$[Cu(Me_4OHO[15]teteneN_4)](ClO_4)$ is very similar to that observed in tetrakis(*N,N'*-dimethyl glyoximato)dicopper(II)[12,13] which shows evidence of weak antiferromagnetic exchange[11] at low temperatures (5–50 K). Further investigations on the effect of 7-membered and larger chelate rings on the coordination geometry and physical and chemical properties of copper(II) complexes are currently in progress.

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Registry No. $[Cu(Me_4OHO[15]teteneN_4)](ClO_4)$, 78149-30-1.

Supplementary Material Available: Tables of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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A Methylene-Bridged Metal–Metal Bond: Neutron Diffraction Study of $(\mu\text{-}CH_2)[(\eta^5\text{-}C_5H_5)Rh(CO)]_2$ at 15 K[1]

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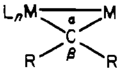
A low-temperature neutron diffraction study of $(\mu\text{-}CH_2)[(\eta^5\text{-}C_5H_5)Rh(CO)]_2$ has been carried out in order to determine the geometry of the bridging methylene group with high precision. The mean methylene C–H bond distance is found to be 1.095 (1) Å, and the H–C–H angle of 110.4 (1)° lies near the tetrahedral value. The dihedral angle between the CH_2 and Rh_2C planes is 84.1°. The cyclopentadienyl ligands are slightly distorted from an ideal pentagonal shape, reflecting the influence of the coordination about rhodium on the five-membered rings. There is no systematic displacement of the hydrogen atoms from the planes of the rings, with respect to the rhodium atom positions. Crystallographic data: space group $P\bar{1}$, $Z = 2$, $a = 7.857$ (2) Å, $b = 8.914$ (2) Å, $c = 9.319$ (2) Å, $\alpha = 74.21$ (2)°, $\beta = 81.25$ (1)°, $\gamma = 82.56$ (2)°, $T = 15$ K. The final unweighted R value based on F^2 for 3054 reflections ($(\sin\theta)/\lambda < 0.70$ Å^{-1}) is 0.036.

Introduction

Over the past 15 years, a tremendously rich chemistry has developed involving metal–carbene complexes,[5] and such complexes have been postulated as intermediates in many catalytic reaction sequences.[6] Recently, a series of novel μ-methylene complexes having structures of the type **1** has



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been prepared and characterized.[7,8] Binuclear complexes with two[9] and three[9,10] bridging methylene groups as well as one with a single bridging methylene and two carbonyls[11] are now known, as are triosmium cluster systems with an Os–Os bond bridged by a hydride and a methylene ligand[12–14] or the dipolar $^-CH(CH_2)(P^+Me_2Ph)$.[15–17] The methylene carbon atom of the bridging ligand in **1** is highly distorted from tetrahedral geometry; a recent survey of structural parameters determined by X-ray diffraction for such compounds has indicated that

Table I. Experimental Details and Refinement Parameters

cryst wt	4.165 mg
cryst vol	2.012 mm^3 (approximately 0.5 × 1.0 × 4.0 mm)
cryst boundary faces	{100}, {001}, {011}
calcd transmission range	0.832–0.910
no. of reflctns measd	3684
no. of independent reflectns (m)	3054
agreement factor for averaging	
$R_c = \Sigma \sum_{i=1}^{n'} \lvert\langle F_o^2\rangle - F_{oi}^2\rvert / \Sigma n' \langle F_o^2\rangle$	0.039
$R(F^2) = \Sigma\lvert F_o^2 - k^2F_c^2\rvert / \Sigma F_o^2$	0.036
$R_w(F^2) = [\Sigma w(F_o^2 - k^2F_c^2)^2 / \Sigma wF_o^4]^{1/2}$	0.038
$S = [\Sigma w(F_o^2 - k^2F_c^2)^2 / k^4(m - n)]^{1/2}$	1.24
no. of variable parameters (n)	263

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(3) Universität Regensburg.
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the internal M–C–M angles α are far less sensitive to the composition and structures of the molecules than the external R–C–R′ angles β.[18] The bonding in bridging methylene complexes has been the subject of theoretical investigations[19] which have pointed out the analogy between these systems and cyclopropanes. The bridging methylene acts as a σ donor and π acceptor. Schultz, Williams, Calvert, Shapley, and Stucky[14] have applied a qualitative molecular orbital scheme to the triosmium clusters,[20] in which the $Os_2(\mu\text{-}H)(\mu\text{-}CH_2)$ interaction is described as a six-electron, four-center bond.

