Stereochemically Nonrigid Organometallic Molecules. XV. The Structure of One of the Isomeric $C_8H_8Ru_2(CO)_6$ Molecules in the Crystalline Compound[1,2]

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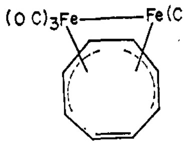
Abstract: The crystal and molecular structures of one of the isomeric (cyclooctatetraene)diruthenium hexacarbonyls have been determined by means of a three-dimensional, X-ray crystal-structure analysis. The intensities of 3141 independent reflections were measured with a counter diffractometer. The structure was solved by Patterson and Fourier methods and refined using anisotropic thermal parameters by full-matrix least squares to a final unweighted discrepancy index of 0.05. Crystallographic data are: space group, $P2_1/n$; unit cell dimensions, $a = 8.906$ Å, $b = 17.96$ Å, $c = 9.245$ Å, $\beta = 90.27°$; $Z = 4$; $\rho_{calcd} = 2.095$ g/cm³, $\rho_{obsd} = 2.091$ g/cm³. The molecule possesses no symmetry in the crystal. It consists of an $(OC)_3Ru\text{-}Ru(CO)_3$ portion which is bonded to the ring by means of a π-allyl–metal bond to one Ru, an olefin–metal bond, and a carbon–metal σ bond to the other Ru (these descriptions are but rough approximations), and there is an uncoordinated C=C bond in the ring. The Ru—Ru line is nearly perpendicular to the unused C=C bond. The implications of this result with respect to the (different) structures previously postulated for the $C_8H_8Fe_2(CO)_6$ having a very similar nmr spectrum and some other molecules are discussed.

A number of the products of reaction of cyclooctatetraene with $Ru_3(CO)_{12}$ have been isolated and characterized.[4-8] One of the products, a substance with the composition $C_8H_8Ru_2(CO)_6$, has an nmr spectrum[8] very similar to that of an iron compound, $C_8H_8Fe_2(CO)_6$, for which Keller, Emerson, and Pettit[9] proposed the structure I. This proposal was based on the nmr spectrum[9] and on the conclusion drawn from the Mössbauer spectrum[9,10] of this and some related molecules[10] that the iron atoms must be in equivalent environments but subject to relatively large field gradients in order to account for the appearance of two Mössbauer absorption bands. The possibility that the observed spectra might be attributed to two nonequivalent iron atoms, differing but slightly in their chemical shifts and quadrupole splittings, was described[10] as "very remote."



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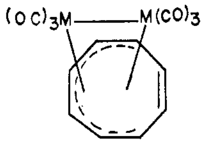

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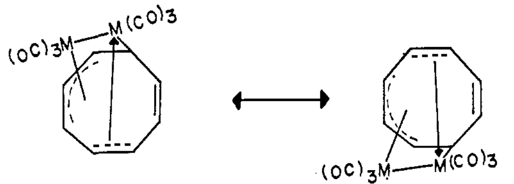

IIIa IIIb

In this laboratory, the nmr spectrum of the ruthenium compound has been studied[6,8] in considerable detail using double and triple irradiation techniques to decouple spins, and it has been concluded that the spectrum is fully consistent with the set of eight proton spins being sorted into four sets of equivalent pairs. No other satisfactory interpretation of the nmr data was considered to be possible, and it was therefore concluded that the "nmr symmetry" of the molecule must be $C_s(m)$ with the single mirror plane passing through the ring so as to be a perpendicular bisector of each of two opposite (1,5) C–C bonds. Structure I is, of course, consistent with, but is not proved correct, by this observation.

In order to determine conclusively the structures of the $C_8H_8Fe_2(CO)_6$ and $C_8H_8Ru_2(CO)_6$ molecules, which might be presumed to be isostructural because of the close similarity of their nmr spectra, a single-crystal X-ray study of the ruthenium compound was undertaken. The results of this study, which *disprove* structure I, are reported here.

Procedure

The compound was prepared and crystallized from pentane solution by Dr. A. Musco. The bright yellow plates so obtained were stable in air through all subsequent operations.

Single crystals were examined by precession and Weissenberg photography and were found to be monoclinic. The systematic absences, $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$, observed on precession films of $hk0$, $0kl$, and $1kl$ levels and on the Weissenberg films of $h0l$ and hll levels, indicate that the space group is $P2_1/n$ (general positions x, y, z; $^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$; $^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$; $\bar{x}, \bar{y}, \bar{z}$). The unit cell dimensions are $a = 8.906 \pm 0.004$, $b = 17.96 \pm 0.03$, $c = 9.245 \pm 0.003$ Å with $\beta = 90.27 \pm 0.04°$ at 23°.

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[1] Research supported by the National Science Foundation under Grant No. GP-7034X.

[2] Part XIV: F. A. Cotton and M. D. LaPrade, *J. Am. Chem. Soc.*, **90**, 2026 (1968).

