the structure of the $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ molecule. Hydrogen atoms are not shown; they are believed to bridge the Ru(1)–Ru(3) and Ru(1)–Ru(4) tetrahedral edges. See text for a further discussion of this point.

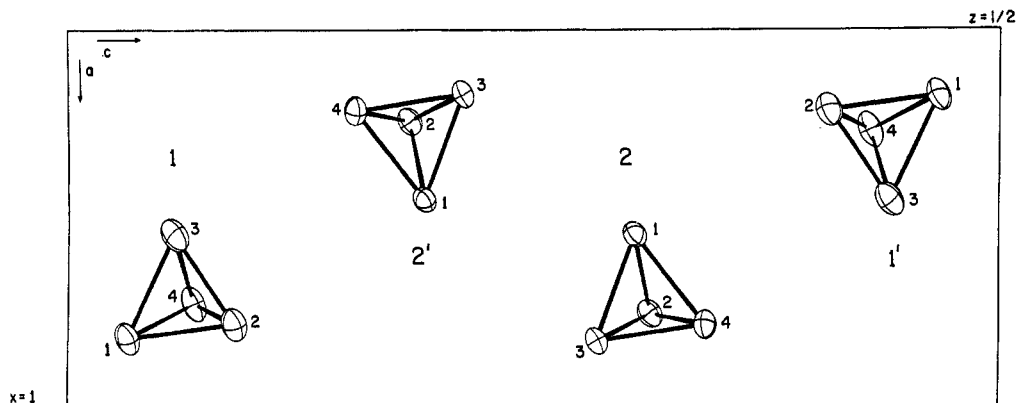


Figure 2.—A schematic view of the packing of the Ru_4 tetrahedra in the unit cell projected onto the ac plane. Only half of the unit cell is shown. The remaining half of the cell is related to that shown by the center of symmetry at $1/2, 1/2, 1/2$. Primes denote molecules related by the twofold screw axis to the corresponding unprimed molecules. The thermal ellipsoids are drawn at the 50% probability level.

from linearity (range 144 (5)–154 (5) $^\circ$; mean 150 (4) $^\circ$). This type of asymmetric bridging carbonyl was also found in $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ ⁹ and $\text{Fe}_4(\text{CO})_{13}^{2-}$,¹⁸ as well as in various other metal carbonyl complexes.³²

Though the hydrogen atoms were not directly located in this study, indirect evidence leads to a conclusion regarding their probable location analogous to that reached by Gilmore and Woodward for $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$.⁹ Situation of the hydrogen atoms as bridges on the Ru(1)–Ru(3) and Ru(1)–Ru(4) tetrahedral edges is con-

sistent with the pattern of metal–metal distances and with the larger Ru–Ru–equatorial C angles³³ associated with the two long edges. These angles (denoted by a in Table III) may be interpreted as resulting from a spreading out of the equatorial carbonyl groups to accommodate a bridging hydrogen atom; they are, as a group, distinctly greater than the corresponding angles (denoted in Table III by b) associated with the two short unbridged tetrahedral edges Ru(1)–Ru(2) and Ru(3)–Ru(4). Average values of the two types of

(32) See for example: (a) E. F. Epstein and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 493 (1970), and references therein; (b) M. R. Churchill and M. V. Veidis, *J. Chem. Soc. A*, 2170 (1971); (c) M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *J. Amer. Chem. Soc.*, **93**, 3073 (1971).

(33) As used in this paper, the term "equatorial" is defined with respect to a particular metal–metal vector and an equatorial carbonyl group is one for which the Ru–Ru–C angle is close to 90 $^\circ$. Angles involving the bridging carbonyl groups are not considered in this comparison.

angle are $a = 107.3^\circ$ and $b = 92.1^\circ$. This reasoning exactly parallels that used to infer the locations of bridging hydrogen atoms in $\text{H}_2\text{Re}_3(\text{CO})_{12}$ ¹² and $\text{H}_2\text{Ru}_6(\text{CO})_{18}$.¹⁴ Placement of the hydrogens in bridging configurations on the Ru(2)–Ru(3) and Ru(2)–Ru(4) edges retains the approximate C_s - m molecular symmetry exhibited by the nonhydrogen atoms.

The root-mean-square thermal displacements of the ruthenium atoms listed in Table IV are reasonable, though it would probably be unwise to attach quantitative significance to them. Likewise, the isotropic temperature factors of the carbon and oxygen atoms show, for the most part, the expected trends. No abnormal intermolecular contacts are observed; most of the shorter contacts (see Table V) occur between carbonyl oxygen atoms, with a minimum intermolecular O...O separation of 2.87 (6) Å.