The synthesis and X-ray structure analyses of the three unsubstituted (R = R′ = H) complexes of type **1** $(\mu\text{-}CH_2)[(Cp)Rh(CO)]_2$ (I)[21,22] and the closely related $(\mu\text{-}CH_2)[(C_5H_4R)Mn(CO)_2]_2$ (II, R = H; III, R = Me)[23,24] have been carried out previously. Here we present the results of a low-temperature neutron diffraction study of the rhodium complex, which has been undertaken in order to determine the geometry of the bridging methylene group with high precision. Results of our neutron diffraction study of the terminal methylene complex $(Cp)_2Ta(Me)CH_2$[25,26] will be presented elsewhere.[27] To our knowledge, only one neutron diffraction study of a compound containing a coordinated methylene group has previously been reported, viz., that of $(\mu\text{-}H)_2(\mu\text{-}CH_2)Os_3(CO)_{10}$ (VIII).[13,14]

Experimental Section

Samples of I were crystallized from pentane in the temperature range 0 to −35 °C.[22] A single crystal with a volume of 2.01 mm^3 was selected for the neutron diffraction measurements. This sample was mounted on an aluminum pin, the end of which had been made hollow in order to reduce the amount of metal in the neutron beam, and was oriented with the crystallographic *a* axis approximately parallel to the pin. The crystal was sealed in an aluminum can under a helium atmosphere and placed in a closed-cycle helium refrigerator[28] mounted on a four-circle diffractometer[29,30] at the Brookhaven high-flux beam reactor. A germanium (220) single-crystal monochromator was employed to obtain a neutron beam of wavelength 1.1621 (2) Å (based on KBr, $a = 6.6000$ Å at $T = 298$ K).[31] The temperature of the sample during data collection was measured to be 15.0 (5) K.[32] Unit-cell parameters were determined at this temperature by a least-squares procedure on the basis of observed $\sin^2\theta$ values of 32 reflections ($60° < 2\theta < 73°$). Crystal data: space group $P\bar{1}$, $Z = 2$, $a = 7.857$ (2) Å, $b = 8.914$ (2) Å, $c = 9.319$ (2) Å, $\alpha = 74.21$ (2)°, $\beta = 81.25$ (1)°, $\gamma = 82.56$ (2)°, $V = 618.1$ (2) Å^3, $M_r = 417.3$, $\rho_c = 2.242$ g cm^{-3}. Experimental details and parameters describing the subsequent structure refinement are listed in Table I.

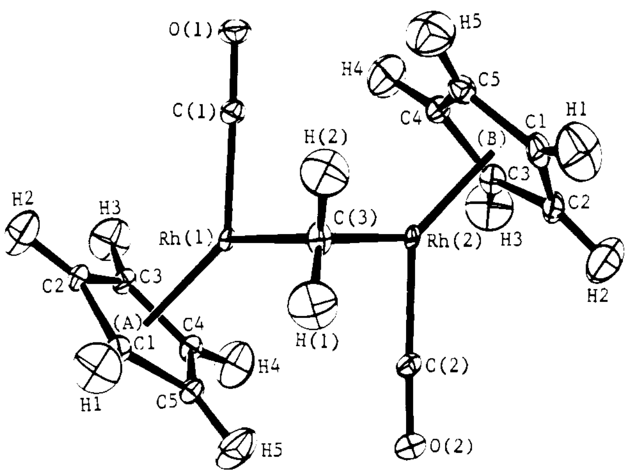

Figure 1. Molecular structure of $(\mu\text{-}CH_2)[(Cp)Rh(CO)]_2$ at 15 K with thermal ellipsoids drawn to enclose 97% probability density.

Reflection intensities were measured in one hemisphere of reciprocal space with $2\theta \le 109°$ ($(\sin\theta)/\lambda \le 0.70$ Å^{-1}) employing a $\theta/2\theta$ step–scan technique. The scan range was varied according to $\Delta 2\theta = (2.94 + 1.24 \tan\theta)°$ for the high-angle data ($60° \le 2\theta \le 109°$) and $\Delta 2\theta = 3.6°$ for the low-angle data. The step size was adjusted to give between 55 and 70 steps in each scan. At each point, counts were accumulated for approximately 2.0 s, with the exact time interval being determined by monitoring the incident beam intensity. As a general check on experimental stability, the intensities of two reflections were monitored every 100 measurements. These monitor intensities did not vary to any significant degree for the duration of data collection.