[3] National Institutes of Health Predoctoral Fellow.

[4] M. I. Bruce, M. Cooke, M. Green, and F. G. A. Stone, *Chem. Commun.*, 523 (1967).

[5] W. K. Bratton, F. A. Cotton, A. Davison, J. W. Faller, and A. Musco, *Proc. Natl. Acad. Sci. U. S.*, **58**, 1324 (1967).

[6] F. A. Cotton, A. Davison, and A. Musco, *J. Am. Chem. Soc.*, **89**, 6796 (1967).

[7] M. J. Bennett, F. A. Cotton, and P. Legzdins, *ibid.*, **89**, 6797 (1967).

[8] F. A. Cotton, A. Davison, and A. Musco, unpublished studies.

[9] C. E. Keller, G. F. Emerson, and R. Pettit, *ibid.*, 87, 1388 (1965).

[10] G. F. Emerson, J. E. Mahler, R. Pettit, and R. Collins, *ibid.*, **86**, 3590 (1964).

The method used to determine a, b, and c, employing copper radiation ($\lambda(K\alpha_1)$ 1.5405 Å, $\lambda(K\alpha_2)$ 1.5443 Å) has been described elsewhere.[11] The crystal used for these measurements and for the subsequent intensity measurements was mounted along its b axis so that β was measured using the ϕ circle of the diffractometer. The uncertainty intervals quoted for all the unit cell constants represent estimates of precision.

The observed density of 2.091 g/cm^3 measured by flotation in aqueous silver nitrate solution agrees well with the calculated density of 2.095 g/cm^3 for a molecular weight of 466.35 g/mole and a unit cell volume of 1479 Å^3 with $Z = 4$.

Intensity data were collected on a General Electric XRD-6 automated diffractometer from a crystal of dimensions 0.219 × 0.128 × 0.073 mm. The intensities of 3141 independent reflections (including space group forbidden reflections in the two nonequivalent sets: hkl, $\bar{h}kl$) within a sphere bounded by $\theta = 26°$ were measured using Mo Kα radiation (λ 0.7107 Å) filtered through zirconium foil. The integrated intensities were measured with a scintillation counter. The pulse height discriminator was set to accept 95% of the Mo Kα radiation with the window centered on the Mo Kα peak. Data were taken using a $\theta/2\theta$ scan of 2.66° at a scan rate of 4°/min with stationary background counts of 20 sec each at $2\theta_{\text{calcd}} - 1.33°$ and $2\theta_{\text{calcd}} + 1.33°$.[12] Periodic checks of two standard reflections showed a variance of ~2% which was random with time and attributable to fluctuation in electronic circuits rather than crystal decomposition. No appreciable variation (~4%) in the intensity of the 040 reflection was observed in the φ scans, and absorption corrections were therefore omitted during refinement.

The data were processed using a general data reduction program[13] which rejected 1842 reflections as unreliable using the two criteria $I \leq 0$ and $I < 3(P + B_1 + B_2)^{1/2}$. The remaining 1299 reflections were corrected for Lorentz and polarization effects and a set of $|F_o|$ was calculated.

Solution and Refinement of the Structure. The positions of the two ruthenium atoms were found from a three-dimensional Patterson map.[14] A three-dimensional electron density map was then calculated using signs provided by the two ruthenium atoms ($R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_c| = 0.31$). All other atoms except hydrogen atoms were identified in this map and trial coordinates assigned.

Refinement[15–17] proceeded with signs computed using all atoms (2Ru, 14C, 6O) and the various stages are summarized in Table I.

Table I. Summary of Steps in Least-Squares Refinement

Parameters varied, etc.	R_1	R_2[a]
1. Only Ru atoms in; positional and isotropic temperature parameters	0.311	0.374
2. Positional and isotropic temperature parameters for all (except H) atoms; three cycles	0.071	0.074
3. Positional parameters of all atoms; fully anisotropic; four cycles	0.050	0.056

[a] $R_2 = (\Sigma w||F_o| - |F_c||)/\Sigma w|F_c|$. σ, the standard deviation of corrected intensities (*cf.* R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967)), is defined as $\sigma(I) = (\Delta I^2 + PI^2)^{1/2}$ where P, the uncertainty factor, was assigned a value of 0.002. The weighting scheme used was $w = 1/\sigma^2$, $\sigma = \sigma(F^2)/2F_o$, where $\sigma(F^2)$ is the Lorentz and polarization corrected $\sigma(I)$.

In the last cycle of refinement there was no parameter shift greater than $^1/_{10}$ of one esd. A final difference Fourier map showed no peaks greater than 0.4 e/Å^3. These were in the vicinity of the metal atoms and were less than 0.01 times the height of the original atom peak observed in the first calculated electron density map.

Final atomic coordinates are listed in Table II.