Discussion

Of the series $[\text{H}_n\text{M}_4(\text{CO})_{13}]^{(2+n)-}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$; $n = 0, 1, 2$), the structures of $[\text{Fe}_4(\text{CO})_{13}]^{2-}$,¹⁸ $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$,⁹ and $\alpha\text{-H}_2\text{Ru}_4(\text{CO})_{13}$ are now known. The structures of the two neutral hydrides are the same in all important respects with the exception of the bond length differences resulting from replacement of one ruthenium atom by an iron atom in the heteronuclear hydride. The arrangement of the carbonyl groups in the two neutral hydrides is quite different from that in $[\text{Fe}_4(\text{CO})_{13}]^{2-}$. For both $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ and $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ the observed infrared absorptions in the bridging carbonyl region⁸ must presumably be attributed to the highly asymmetric carbonyl bridges. The differences in the bridging carbonyl bands for the two hydrides are not attributable to any gross differences in carbonyl group function other than the presence of Fe–C...Ru bridges in one case and Ru–C...Ru bridges in the other. No systematic study of the effect of the asymmetry of bridging carbonyl groups on their infrared absorption frequencies has been made and neither is a simple theoretical picture of the bonding in these groups available.^{34–36} To date, observation of highly asymmetric bridging carbonyl groups has largely been confined to complexes of the iron group

(34) A molecular orbital calculation for $\text{Mn}_2(\text{CO})_{10}$ has yielded results which were interpreted as favoring a significant Mn...C interaction across the metal–metal bond.³⁵ Existence of this type of "incipient bridge carbonyl bonding" had previously been proposed for a variety of systems by Berry, *et al.*³⁵ One thus could envision a broad range of metal–carbonyl–metal interactions from symmetric bridging through varying degrees of asymmetry to "incipient bridging."

(35) D. A. Brown, W. J. Chambers, N. J. Fitzpatrick, and R. M. Rawlinson, *J. Chem. Soc. A*, 720 (1971).

(36) A. D. Berry, E. R. Corey, A. P. Hagen, A. G. MacDiarmid, F. E. Saalfeld, and B. B. Wayland, *J. Amer. Chem. Soc.*, **92**, 1940 (1970).

metals (an exception is the Rh...C–Fe bridge in $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_2(\text{CO})_8$);^{32b} in fact $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ contains the first examples of such bridges in which neither of the bridged atoms is an iron atom.^{36a} The presence of bridging carbonyl groups in $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ has been used in accounting for the ease with which this compound reacts with hydrogen to form $\text{H}_4\text{Ru}_4(\text{CO})_{12}$.³⁷

It is tempting to speculate on the possible structures of $\beta\text{-H}_2\text{Ru}_4(\text{CO})_{13}$ and $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ and the relationship of these structures to that of $\alpha\text{-H}_2\text{Ru}_4(\text{CO})_{13}$. The strong similarity of the infrared spectra of α - and $\beta\text{-H}_2\text{Ru}_4(\text{CO})_{13}$ in the carbonyl region implies that the carbonyl groups are similarly disposed in the two forms, while the differences in H nmr spectra (*vide supra*) require a different hydrogen atom environment in the β form. Terminal or triply bridging hydrogen atoms are the obvious alternatives; we favor the latter on the basis that it would require smaller adjustments of the carbonyl group configurations. Static equivalence of the two protons (consistent with but not required by the nmr data) could be maintained if they bridged the Ru(1)–Ru(2)–Ru(4) and Ru(1)–Ru(2)–Ru(3) faces. The earlier report of the existence of two isomeric forms of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ ¹ has been called into question.³⁷ If indeed only a single isomer exists, a D_{2d} structure with four doubly bridging hydrogens (Figure 2e of ref 1) would appear to be most consistent with the observed ir and nmr data.³⁸

All of the metal atom clusters of the $[\text{H}_n\text{M}_4(\text{CO})_{13}]^{(2+n)-}$ and $\text{H}_4\text{M}_4(\text{CO})_{12}$ molecules contain a number of electrons consistent with the noble gas formalism. Though valence-bond structures exist which allow each metal atom separately to attain a noble gas configuration, the drawing of such structures adds little to our understanding of these systems and is probably not a useful exercise. Molecular orbital treatments which allow for considerable electron delocalization will undoubtedly be needed to account fully for the structural and chemical properties of this type of molecule.

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(36a) NOTE ADDED IN PROOF.—Highly asymmetric Co—C...Co bridges have recently been reported in a cobalt carbonyl derivative which contains a tetrahedral cobalt atom cluster: F. W. B. Einstein and R. D. G. Jones, *J. Chem. Soc. A*, 3359 (1971).

(37) H. D. Kaesz, S. A. R. Knox, J. W. Koepke, and R. B. Salliant, *Chem. Commun.*, 477 (1971).

(38) Since submission of this paper, a similar conclusion has been reported by S. A. R. Knox and H. D. Kaesz, *J. Amer. Chem. Soc.*, **93**, 4595 (1971).