Integrated intensities were obtained by a modification of the Lehmann and Larsen profile analysis,[33] with a program[34] that employs an interactive CRT display. Observed intensities were corrected for absorption ($\mu = 2.127$ cm^{-1}) by means of numerical integration over a Gaussian grid of points[35] and converted to squared structure factors, $F_o^2 = I \sin 2\theta$. Variances were estimated as

$$\sigma^2(F_o^2) = \sigma^2(\text{count}) + A \cdot F_o^4 + B$$

where σ^2(count) is the variance based on counting statistics. Coefficients *A* and *B* were estimated to be 0.0016 and 2.56, respectively on an absolute scale with F_o^2 in barn, on the basis of the discrepancies between Friedel-related reflections $h0l$ and $\bar{h}0\bar{l}$. Multiple observations of the same and Friedel-related reflections were averaged to give 3054 independent values of F_o^2.

Atomic coordinates[21b] of the nonhydrogen atoms from the X-ray determination defined the initial model for the refinement on the basis of the neutron data. After a few cycles, a difference scattering density synthesis indicated the locations of all hydrogen atoms. A total of 263 parameters, comprised of positional and anisotropic thermal factors

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Table II. Positional and Thermal Parameters[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh(1)	0.146 41 (8)	0.209 23 (7)	0.079 93 (7)	0.0033 (3)	0.0043 (2)	0.0064 (2)	0.0015 (2)	−0.0026 (2)	−0.0012 (2)
Rh(2)	0.351 07 (8)	0.253 04 (7)	0.264 97 (7)	0.0040 (3)	0.0061 (3)	0.0071 (2)	0.0020 (2)	−0.0033 (2)	−0.0024 (2)
C(1)	−0.027 19 (8)	0.190 41 (7)	0.238 45 (6)	0.0060 (3)	0.0099 (2)	0.0085 (2)	0.0009 (2)	−0.0011 (2)	−0.0019 (2)
C(2)	0.523 24 (8)	0.283 70 (7)	0.105 82 (7)	0.0054 (2)	0.0110 (2)	0.0103 (2)	−0.0001 (2)	−0.0007 (2)	−0.0038 (2)
C(3)	0.304 42 (8)	0.051 97 (7)	0.216 80 (7)	0.0094 (3)	0.0066 (2)	0.0104 (2)	0.0025 (2)	−0.0050 (2)	−0.0019 (2)
O(1)	−0.137 8 (1)	0.176 58 (9)	0.336 57 (8)	0.0087 (3)	0.0151 (3)	0.0111 (3)	−0.0006 (2)	0.0017 (2)	−0.0033 (2)
O(2)	0.636 3 (1)	0.299 99 (9)	0.010 22 (8)	0.0087 (3)	0.0180 (3)	0.0126 (3)	−0.0029 (2)	0.0011 (2)	−0.0048 (3)
H(1)	0.406 7 (2)	−0.006 8 (2)	0.152 2 (2)	0.0216 (7)	0.0246 (6)	0.0309 (7)	0.0095 (5)	−0.0045 (5)	−0.0126 (5)
H(2)	0.247 1 (2)	−0.032 9 (2)	0.315 0 (2)	0.0282 (7)	0.0196 (6)	0.0235 (6)	−0.0035 (5)	−0.0046 (5)	0.0011 (5)
C(1A)	0.199 98 (8)	0.133 35 (7)	−0.136 86 (6)	0.0075 (3)	0.0081 (2)	0.0094 (2)	0.0012 (2)	−0.0020 (2)	−0.0031 (2)
C(2A)	0.025 70 (8)	0.200 46 (7)	−0.120 54 (6)	0.0058 (2)	0.0086 (2)	0.0092 (2)	−0.0002 (2)	−0.0026 (2)	−0.0020 (2)
C(3A)	0.028 68 (8)	0.363 68 (7)	−0.126 03 (6)	0.0058 (2)	0.0077 (2)	0.0091 (2)	0.0013 (2)	−0.0027 (2)	−0.0006 (2)
C(4A)	0.203 22 (8)	0.395 63 (7)	−0.142 62 (6)	0.0076 (3)	0.0074 (2)	0.0093 (2)	−0.0004 (2)	−0.0022 (2)	−0.0010 (2)
C(5A)	0.309 83 (8)	0.251 97 (7)	−0.144 96 (6)	0.0057 (2)	0.0095 (2)	0.0095 (2)	0.0008 (2)	−0.0015 (2)	−0.0024 (2)
H(1A)	0.241 1 (2)	0.013 7 (2)	−0.140 0 (2)	0.0260 (7)	0.0147 (5)	0.0314 (7)	0.0034 (5)	−0.0042 (5)	−0.0079 (5)
H(2A)	−0.087 9 (2)	0.140 3 (2)	−0.111 7 (2)	0.0160 (6)	0.0259 (6)	0.0320 (7)	−0.0070 (5)	−0.0050 (5)	−0.0091 (5)
H(3A)	−0.084 5 (2)	0.447 3 (2)	−0.117 2 (2)	0.0174 (6)	0.0202 (6)	0.0296 (6)	0.0072 (5)	−0.0059 (5)	−0.0060 (5)
H(4A)	0.248 8 (2)	0.506 5 (2)	−0.146 7 (2)	0.0258 (7)	0.0164 (6)	0.0318 (7)	−0.0056 (5)	−0.0053 (5)	−0.0056 (5)
H(5A)	0.449 2 (2)	0.238 0 (2)	−0.158 5 (2)	0.0102 (6)	0.0273 (6)	0.0331 (7)	0.0013 (5)	−0.0033 (5)	−0.0097 (5)
C(1B)	0.389 93 (9)	0.199 67 (7)	0.508 12 (7)	0.0109 (3)	0.0127 (3)	0.0104 (2)	0.0046 (2)	−0.0060 (2)	−0.0036 (2)
C(2B)	0.451 18 (8)	0.348 40 (8)	0.429 84 (7)	0.0077 (3)	0.0151 (3)	0.0131 (3)	0.0011 (2)	−0.0041 (2)	−0.0070 (2)
C(3B)	0.306 22 (8)	0.455 22 (7)	0.379 51 (7)	0.0108 (3)	0.0092 (3)	0.0124 (2)	0.0009 (2)	−0.0029 (2)	−0.0045 (2)
C(4B)	0.157 32 (8)	0.371 45 (7)	0.421 54 (7)	0.0069 (3)	0.0102 (2)	0.0099 (2)	0.0026 (2)	−0.0022 (2)	−0.0031 (2)
C(5B)	0.269 02 (8)	0.213 16 (7)	0.498 45 (6)	0.0106 (3)	0.0100 (3)	0.0086 (2)	0.0008 (2)	−0.0016 (2)	−0.0019 (2)
H(1B)	0.467 4 (2)	0.096 7 (2)	0.563 5 (2)	0.0327 (8)	0.0246 (6)	0.0284 (7)	0.0119 (6)	−0.0147 (6)	−0.0037 (5)
H(2B)	0.584 1 (2)	0.376 6 (2)	0.415 7 (2)	0.0150 (7)	0.0420 (8)	0.0364 (8)	−0.0046 (6)	−0.0053 (6)	−0.0161 (7)
H(3B)	0.309 8 (2)	0.577 3 (2)	0.317 7 (2)	0.0343 (8)	0.0152 (6)	0.0322 (7)	−0.0026 (5)	−0.0048 (6)	−0.0023 (5)
H(4B)	0.027 7 (2)	0.417 4 (2)	0.397 3 (2)	0.0143 (6)	0.0297 (7)	0.0281 (6)	0.0052 (5)	−0.0060 (5)	−0.0078 (5)
H(5B)	0.123 3 (2)	0.120 7 (2)	0.545 1 (2)	0.0295 (8)	0.0223 (6)	0.0285 (6)	−0.0092 (6)	0.0001 (6)	−0.0024 (5)