Table II. Final Atomic Positional Parameters[a]

Atom	x	y	z
Ru$_1$	0.2310 (1)	0.1167 (1)	0.1720 (1)
Ru$_2$	0.5177 (1)	0.1715 (1)	0.2652 (1)
C$_1$	0.5823 (17)	0.1610 (10)	0.0727 (18)
C$_2$	0.4692 (20)	0.2752 (11)	0.2619 (20)
C$_3$	0.7121 (19)	0.1895 (10)	0.3342 (19)
C$_4$	0.2730 (19)	0.1056 (11)	−0.0334 (21)
C$_5$	0.0301 (22)	0.0834 (12)	0.1533 (22)
C$_6$	0.1800 (17)	0.2170 (11)	0.1624 (18)
C$_7$	0.2561 (18)	−0.0050 (9)	0.2438 (21)
C$_8$	0.4004 (17)	0.0213 (8)	0.2178 (16)
C$_9$	0.5125 (16)	0.0512 (9)	0.3237 (17)
C$_{10}$	0.4913 (15)	0.0940 (9)	0.4466 (16)
C$_{11}$	0.3722 (16)	0.1444 (9)	0.4636 (17)
C$_{12}$	0.2150 (16)	0.1273 (8)	0.4017 (16)
C$_{13}$	0.1659 (17)	0.0542 (11)	0.4639 (19)
C$_{14}$	0.1885 (18)	−0.0071 (10)	0.3924 (21)
O$_1$	0.6271 (16)	0.1556 (9)	−0.0430 (15)
O$_2$	0.4481 (16)	0.3378 (8)	0.2695 (21)
O$_3$	0.8322 (14)	0.2017 (8)	0.3692 (15)
O$_4$	0.2968 (16)	0.1012 (9)	−0.1542 (14)
O$_5$	−0.0892 (15)	0.0638 (10)	0.1458 (18)
O$_6$	0.1431 (15)	0.2782 (8)	0.1613 (14)

[a] Figures in parentheses are standard deviations occurring in the last significant figure given.

Anisotropic thermal parameters and equivalent isotropic atomic thermal parameters (B's) are listed in Table III. A listing of observed structure amplitudes and calculated structure factors is to be found in Table IV.[18] Intramolecular distances and bond angles are tabulated in Tables V and VI, while the shortest intermolecular contacts are collected in Table VII.

Two views of the molecule are shown in Figures 1 and 2 and a schematic bonding diagram is given in Figure 3. Figure 4 illustrates the arrangement of the four molecules in one unit cell.

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(11) M. J. Bennett, F. A. Cotton, and J. Takats, *J. Am. Chem. Soc.*, **90**, 903 (1968).

(12) Diffractometer settings were calculated using the program MIXG2A, a modified version of MIXG2 by D. P. Shoemaker (1962) adapted to yield control cards for the Datex-controlled G.E. automated diffractometer.

(13) M. J. Bennett, PMMO, Massachusetts Institute of Technology, 1967.

(14) All Fourier calculations were carried out using FORDAP II, "A General Crystallographic Fourier Program for the IBM 360/65," adapted by B. M. Foxman, Massachusetts Institute of Technology, 1967, from A. Zalkin's FORDAP program.

(15) The atomic scattering factors used were taken from D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(16) Refinement was carried out using SFLS5, Version 2, 1967, a full-matrix, least-squares program for the IBM 360/65. In this program the function minimized is $\Sigma w(|F_o| - |F_c|)^2$.

(17) Anomalous dispersion corrections, real ($\Delta f' = -1.30$ e) and imaginary ($\Delta f'' = +1.0$ e) parts, applied to the ruthenium scattering factors were taken from "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, p 216.

(18) This table has been deposited as Document No. NAPS-00031 with the ASIS National Auxiliary Publication Service, ℅ CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and by remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

