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CARBON COMPOUNDS OF THE TRANSITION METALS
V. THE STRUCTURE OF BIS(CYCLOPENTADIENYLDICARBONYLRUTHENIUM)

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Complexes of composition $Cp_2M_2(CO)_4$ (I) have been prepared for M = Fe, Ru and Os[1-6]. These complexes are of special interest structurally since they exist in solution in two isomeric molecular forms, the proportions of which are temperature dependent. The "low temperature" form (II) contains two bridging and two non-bridging carbonyl groups whilst the "high temperature" form (III) contains no bridging groups. In the case of (I; M = Fe) the form which occurs in the solid, at room temperature, is (IV), a centrosymmetric modification of the "low" form (II)[7]. In solution, at room temperature, the "low" form predominates, but since these solutions are polar, *e.g.* in benzene $\mu = 3.10 \pm 0.10$ D[8], this form cannot be the form (IV). Solutions of (I; M = Ru) are also polar, $\mu = 2.75 \pm 0.12$ D[5], and contain both isomers; at room temperature approximately equal proportions of both forms occur[9]. The infrared spectrum of the solid is similar to that of the iron complex with absorptions in the region of 1946 and 1764 cms^{-1} indicative of bridging carbonyl groups. We have undertaken the analysis of the ruthenium complex to establish the structure in the solid and to obtain values of Ru–Ru and Ru–C bond lengths. The structure of the osmium complex, which appears to exist in both solution and solid as the "high" form (III) is also under investigation.

DISCUSSION

The crystal structure of $Cp_2Ru_2(CO)_4$ is very similar to that of $Cp_2Fe_2(CO)_4$. The molecules are centrosymmetric with two bridging and two non-bridging carbonyl groups and so have the cyclopentadienyl groups arranged *trans* to one another. The bridging carbonyl groups and the ruthenium atoms are coplanar. The terminal carbonyl groups make an angle of 93.3° and the normals to the cyclopentadiene rings

TABLE 1
INTERATOMIC DISTANCES (*d*)

Bond	*M = Fe*	*M = Ru*	d_{Ru}–d_{Fe}
$\frac{1}{2}$(M–M)	1.24_5	1.36_7	0.12_2
M–CO(terminal)	1.75	1.86	0.11
M–CO(bridge)	1.85	1.99	0.14
M–C(ring)	2.12	2.26	0.14

40.6° to this plane. The bridging groups are symmetrical with a mean Ru–C distance of 1.99 Å, which is 0.13 Å longer than the Ru–C(terminal) value. Table 1 illustrates that the differences in bond lengths between the ruthenium and iron complexes can be accounted for by the increased size of the ruthenium atom. All the differences are consistent with an increase in metal radius of 0.12 Å.

The cyclopentadienyl rings are planar to within 0.01 Å and the metal–ring plane distance is 1.91 Å. The cyclopentadienyl rings lie symmetrically with respect to the ruthenium atoms. Thus the vector from the ruthenium atom to the centroid of the ring makes an angle of only 1° with the normal to the ring plane. The average Ru–C(ring) separation, 2.26 Å, is larger than that observed in ruthenocene[10], 2.21 Å, and this parallels the trend shown between $Cp_2Fe_2(CO)_4$, 2.11 Å, and ferrocene, 2.05 Å[11]. Individual C–C distances in the rings are not significantly different.

The Ru–Ru distance, 2.73_5 Å, is significantly longer than the separation found in the metal itself. No other Ru–Ru distances are available for comparison.

EXPERIMENTAL

A crystalline sample of bis(cyclopentadienyldicarbonylruthenium) was kindly supplied by Professor E. O. Fischer. The unit cell and space-group were determined from precession and cone axis photographs taken with molybdenum radiation. The crystal data are compared with those of the iron complex in Table 2.

TABLE 2

CRYSTAL DATA OF BIS(CYCLOPENTADIENYLDICARBONYLRUTHENIUM AND -IRON)

	$C_{14}H_{10}O_4Ru_2$	$C_{14}H_{10}O_4Fe_2$ (*ref.* 7)
System	Monoclinic	Monoclinic
Mol. wt.	444.36	353.92
a (Å)	7.10	7.07
b (Å)	12.48	12.46
c (Å)	8.04	7.99
β	104.33°	108.41°
U (Å^3)	690(6)	668(6)
Z	2	2
D_m(flotation) (g.cm^{-3})	2.13(2)	1.77(1)
D_c (g.cm^{-3})	2.14	1.76
Space-group	$P2_1/c$ (C_{2h}^5, No. 14)	$P2_1/c$ (C_{2h}^5, No. 14)
Radiation	Mo-K_α	Co-K_α
hkl	three-dimensional	two-dimensional