[a] Thermal parameters are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12} + ...)]$.

for all 29 atoms, a scale factor k, and a type I isotropic extinction parameter,[36] was varied by a full-matrix least-squares procedure minimizing $\sum w(F_o^2 - k^2F_c^2)^2$.[37] Weights were taken as $w = 1/\sigma^2(F_o^2)$. The most significant extinction correlation applied to F_c^2 was 0.65 for reflection 020. Neutron-scattering lengths were taken to be $b_{Rh} = 0.588 \times 10^{-12}$, $b_O = 0.580 \times 10^{-12}$, $b_C = 0.665 \times 10^{-12}$, and $b_H = -0.374 \times 10^{-12}$ cm.[38] The individual rhodium atom scattering lengths were allowed to vary, but the resulting values agreed within their standard deviations with the literature value quoted above, which was employed in the latter cycles. The refinement was terminated when the maximum shift/esd for any parameter was less than 0.1. A difference synthesis computed at this stage was essentially featureless. Final agreement factors are included in Table I, while positional and thermal parameters for all atoms are listed in Table II.[39]

Results and Discussion

The molecular structure of $(\mu\text{-CH}_2)[(Cp)Rh(CO)]_2$ at 15 K is illustrated in Figure 1.[40] An approximate local twofold axis relating the halves of the dimer passes through the methylene carbon C(3). Intramolecular bond distances and angles are indicated in Figure 2 and Table III, while a stereoscopic view of the packing of four molecules intersecting one unit cell is presented in Figure 3. There are no unusual intra- or intermolecular nonbonded contacts.