Table III. Components of Anisotropic Thermal Tensors (×10⁴) and Equivalent Isotropic Thermal Parameters[a,b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B
Ru_1	85 (2)	27 (1)	87 (2)	12 (1)	−14 (1)	−7 (1)	3.06
Ru_2	80 (2)	19 (1)	91 (2)	3 (1)	10 (1)	4 (1)	2.69
C_1	102 (24)	43 (9)	75 (23)	3 (11)	1 (19)	20 (11)	3.77
C_2	146 (31)	34 (8)	144 (30)	20 (13)	16 (23)	3 (13)	4.62
C_3	84 (24)	40 (9)	160 (31)	−8 (11)	8 (22)	−4 (12)	4.42
C_4	137 (28)	39 (9)	142 (30)	17 (12)	−9 (23)	−38 (14)	4.77
C_5	103 (29)	45 (10)	216 (39)	12 (13)	20 (28)	−14 (15)	5.46
C_6	75 (23)	40 (9)	98 (25)	−10 (11)	−35 (19)	4 (12)	3.64
C_7	96 (24)	18 (6)	195 (33)	−3 (10)	−11 (22)	9 (11)	4.02
C_8	115 (25)	15 (6)	100 (23)	17 (9)	0 (18)	10 (9)	2.97
C_9	106 (25)	20 (6)	84 (22)	−1 (9)	23 (10)	0 (9)	2.94
C_{10}	86 (21)	24 (6)	86 (21)	1 (9)	48 (17)	21 (9)	2.90
C_{11}	74 (21)	27 (6)	108 (23)	−8 (9)	−1 (17)	15 (9)	3.14
C_{12}	104 (23)	20 (6)	85 (21)	0 (9)	3 (17)	− 6 (9)	2.92
C_{13}	74 (23)	35 (8)	153 (29)	−8 (11)	2 (20)	15 (12)	4.03
C_{14}	98 (25)	27 (7)	180 (34)	3 (11)	−21 (23)	9 (13)	4.27
O_1	253 (28)	65 (9)	148 (22)	−7 (11)	80 (20)	7 (11)	7.16
O_2	195 (25)	29 (63)	429 (42)	23 (10)	10 (24)	−9 (13)	8.23
O_3	116 (20)	53 (7)	223 (25)	−3 (9)	−13 (18)	−11 (10)	6.03
O_4	265 (28)	72 (8)	114 (20)	29 (12)	12 (19)	−34 (11)	7.22
O_5	116 (23)	78 (9)	341 (35)	−8 (11)	−27 (22)	−49 (14)	8.49
O_6	231 (27)	46 (7)	149 (21)	45 (21)	−48 (18)	5 (10)	6.10

[a] Figures in parentheses are standard deviations occurring in the last significant figure given. [b] Anisotropic thermal parameters are of the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}\,kl)$.

Table V. Intramolecular Distances (Å)[a]

Atoms	Distance	Atoms	Distance
Ru_1-Ru_2	2.865 (2)	C_1-O_1	1.15 (2)
Ru_2-C_1	1.88 (2)	C_2-O_2	1.14 (2.5)
Ru_2-C_2	1.91 (2)	C_3-O_3	1.14 (2)
Ru_2-C_3	1.87 (2)	C_4-O_4	1.14 (2)
Ru_1-C_4	1.95 (2)	C_5-O_5	1.12 (2.5)
Ru_1-C_5	1.89 (2)	C_6-O_6	1.15 (2.5)
Ru_1-C_6	1.86 (2)	C_7-C_8	1.39 (2)
Ru_1-C_7	2.30 (2)	C_8-C_9	1.50 (2)
Ru_1-C_8	2.32 (1.5)	C_9-C_{10}	1.39 (2)
Ru_1-C_9	3.10 (1.5)	$C_{10}-C_{11}$	1.40 (2)
Ru_1-C_{10}	3.45 (1.5)	$C_{11}-C_{12}$	1.54 (2)
Ru_1-C_{11}	3.01 (1.5)	$C_{12}-C_{13}$	1.50 (2.5)
Ru_1-C_{12}	2.14 (1.5)	$C_{13}-C_{14}$	1.30 (2.5)
Ru_1-C_{13}	2.98 (2)	$C_{14}-C_7$	1.50 (2.5)
Ru_1-C_{14}	3.04 (2)		
Ru_2-C_7	3.94 (1.5)		
Ru_2-C_8	2.93 (1.5)		
Ru_2-C_9	2.23 (1.5)		
Ru_2-C_{10}	2.19 (1.5)		
Ru_2-C_{11}	2.30 (1.5)		
Ru_2-C_{12}	3.09 (1.5)		
Ru_2-C_{13}	4.21 (2)		
Ru_2-C_{14}	4.51 (2)		

[a] Figures in parentheses are standard deviations occurring in the last significant figure given.

Table VI. Bond Angles (Degrees)[a]

