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CARBON COMPOUNDS OF THE TRANSITION METALS
VIII. THE STRUCTURE OF TRIS(π-CYCLOPENTADIENYLCARBONYLRHODIUM)

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INTRODUCTION

Although the monomeric species cyclopentadienyldicarbonylcobalt[1,2], C_5H_5-$Co(CO)_2$, and the corresponding rhodium compound[3] (I) are stable, both give rise to a series of polynuclear metal cyclopentadienyl carbonyls in a manner somewhat analogous to the metal carbonyls themselves.

In the case of the rhodium species at least four polynuclear complexes have been prepared[4,5]; two have been reported for the cobalt series, both trimers[6]. Irradiation of hexane solutions of (I) with ultraviolet light yields a binuclear species with loss of CO, whilst under prolonged exposure higher polynuclear species occur. One of these (II) is a black crystalline material, only sparingly soluble in organic solvents. The infrared spectrum of (II), measured from a KBr disc[5], showed no absorption in the region 1950–2200 cms^{-1} but strong absorptions in the 1700–1825 cms^{-1} region. This suggests the absence of terminal CO groups and the presence of bridging carbonyls. The low solubility of the complex made NMR measurements difficult but the results were consistent with only one kind of hydrogen atom. The mass spectrum is consistent with a trimer which is the structure determined from our X-ray analysis[7].

EXPERIMENTAL

Crystal data

Tris(cyclopentadienylcarbonylrhodium), $C_{18}H_{15}O_3Rh_3$, mol.wt. 588.0, monoclinic, $a = 7.06 \pm 0.04$, $b = 12.92 \pm 0.05$, $c = 9.47 \pm 0.04$ Å, $\beta = 94°45' \pm 9'$, $U = 861$ Å^3, $D_c = 2.27$ g·cms^{-3} (based on two trimers per cell), systematic absences $0k0$ when k odd, spacegroup $P2_1$ (C_2^2, No. 4) or $P2_1/m$ (C_{2h}^2, No. 11), $\mu = 27.7$ cms^{-1} for Mo–K_α radiation.

A crystalline sample of the air-stable compound in the form of rather small, black, very thin platelets was kindly supplied by Professor E. O. Fischer. Unit-cell dimensions and intensity data were measured from precession photographs taken with Mo–K_α radiation (λ 0.7107 Å). For the intensity measurements, a very thin plate of dimensions $0.6 \times 0.15 \times 0.01$ mm was used with the long dimension, which was

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parallel to the *a* axis, almost aligned along the spindle axis (a^*). Intensities were estimated visually from the levels *hkn*, $n=0, 1, 2$ and *hnl*, $n=0, 1, 2, 3$. After Lorentz and polarisation corrections had been applied the inter-level scale factors were determined by the method of Hamilton, Rollett and Sparks[8]. Altogether some 802 reflexions, of which 62 were immeasurably weak, were estimated from these films; 699 of these reflexions, including 51 of zero intensity, were crystallographically unique. No correction for absorption was applied.

Solution of the structure and refinement

Although the systematic absences leave the space group in some doubt, the interpretation of the Patterson function should be capable of resolution of the ambiguity. Thus for the lower spacegroup $P2_1$, the molecule has no symmetry imposed upon it when there are two molecules per unit cell, whilst for the higher space group the molecule must exhibit mirror symmetry since the alternative permitted by the space group, namely a centre of symmetry, is incompatible with an odd number of metal atoms, cyclopentadienyl groups and carbonyl groups. The rhodium atoms must therefore either all lie in the mirror plane, or be arranged in a plane perpendicular to the mirror plane with one atom on the intersection of the two planes and the other two symmetrically above and below the mirror plane. The positions of the major peaks in the Patterson synthesis were compatible with this latter arrangement. We concluded that the spacegroup was $P2_1/m$ and the structure was subsequently solved and refined with the symmetry of this spacegroup. The first Fourier synthesis of electron density, with phases based upon the rhodium atom positions determined from the Patterson synthesis, revealed the positions of all the light atoms.