Table III. Geometry around the Rh-Rh Core

(a) Rh–C Distances (Å)

Rh(1)–C(1A)	2.264 (1)	Rh(2)–C(1B)	2.245 (1)
Rh(1)–C(2A)	2.244 (1)	Rh(2)–C(2B)	2.226 (1)
Rh(1)–C(3A)	2.282 (1)	Rh(2)–C(3B)	2.298 (1)
Rh(1)–C(4A)	2.302 (1)	Rh(2)–C(4B)	2.304 (1)
Rh(1)–C(5A)	2.249 (1)	Rh(2)–C(5B)	2.247 (1)

(b) Ring Center–Rh–X Angles (Deg)

ring A–Rh(1)–Rh(2)	132.85 (4)	ring B–Rh(2)–C(2)	134.61 (5)
ring B–Rh(2)–Rh(1)	132.20 (3)	ring A–Rh(1)–C(3)	130.94 (4)
ring A–Rh(1)–C(1)	134.70 (4)	ring B–Rh(2)–C(3)	130.87 (4)

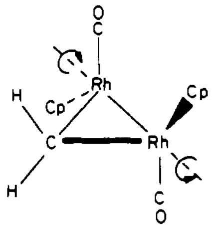
(c) Dihedral Angles (Deg)

[Rh(1),Rh(2),C(3)]–[C(3),H(1),H(2)]	84.1
[Rh(1),Rh(2),C(3)]–[Rh(1),Rh(2),C(1),C(2)]	89.7
ring A–ring B	29.9

(d) Torsion Angle (Deg)[42]

C(1)–Rh(1)–Rh(2)–C(2)	−176.91 (5)

The mean[41] C–H distance in the methylene group is found to be 1.095 (1) Å and the H–C–H angle 110.4 (1)°. The dihedral angle between the CH_2 and Rh_2C planes is 84.1°; consonant with this small rotation from the favored[19] perpendicular conformation, the Rh–C–H angles fall into two groups with mean values 112.3 (7) and 119.3 (3)°. There is also a slight twisting of the Rh(Cp)(CO) units about the Rh–Rh bond as indicated in **2**, so that the C(1)–Rh(1)–Rh(2)–C(2) torsion angle is −176.9°. The rotation of the CH_2 plane is in the expected direction, maintaining optimum overlap between the CH_2 p orbital and the metal–metal antibonding π_{xy}^* **3**. The geometry of coordinated methylene ligands will



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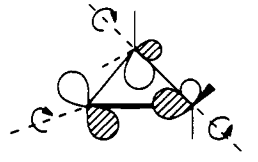

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(36) P. Becker and P. Coppens, *Acta Crystallogr., Sect. A*, **A31**, 417 (1975).

(37) Least-squares refinements were carried out with LINEX79, a modified version of ORFLS: W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, TN, 1962.

(38) L. Koester in "Neutron Physics", Springer-Verlag, Berlin, Heidelberg, New York, 1977, p 36.

(39) The nomenclature here is somewhat different than that employed in ref 21, viz., H(1) = H(3A), H(2) = H(3B), C(1A)–C(5A) = C(4)–C(8), C(1B)–C(3B) = C(11)–C(13), C(4B) = C(9), and C(5B) = C(10).

(40) C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

(41) Standard deviations of mean values have been estimated as $\sigma(\langle x\rangle) = [\sum_{i=1}^{n}(x_i - \langle x\rangle)^2/n(n-1)]^{1/2}$, except where $n = 2$ when the average of the individual esd's has been used if this exceeds $\sigma(\langle x\rangle)$.

(42) IUPAC-IUB Commission on Biochemical Nomenclature, *J. Mol. Biol.*, **52**, 1 (1970).

Table IV. Geometry of the M-μ-CH$_2$-M Core in Compounds with Bridging CH$_2$ Ligands

compd	method[a]	dist, Å			angles, deg			ref
		M-M	M-C[b]	C-H[b]	M-C-M(α)	H-C-H(β)	dihedral[c]	
$(\mu\text{-}CH_2)[(Cp)Rh(CO)]_2$ (I)	N	2.662 (1)	2.050 (1)	1.095 (2)	81.0 (1)	110.4 (1)	84.1	this work
$(\mu\text{-}CH_2)[(Cp)Mn(CO)_2]_2$ (II)	X[d]	2.799 (1)	2.025 (1)	0.93 (2)	87.43 (7)	108.8 (1.5)	88.0	24a
$(\mu\text{-}CH_2)[(MeCp)Mn(CO)_2]_2$ (III)	X	2.779 (1)	2.013 (5)	0.90 (5)	87.3 (2)	92 (8)	87.5	24b
$(\mu\text{-}CH_2)(\mu\text{-}CO)_2[Fe(CO)_3]_2$ (IV)	X[e]	2.504 (1)	2.015 (1)	*f*	76.6 (1)	*f*	90[g]	11b
$(\mu\text{-}CH_2)_3[Ru(PMe_3)_3]_2$ (V)	N	2.643 (4)	2.116 (5)	1.086 (2)	77.3 (2)[b]	107 (2)[b]	88.5 (3)	10
$(\mu\text{-}CH_2)_2(\mu\text{-}Me)[Ru(PMe_3)_3]_2BF_4$ (VI)	X	2.732 (1)	2.090 (7)	*h*	81.6 (4)	*h*	*h*	9b
$(\mu\text{-}CH_2)_2[Ru(PMe_3)_3]_2(BF_4)_2$ (VII)	X	2.641 (1)	2.071 (5)	0.92 (5)	79.2 (2)	102 (4)	87.3	9b
$(\mu\text{-}H)_2(\mu\text{-}CH_2)Os_3(CO)_{10}$ (VIII)	N	2.824 (3)	2.151 (6)	1.09 (1)	82.1 (2)	106.0 (8)	88.8	14