Atoms	Angle	Atoms	Angle
$Ru_1-C_4-O_4$	178.1 (1.6)	$Ru_1-Ru_2-C_1$	87.6 (0.5)
$Ru_1-C_5-O_5$	178.3 (1.8)	$Ru_1-Ru_2-C_2$	97.4 (0.5)
$Ru_1-C_6-O_6$	176.6 (1.4)	$Ru_1-Ru_2-C_3$	169.8 (0.5)
$Ru_2-C_1-O_1$	177.5 (1.6)	$Ru_2-Ru_1-C_4$	98.8 (0.5)
$Ru_2-C_2-O_2$	174.3 (1.7)	$Ru_2-Ru_1-C_5$	167.4 (0.6)
$Ru_2-C_3-O_3$	176.5 (1.6)	$Ru_2-Ru_1-C_6$	84.2 (0.5)
$C_4-Ru_1-C_5$	93.7 (0.8)	$C_7-Ru_1-C_8$	35.1 (0.5)
$C_4-Ru_1-C_6$	95.8 (0.7)	$C_9-Ru_2-C_{10}$	36.5 (0.5)
$C_5-Ru_1-C_6$	94.1 (0.8)	$C_{10}-Ru_2-C_{11}$	36.3 (0.5)
$C_1-Ru_2-C_2$	98.8 (0.7)	$Ru_1-C_{12}-C_{13}$	108.9 (1.0)
$C_1-Ru_2-C_3$	92.9 (0.8)	$Ru_1-C_{12}-C_{11}$	108.8 (0.9)
$C_2-Ru_2-C_3$	92.6 (0.7)		
$C_7-C_8-C_9$	128.5 (1.4)		
$C_8-C_9-C_{10}$	130.0 (1.3)		
$C_9-C_{10}-C_{11}$	123.7 (1.3)		
$C_{10}-C_{11}-C_{12}$	121.1 (1.3)		
$C_{11}-C_{12}-C_{13}$	107.3 (1.2)		
$C_{12}-C_{13}-C_{14}$	120.0 (1.5)		
$C_{13}-C_{14}-C_7$	120.4 (1.4)		
$C_{14}-C_7-C_8$	122.8 (1.5)		

[a] Figures in parentheses are standard deviations occurring in the last significant figure given.

Table VII. Selected Intermolecular Contacts

Atom I	Atom J	Vector from molecule containing I to molecule containing J	Contact
C_6	C_3	$^1/_2 + x,\ ^1/_2 - y,\ ^1/_2 + z$	3.481
O_6	C_8	$^1/_2 + x,\ ^1/_2 - y,\ ^1/_2 + z$	3.144
O_3	C_6	$^1/_2 + x,\ ^1/_2 - y,\ ^1/_2 + z$	3.370
O_2	C_7	$^1/_2 - x,\ ^1/_2 + y,\ ^1/_2 - z$	3.359
O_1	C_7	$-x,\ -y,\ -z$	3.444
O_2	C_{14}	$^1/_2 - x,\ ^1/_2 + y,\ ^1/_2 - z$	3.384
O_2	O_4	$^1/_2 + x,\ ^1/_2 - y,\ ^1/_2 + z$	3.365
O_5	O_4	$-x,\ -y,\ -z$	3.493
C_{10}	O_6	$^1/_2 + x,\ ^1/_2 - y,\ ^1/_2 + z$	3.318
C_{11}	O_6	$^1/_2 + y,\ ^1/_2 - y,\ ^1/_2 + z$	3.325
O_1	O_6	$^1/_2 + x,\ ^1/_2 - y,\ ^1/_2 + z$	2.984
O_3	O_6	$^1/_2 + x,\ ^1/_2 - y,\ ^1/_2 + z$	3.210

Discussion

As may be seen in Figures 1 and 2, the molecule consists of two $Ru(CO)_3$ moieties lying on the same side of the C_8H_8 ring and connected to each other by a metal–metal bond. The $Ru_2(CO)_6$ group by itself has mm symmetry, consisting of a "sawhorse" arrangement, $Ru_2(CO)_4$, with the two additional CO groups (C_3–O_3, C_5–O_5) lying almost colinear with the pair of Ru atoms. The Ru–Ru distance, 2.865 Å, indicates the existence of a metal–metal single bond and may be compared with the average Ru–Ru bond lengths, 2.85 Å in $Ru_3(CO)_{12}$[19] and 2.89 Å in $(C_8H_8)_2Ru_3(CO)_4$.[7]

According to the usual views regarding the electronic structures of metal carbonyl compounds, each Ru atom of this $Ru_2(CO)_6$ group would be considered to have the capacity to interact with a ligand or ligands

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[19] E. R. Corey and L. F. Dahl, submitted for publication.

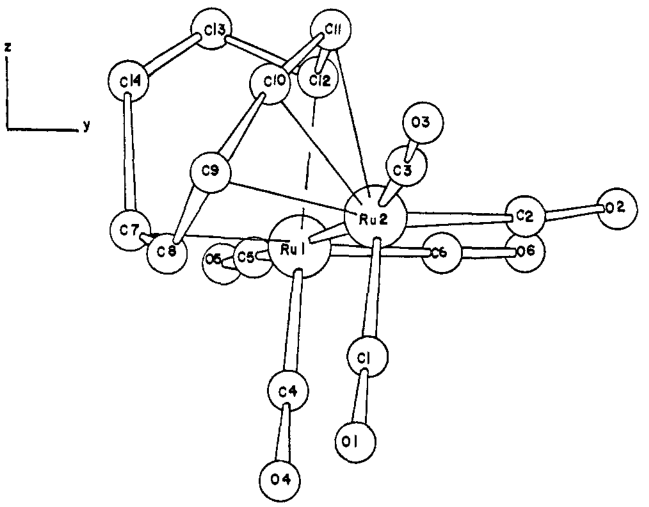

Figure 1. A perspective view of the molecule tilted 15° with respect to the x axis of the orthogonal coordinate system x, y, z corresponding to a, b, c^*.