Three-dimensional intensity data were estimated visually from precession photographs of the levels nkl; $n = 0, 1, 2, 3$ and hkn; $n = 0, 1, 2, 3$. The crystal used was of maximum dimension 0.35 mm and absorption corrections were not applied (μ for Mo-K_α radiation = 23.8 cm^{-1}). The data were correlated by the iterative least-squares procedure suggested by Hamilton, Rollett and Sparks[12] and coded for the Atlas computer. In all some 1413 independently observed reflexions were used. The structure was solved from Patterson and electron-density syntheses. The final refinement was based on 1296 reflexions subsequent to the observation that 117 reflexions in a well defined region of reciprocal space on some photographs were repeatedly calculated with higher intensities than those observed. That this was associated with the use (or misuse) of the 3 mm annulus screens seems most likely since a later trial photograph taken with 5 mm screens showed no attenuation of intensity for these reflexions.

The structure was refined by the full-matrix least-squares method. The programme used was a modification of that of Busing, Martin and Levy[13]. Analysis of the distribution of $\Sigma\, w\Delta F^2$ against F_o and $\sin^2\theta/\lambda^2$ showed that the weighting scheme used, $w^{-1} = 1 + 0.001F_o^2$, gave a uniform distribution of errors. Unobserved reflexions, which were included in the data with $F_o = 0$, were given zero weight if $F_c < 2.0$ (the lowest recorded non-zero value of F_o); if $F_c \geqslant 2.0$ then ΔF was set to $\pm 2.0\ F_c$ with a weight of 0.6. This arbitrarily adjusted weight brought the value of $\Sigma w\Delta F^2$ for unobserved reflexions into line with the main body of reflexions. Four cycles of least-squares were sufficient to make all shifts, positional and isotropic thermal, less than 0.4 e.s.d. ($R = 11.5\%$). A difference synthesis, however, showed clearly that the ruthenium atom should be treated anisotropically. When this was done the R value improved to 9.2%. Attempts to locate hydrogen atoms, based on probable positions calculated on the assumption of sp^2 directions from the rings, were inconclusive and they were not included in the refinement. The light atoms were not refined anisotropically.

The final atomic parameters are listed in Table 3. A sketch of the molecule, showing the more important interatomic distances and angles, but without standard deviations, is shown in Fig. 1. A fuller list, together with estimated standard deviations calculated from the inverse of the fullmatrix, is given in Table 4. Fig. 2 shows a projection of the structure down the b axis.

TABLE 3

ATOMIC PARAMETERS

Atom	x/a	y/b	z/c	$B(\AA^2)$
Ru	0.0894(1)	0.0646(1)	0.1336(1)	
C(bridge)	−0.1017(19)	−0.0556(8)	0.1086(19)	2.76(20)
O(bridge)	−0.1884(17)	−0.1028(8)	0.2044(18)	4.88(21)
C(terminal)	−0.1061(20)	0.1668(9)	0.0808(20)	3.42(21)
O(terminal)	−0.2236(17)	0.2303(8)	0.0494(17)	5.19(23)
C1(ring)	0.3528(22)	−0.0275(10)	0.2886(22)	4.02(24)
C2(ring)	0.2401(25)	0.0081(11)	0.4001(27)	4.80(30)
C3(ring)	0.2405(23)	0.1219(10)	0.3945(24)	4.16(25)
C4(ring)	0.3504(24)	0.1556(11)	0.2858(24)	4.49(28)
C5(ring)	0.4212(27)	0.0636(10)	0.2127(27)	4.64(31)

The quantities enclosed in brackets are the estimated standard deviations estimated from the inverted least-squares matrix of the final cycle of refinement and are in units of the last place of decimals given.

The anisotropic temperature coefficients for the ruthenium atom are:

$b_{11} = 0.01329(25)$ $b_{22} = 0.00420(6)$ $b_{33} = 0.00862(21)$
$b_{12} = 0.00049(8)$ $b_{13} = 0.00307(25)$ $b_{23} = 0.00059(7)$

where expression for the temperature factor is:

$$\exp -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$$

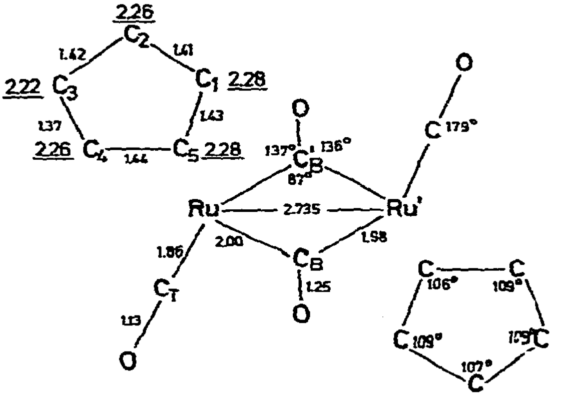

Fig. 1. Sketch showing main interatomic distances and angles.