[a] N = neutron diffraction, X = X-ray diffraction. [b] Mean value. [c] Dihedral angle defined by M-C-M and CH$_2$. [d] Low-temperature (130 K) study. [e] Low-temperature (238 K) study. [f] Methylene hydrogen atoms placed at idealized positions. [g] Required by crystallographic symmetry. [h] Positions of methylene hydrogen atoms not determined.

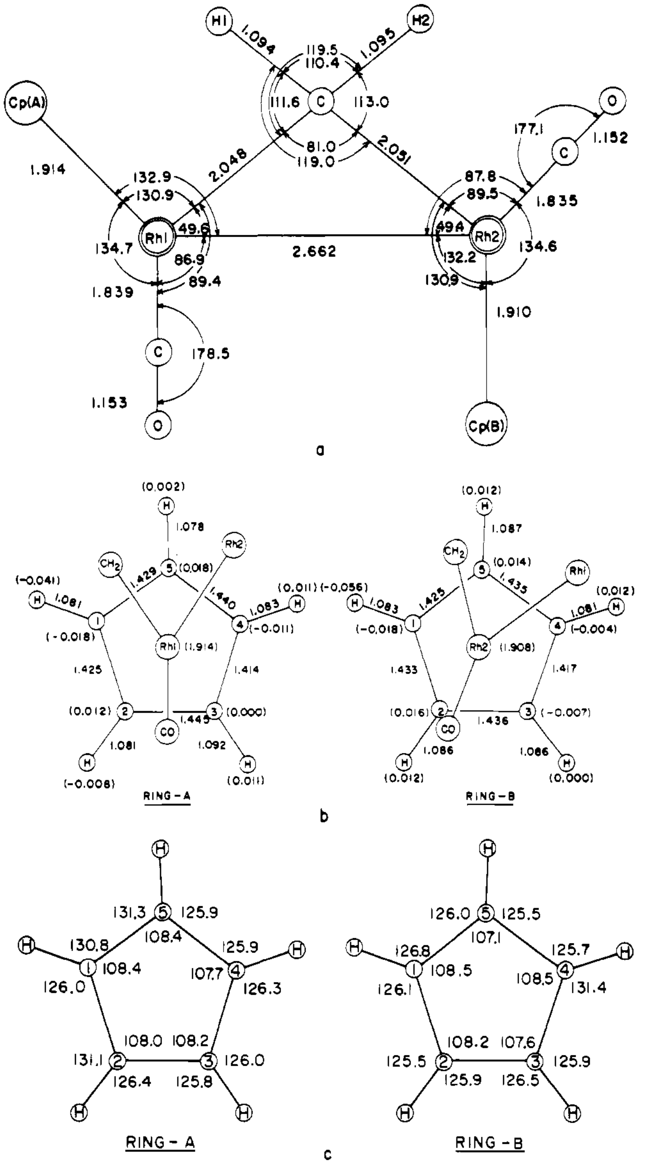

Figure 2. Bond distances and angles (a) around the rhodium atoms. (b and c) within the Cp rings. Estimated standard deviations of all distances are 0.001 Å or less except for C-H bonds (0.002 Å). Esd's of angles are 0.1° or less. Displacements from the least-squares plane through the carbon atom of each Cp ring are indicated in parentheses in part b. Esd's in these displacements are 0.001-0.002 Å for carbon and rhodium atoms and 0.003-0.004 Å for hydrogen atoms.

be discussed further (vide infra).