It can be seen that the $Ru_2(CO)_6$ moiety is not oriented in any symmetrical way to the ring. It is not therefore possible to offer any neat, simple, symmetry-restricted description of the metal-to-ring bonding, but the following formulation seems to be consistent with all the main structural features.

Ru_2 is related to C_9, C_{10}, C_{11} as though a π-allyl-metal complex exists in this region of the molecule. All of the dimensions within this set of four atoms are similar to those found in various other π-allyl-metal complexes.[20]

Ru_1 is so placed relative to C_7 and C_8 (which are separated by 1.39 Å from each other and 2.31 ± 0.01 Å from Ru_1) that the existence of an olefin-metal complex involving these three atoms may be said to exist. Least-squares plane calculations show that the plane containing C_{14}, C_7, C_8, and C_9 makes an angle of 93° with a plane through the midpoint of the C_7–C_8 bond containing Ru_1. This is further evidence for an olefin-metal bond at this point. At the same time the very short C_{12}–Ru_1 distance is indicative of a metal-carbon σ bond,[21] and the assumption that there is such a bond is supported by the nearly tetrahedral bond angles at C_{12} (Ru_1–C_{12}–C_{11} = 108.8 ± 0.9°; Ru_1–C_{12}–C_{13} = 108.9 ± 1.0°) and the C_{12}–C_{13} and C_{12}–C_{11} bond lengths of 1.52 ± 0.02 Å.

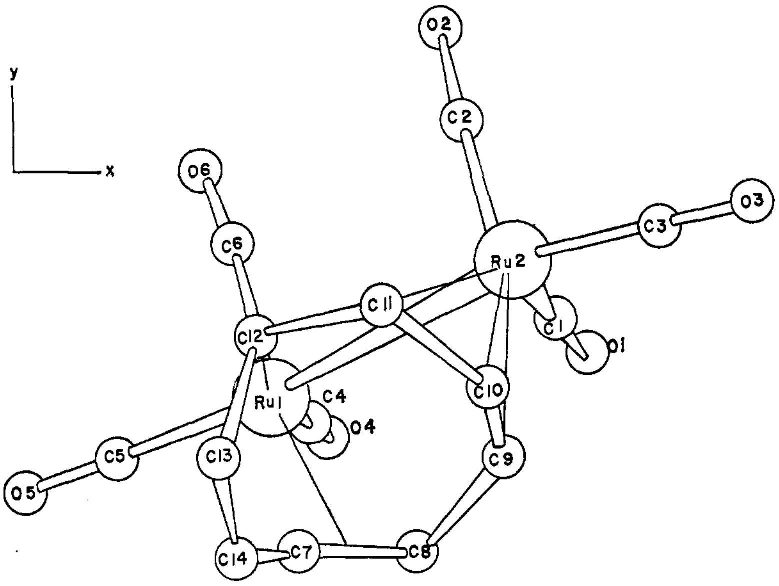

Figure 2. A perspective view of the molecule tilted 15° with respect to the z axis of the orthogonal coordinate system x, y, z corresponding to a, b, c^*.

capable of utilizing up to two orbitals and providing three electrons.

It is clear from Figures 1 and 2 and Table V that Ru_1 and Ru_2 each lie within bonding distance of three ring carbon atoms. Ru_2 lies 2.23, 2.19, and 2.30 Å from C_9, C_{10}, and C_{11}, respectively, while lying upwards of 2.93 Å from the other five ring atoms. Ru_1 lies 2.30, 2.32, and 2.14 Å, from C_7, C_8, and C_{12}, respectively, and upwards of 2.98 Å from all other ring atoms. Considering the relation of ring atoms to the metal atoms, six ring atoms, C_7–C_{12}, lie 2.14–2.32 Å from one or the other metal atom, while two ring atoms, C_{13} and C_{14}, do not lie within effective bonding distance of either metal atom. These two ring atoms are separated from each other by only 1.30 Å and the C-C-C bond angles subtended at each of them are 120 ± 2°. Clearly C_{13} and C_{14} make up an uncoordinated olefinic portion of the ring. The $Ru_2(CO)_6$ group is bonded to the other six carbon atoms.

Based on the above considerations, the bonding scheme shown in Figure 3 is proposed as a formal description of the metal-ring bonding in $C_8H_8Ru_2(CO)_6$ as the molecule occurs in the crystals. Comparison of this, and also Figures 1 and 2 with the structure and bonding scheme shown represented by I, indicates that $C_8H_8Ru_2(CO)_6$ is constituted quite differently from the proposal embodied in I. A number of further questions are thereby raised.

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(20) *Cf.* F. A. Cotton and J. Takats, *J. Am. Chem. Soc.*, **90**, 2031 (1968), and earlier work cited therein.