TABLE 4

INTRAMOLECULAR DISTANCES AND ESTIMATED STANDARD DEVIATIONS

Ru–Ru	2.735(2)	Ru–C5	2.282(18)
Ru–C_B	1.998(13)	C–O_B	1.247(18)
Ru–C'_B	1.975(13)	C–O_T	1.132(18)
Ru–C_T	1.855(14)	C1–C2	1.413(24)
Ru–C1	2.284(15)	C2–C3	1.421(24)
Ru–C2	2.259(18)	C3–C4	1.374(23)
Ru–C3	2.225(16)	C4–C5	1.436(25)
Ru–C4	2.257(17)	C5–C1	1.431(24)

INTRAMOLECULAR ANGLES AND ESTIMATED STANDARD DEVIATIONS

C_B–Ru–C'_B	93.0(5)	C_B–Ru–Ru'	46.1(4)
C_T–Ru–C_B	92.4(6)	C'_B–Ru–Ru'	46.8(4)
C_T–Ru–C'_B	91.5(6)	C_1–C_2–C_3	107(1)
Ru–C_B–Ru'	87.0(5)	C_2–C_3–C_4	109(1)
Ru–C_B–O_B	136(1)	C_3–C_4–C_5	109(1)
Ru–C'_B–O'_B	137(1)	C_4–C_5–C_1	106(1)
Ru–C_T–O_T	179(1)	C_5–C_1–C_2	109(1)

The angles subtended at a carbon atom of the ring by the ruthenium atom and an adjacent carbon atom vary between 70 and 73° with e.s.d. 1° and avarage value of 71.8°. The angles subtended at the ruthenium atom by two adjacent carbon atoms in the ring vary between 36 and 37° with e.s.d. 0.6° and average value 36.4°. C_B = C(bridge); C_T = C(terminal).

Best least-squares planes through atomic positions

In the following equations the quantities X, Y, Z refer to orthogonal coordinates obtained by the transformation

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

(*i*) Plane through Ru, C(bridge) and the origin *i.e.* the molecular centre of symmetry.

$$0.7128X - 0.6537Y + 0.2542Z = 0$$

The oxygen atom of the bridging carbonyl group is within 0.001 Å of this plane.

(*ii*) Plane through C1, C2, C3, C4 and C5:

$$0.6546X + 0.0123Y + 0.7558Z = 2.9520$$

Distances of atoms from this plane

C1	0.006 Å	C2	0.000	C3	−0.007
C4	0.010	C5	−0.010	Ru	1.910

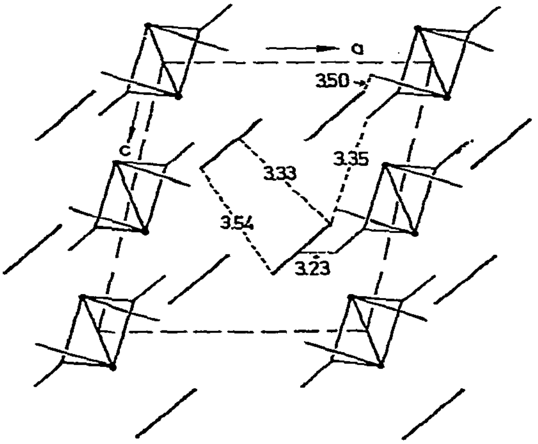

Fig. 2. Projection of structure along the *b* axis. The shortest non-bonding distances are shown.

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SUMMARY

The structure of bis(cyclopentadienyldicarbonylruthenium) has been determined in the solid at room temperature. The crystals are monoclinic with $a = 7.10$, $b = 12.48$, $c = 8.04$ Å and $\beta = 104.33°$. The cell dimensions, space-group and structure are compared with those of bis(cyclopentadienyldicarbonyliron). The Ru–Ru distance is 2.73 Å, Ru–C(terminal CO) 1.86 Å, Ru–C(bridging CO) 1.99 Å and Ru–C(ring) 2.26 Å. In the solid the structure is centrosymmetrical.

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