The molecular geometry is in generally good agreement with that found by X-ray diffraction at room temperature,[21] except for discrepancies in bond distances and angles involving hydrogen atoms and some differences in the dimensions of the Cp rings. Most of the latter differences may be ascribed to the foreshortening of C-C bonds caused by librational motion of the Cp rings at room temperature, which is greatly reduced at 15 K.[43] However, small systematic distortions of the rings from D_{5h} symmetry become apparent with the increased precision of the neutron study. In both rings, there is a tendency for the 1-5, 2-3 and 4-5 C-C bonds, which eclipse the Rh-Rh or Rh-C bonds, to be slightly longer than the 1-2 and 3-4 C-C bonds (see Figure 2b). The mean C-C distances for the two sets of bonds are 1.435 (3) and 1.422 (4) Å, respectively. Distortions of Cp rings from D_{5h} symmetry have also been detected in CpM(CO)$_3$ (M = Mn, Re),[44] $C_6H_6Cr(CO)_3$,[45] and $(CH_3)_6C_6Mo(CO)_3$[46] and may be rationalized on the basis of molecular orbital calculations.[47] In the case of the rhodium dimer, the alternation in bond distances is more pronounced[48] for ring A, which takes a conformation in which the Rh-Rh and Rh-C bonds lie almost directly over the ring C-C bonds, than for ring B, which is rotated toward an alternative conformation where Rh(2)-C(2) eclipses C(2B). Barriers to this type of rotation of the Cp ring in Cp-M(CO)$_3$ complexes are calculated to be very small.[47]

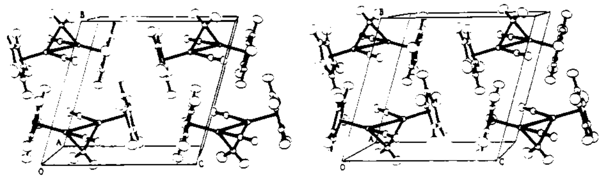

Figure 3. Stereoscopic view of the packing of four molecules intersecting one unit cell viewed along *a**, with thermal ellipsoids as in Figure 1.

Out-of-plane displacements of the atoms in the Cp rings are given in Figure 2b. Both rings show small deviations of the carbon atoms from planarity with carbons 2 and 5 displaced toward the rhodium atom and carbons 1 and 4 displaced away

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[43] Mean C-C bond distances are 1.430 (3) Å from the present neutron work and 1.406 (13) Å from the X-ray study of ref 21b. After correction for the effects of rigid-body libration with the method described by D. W. J. Cruickshank, *Acta Crystallogr.*, **9**, 754 (1956), mean C-C distances from the neutron and X-ray studies are 1.432 (3) and 1.433 (12) Å, respectively. The calculated root-mean-square amplitudes of libration about axes normal to the rings are as follows (the larger values refer to the room temperature X-ray results): ring A, 2.2 (2) vs. 8.0 (5)°; ring B, 3.0 (4) vs. 14 (1)°.

[44] P. J. Fitzpatrick, J. Sedman, I. S. Butler, and Y. Le Page, "Abstracts of Papers" 179th National Meeting of the American Chemical Society, Houston, TX, 1980, Paper INOR 201; P. J. Fitzpatrick, Y. Le Page and I. S. Butler, *Acta Crystallogr.*, in press.

[45] B. Rees and P. Coppens, *Acta Crystallogr., Sect. B*, **B29**, 2516 (1973); M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1314 (1965).

[46] D. E. Koshland, S. E. Meyers, and J. P. Chesick, *Acta Crystallogr., Sect. B*, **B33**, 2013 (1977).

[47] T. A. Albright, P. Hofmann, and R. Hoffmann, *J. Am. Chem. Soc.*, **99**, 7546 (1977).

[48] For the individual rings the mean "long" and "short" C-C distances are 1.438 (5) and 1.420 (6) Å for ring A and 1.432 (4) and 1.425 (8) Å for B.

from rhodium. There is no clear trend in the hydrogen atom displacements, which are probably dominated by intramolecular steric and crystal-packing forces. The rhodium atoms lie very nearly over the centers of the Cp rings: the angles between the Rh-ring center vectors and the normals to the ring planes are 1.3 and 2.3° for rings A and B, respectively. The angles defined by ring center–Rh–Rh or ring center–Rh–C are also very similar, with a mean value of 133 (1)°.