(21) *Cf.* the Mo–C σ-bond distance (2.38 Å) in π-$C_5H_5Mo(CO)_3C_2H_5$ reported by M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 273 (1963).

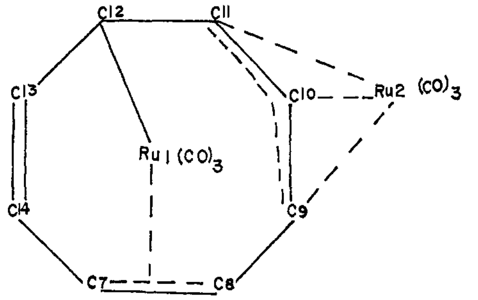

Figure 3. A schematic diagram of the bonding (formalized) in $C_8H_8Ru_2(CO)_6$.

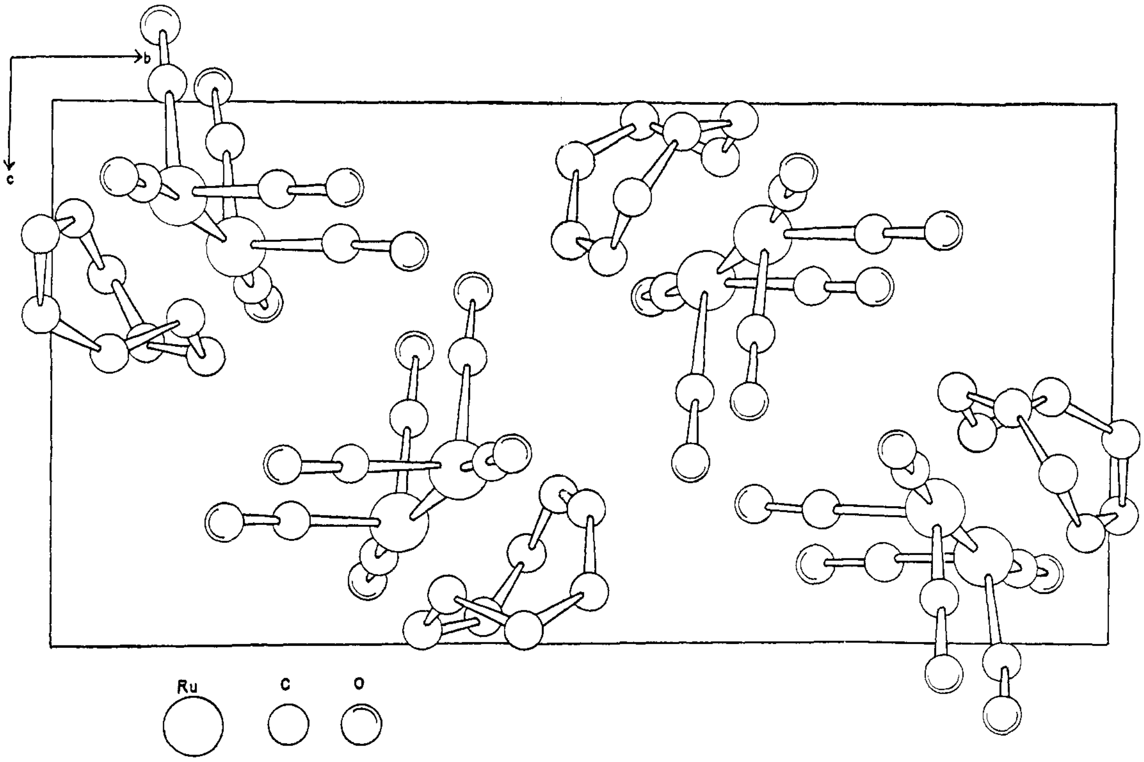

Figure 4. The contents of one unit cell projected onto (100).

First, there is the fact that the molecular structure we have found in the crystal does not have a plane of symmetry and cannot therefore provide a straightforward explanation for the $A_2B_2C_2X_2$ nmr spectrum. There would appear to be three possible ways to reconcile the observed asymmetric structure observed for the molecule in the crystal with the spectrum observed for the solution. (1) Assume that the molecule rearranges drastically to structure I when released from the crystal environment. (2) Assume that the molecule rearranges moderately to give structure II, a rigid structure with mirror symmetry, when released from the crystal. (3) Assume that the molecule is fluxional in the manner indicated by the rearrangement IIIa ↔ IIIb; this implies that the structure observed in the crystal is the one of lowest energy but that there is a rather low barrier, *via* structure II, separating it from its equivalent mirror image.

At present, there is no conclusive evidence for or against any of these hypotheses. However, there are some considerations which lead to an order of preference among the possibilities. First, we think assumption 1 is the least likely, and, in fact, consider it very improbable. Such a gross difference between structures in the crystalline and solution phases is a rare occurrence and is thus an unappealing idea so long as some other more plausible hypotheses are available. Assumption 2 is more attractive, since the degree of rearrangement required is relatively small. However, if II is the structure in solution, it is a little difficult to see why there is such a large amount of distortion in the crystal. It seems as likely that the instantaneous structure of the molecule in solution is an unsymmetrical one, very similar to or virtually identical with that found in the crystal, with the molecule executing the rearrangement IIIa ↔ IIIb rapidly enough at room temperature to give nmr symmetry corresponding to a mirror plane as observed at room temperature. There is, however, no firm basis for choice between assumptions 2 and 3 at the present time. Experiments which may afford a clear distinction between the possibilities will be described in a later paper in this series.

A second question raised by the crystallographic results reported here concerns the structure of the iron compound, $C_8H_8Re_2(CO)_6$, for which structure I has been suggested. It is clear from the reported nmr results[6,9] that the iron and ruthenium compounds must have the same or very similar structures in solution. If the tentative conclusion drawn above as to the structure of $C_8H_8Ru_2(CO)_6$ in solution is accepted (*i.e.*, that it is IIIa ↔ IIIb or possibly II), then the same conclusion applies to $C_8H_8Fe_2(CO)_6$. Then, just as for the ruthenium compound, a drastic structural change, such as II → I or III → I, seems unlikely on going from solution to the crystalline phase, and we are led to doubt that I is the correct structure for $C_8H_8Fe_2(CO)_6$ in the crystal.

In order to sustain such a doubt, however, it is necessary to rebut or at least seriously undermine the argument used by Keller, Emerson, and Pettit[9] to support structure I with Mössbauer data. While their argument is certainly a sensible one, it is not rigorous. In fact, it could well be yet another example of one of the most insidious of spectroscopic fallacies, namely, that high symmetry is proved by failure to observe bands or resolve splittings which should in principle be present for a lower symmetry structure.

The argument used[9] to support the postulate that the two iron atoms of $C_8H_8Fe_2(CO)_2$ are chemically identical in the crystal was not stated in detail but it seems clearly implied[9] that it is the same as the one used earlier[10] with regard to the $C_8H_{10}Fe_2(CO)_6$ and C_7H_8-$Fe_2(CO)_6$ molecules. It is, simply, that each iron atom should give rise to two Mössbauer resonances due to nuclear quadrupole splitting arising from the electric field gradient and that the possibility of the chemical shift and splitting parameters for the two iron nuclei being so similar as to lead to a spectrum containing only two resolved lines of very similar width is "extremely remote" unless the two iron nuclei are in fact equivalent. Such an occurrence, though perhaps in general remote, is not impossible, and examples of it were known for other organoiron carbonyl molecules. Thus[22] the compound $(\pi\text{-}C_5H_5)Fe(CO)_2\text{–}CH_2CH_2C(O)\text{–}Fe(CO)_2(\pi\text{-}C_5H_5)$, in which the two iron atoms are not equivalent, shows only two lines (separated by 1.66 mm/sec) of slightly unequal intensity and only slightly different widths (ratio 1.13). Again, for the compound $C_8H_6S[Fe(CO)_3]_2$, in which it would scarcely seem possible to have a symmetrical structure,[23] the Mössbauer spectrum consists of only two lines of essentially equal intensities and practically equal widths (ratio, 1.13) separated by 1.11 mm/sec. Finally, the compound $C_4H_4Fe_2(CO)_6$ has a two-line spectrum which Wertheim, *et al.*, did not resolve although Emerson, Mahler, Pettit, and Collins did achieve resolution of one peak. However, the deviation from a spectrum of two virtually identical single lines is not great, even here where the environments of the two iron atoms are very different indeed according to the postulated structure.[24] We think that a structure of type II or III could well lead to a two-line Mössbauer spectrum.

Finally, if the structure of $C_8H_8Fe_2(CO)_6$ is not I but III (or II), the correctness of the structures proposed[10] for $C_8H_{10}Fe_2(CO)_6$ and $C_7H_8Fe_2(CO)_6$ is open to question. We believe that X-ray investigations of these and some other related compounds are clearly worthwhile in order to resolve all doubts about their structures and a program of such studies is now underway.

Acknowledgments. We are grateful to Dr. M. J. Bennett and Professor A. Davison for their interest and counsel and to Professor R. H. Herber of Rutgers University for guidance concerning the interpretation of Mössbauer spectra.

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[22] *Cf.* G. K. Wertheim, R. B. King, and R. H. Herber, *Inorg. Chem.*, 3, 101 (1964).

[23] Only structures having nonequivalent iron atoms have been considered acceptable on other evidence by R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 4557 (1960); **83**, 3600 (1961).

[24] H. D. Kaesz, R. B. King, T. A. Manuel, L. D. Nichols, and F. G. A. Stone, *ibid.*, **82**, 4749 (1960).