In reviewing the available structural results for μ-methylene complexes (**1**), Herrmann, Schweizer, Creswick, and Bernal[18] noted that the M–C–M angles (α) fall the range 75–87° and the R–C–R′ (β) angles in the range 92–115°. All known structures have the carbene ligand oriented approximately perpendicular to the M–M bond. Here we focus our attention on unsubstituted complexes, the geometries of which are summarized in Table IV. Application of the 18-electron rule to compounds I–VI predicts a formal M–M bond order of 1, which is consistent with results of a molecular orbital analysis of compound I.[19] Interestingly, the manganese dimers (II and III) have longer M–M distances than the rhodium dimer (I), and both II and III possess substantially the largest α angles in the group.[24a,b] In fact, in view of the differences in composition, the relative constancy of the α angles in the remaining six compounds is perhaps surprising. The H–C–H (β) angles from the present neutron diffraction study of I and that of VIII[13,14] are quite close to the tetrahedral value. By way of further comparison, in our recent neutron diffraction study of the terminal complex $(Cp)_2Ta(Me)CH_2$,[27] the methylene H–C–H angle is found to be 112.3 (2)°. The inadequacy of simple hybridization arguments in rationalizing these angles has been pointed out.[14] In the MO analysis of the bonding in I, Hofmann[19] has indicated that the H–C–H angle in such systems depends upon the details of a repulsive interaction between the low-lying filled π_{CH_2} orbital and the metal–metal bonding π_{xz} orbital extending normal to the M–C–M plane. Optimization of the H–C–H angle for compounds I and II has led to calculated[49] minimum energy angles of between 109 and 110° for I, in agreement with our experimental value, and about 100° for II compared to the value of 108.8 (1.5)° from the low-temperature X-ray study.[24a]

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Registry No. I, 65138-22-9.

Supplementary Material Available: A listing of observed and calculated squared structure factors (18 pages). Ordering information is given on any current masthead page.

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[49] P. Hofmann, personal communication, 1980.

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Boulder, Colorado 80309

Syntheses, Structures, and Reactions of Molybdenum Complexes with Sulfido and Disulfido Ligands

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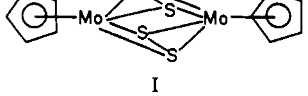
The reaction of elemental sulfur with $(CH_3)_5C_5Mo(CO)_3H$ produced $[(CH_3)_5C_5MoS_2]_2$ (II) and $[(CH_3)_5C_5MoS_5]_2$ (IV) in 65% and 10% yields, respectively. The remaining product was an insoluble, presumably polymeric, material. Complex II crystallizes in space group $P2_1/n$ with $a = 10.069$ (20) Å, $b = 15.107$ (4) Å, $c = 7.889$ (2) Å, and $\beta = 104.81$ (2)°. The molecule contains a planar $Mo_2(\mu\text{-}S)_2$ unit with terminal sulfido ligands in the anti configuration. In the presence of oxygen, complex II is converted to $[(CH_3)_5C_5MoO(S)]_2$, which crystallizes in space group $P4_2/n$ with $a = b = 16.342$ (3) Å and $c = 8.456$ (1) Å. The molecule is similar to complex II with oxo ligands replacing the terminal sulfido ligands. Complex IV crystallizes in space group $Fdd2$ with $a = 15.233$ (3) Å, $b = 45.205$ (7) Å, and $c = 8.051$ (2) Å. The metal ions in this dimer are each coordinated to a single sulfur atom of a bridging disulfide ligand. The coordination sphere of each molybdenum ion also includes two $\eta^2\text{-}S_2$ ligands and the $\eta^5\text{-}(CH_3)_5C_5$ ligand. The reactions of $[CH_3C_5H_4Mo(CO)_3]_2$ and of $[C_5H_5Mo(CO)_3]_2$ with elemental sulfur resulted primarily in the formation of insoluble materials. The dimer $[CH_3C_5H_4MoS_2]_2$ (III) was isolated from the former reaction in very low yields. An X-ray diffraction study of this product confirms that it is also an anti isomer of a $[MoS(\mu\text{-}S)]_2$ dimer. The complex crystallizes in space group $P2_1/n$ with $a = 7.023$ (4) Å, $b = 6.703$ (2) Å, $c = 16.227$ (8) Å, and $\beta = 95.86$ (4)°. Complexes II–IV, as well as the insoluble products from these reactions, react with hydrogen under mild conditions to form in each case a complex with hydrosulfido ligands. In addition, III reacts with ethylene and acetylene at room temperature to form the known dimers with bridging ethane- and ethenedithiolate ligands, respectively. The insoluble materials $[(CH_3)_nC_5H_{5-n}MoS_x]_y$ ($n = 1, 5$) also react with these unsaturated hydrocarbons to form the same dithiolate-bridged dimers.

Introduction

A cyclopentadienylmolybdenum dimer with two bridging disulfide ligands (structure I) has been reported as a product of the reaction of episulfides with cyclopentadienylmolybdenum carbonyl hydrides.[1] Recently we reported that our efforts to reproduce this synthesis resulted in the formation of dimeric complexes with bridging alkanedithiolate ligands.[2] The bridging sulfur atoms in the latter complexes were found to undergo unusual reactions with unsaturated molecules, and



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