The initial structure refinement was achieved by the use of an *R*-factor Minimisation programme[9] written by us for the Atlas computer. In this programme the positional parameters which were permitted to be changed were varied systematically during two cycles. In the first cycle, the *x*, *y* and *z* coordinates of each atom were successively altered in steps of 0.01 of a cell edge and the value of $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ evaluated at each step. The coordinate selected was that which corresponded to the minimum value of *R*. In the second cycle the step interval was reduced to 0.001. Throughout this procedure the temperature factors were kept constant at an arbitrary value of 3 Å^2. For this process some 322 reflexions were used which satisfied the conditions that $\sin\theta/\lambda<0.5$, $F_o>14.4$e, and that not more than 60 reflexions came from any one film. Systematic changes of the scale factors for these films were also investigated during the programme. As a result of these two cycles the *R* factor for the 322 reflexions improved from 13.9% to 7.8%; the *R* factor for all the 802 planes at the completion of these adjustments was 11.0%.

After four cycles of conventional full-matrix least-squares refinement with variable isotropic temperature factors the *R* factor was 9.1% for the 802 reflexions. The weighting scheme used was:

$$w=0.27 \text{ if } F_o<1 \text{ electron}$$

$$w=0.7/(1+0.0006\,F_o^2+0.1\,F_o)^{\frac{1}{2}} \text{ if } 1<F_o<16$$

$$w=1/(1+0.0006\,F_o^2+0.1\,F_o)^{\frac{1}{2}} \text{ if } F_o>16$$

where the coefficients were chosen so that the weighting analysis showed a uniform distribution of weighted differences when sampled in increasing values of sin θ/λ or F_o.

Finally, the rhodium atoms were treated anisotropically and hydrogen atoms, whose positions were not refined, were included at calculated positions so that the C–H distance was 1.08 Å. The 802 separately estimated reflexions were combined to give the set of 699 crystallographically unique reflexions and after two further cycles of least-squares refinement the convergence was judged complete since the largest change in any parameter was less then one half of the corresponding standard deviation. The final R factor was 8.0% for the 648 non-zero unique reflexions and 9.1% for the 699 unique reflexions*. All the programmes used in the analysis were written for the Atlas computer by members of our laboratory.

TABLE 1

ATOMIC PARAMETERS

Atom	*x/a*	*y/b*	*z/c*	*B* (Å^2)
Rh 1	−0.3291 (2)	−0.1485 (2)	0.2668 (2)	
Rh 2	−0.3680 (3)	−0.2500	0.0269 (3)	
C 1	−0.1223 (32)	−0.1955 (23)	−0.0989 (28)	4.0 (5)
C 2	−0.2977 (37)	−0.1652 (26)	−0.1620 (34)	4.5 (6)
C 3	−0.4097 (46)	−0.2500	−0.2110 (43)	3.4 (7)
C 4	−0.0373 (40)	−0.1049 (29)	0.3717 (31)	5.4 (7)
C 5	−0.0632 (41)	−0.0499 (31)	0.2573 (35)	5.4 (7)
C 6	−0.2251 (39)	0.0151 (27)	0.2613 (34)	4.6 (6)
C 7	−0.2969 (35)	0.0016 (26)	0.3819 (31)	3.9 (5)
C 8	−0.1879 (46)	−0.0782 (33)	0.4540 (39)	6.7 (8)
C 9	−0.4949 (41)	−0.2500	0.3559 (37)	3.0 (6)
C 10	−0.5360 (30)	−0.1439 (21)	0.1095 (28)	3.0 (4)
O 1	−0.6116 (30)	−0.2500	0.4387 (26)	3.5 (5)
O 2	−0.6745 (22)	−0.1005 (16)	0.0759 (19)	3.9 (3)
H 1	−0.0079	−0.1434	−0.0573	6.0
H 2	−0.3461	−0.0880	−0.1764	6.0
H 3	−0.5504	−0.2500	−0.2690	6.0
H 4	0.0791	−0.1596	0.3985	6.0
H 5	0.0395	−0.0630	0.1774	6.0
H 6	−0.2847	0.0698	0.1775	6.0
H 7	−0.4095	0.0457	0.4193	6.0
H 8	−0.2138	−0.1187	0.5570	6.0

Anisotropic temperature coefficients for the rhodium atoms:

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Rh 1	0.0126 (3)	0.0054 (1)	0.0080 (3)	−0.0004 (2)	0.0000 (2)	−0.0002 (3)
Rh 2	0.0127 (5)	0.0050 (2)	0.0068 (3)		0.0009 (3)	

The expression for the temperature factor used was:

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

The quantities in parentheses are the 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.

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* Atomic scattering factors were taken from the following sources: (*i*) for C and O, ref 10(a); (*ii*) for H, ref. 10(b); (*iii*) for Rh, ref. 10(c) with dispersion correction given in ref. 10(b).

The final atomic coordinates and estimated standard deviations are listed in Table 1, and details of molecular geometry in Table 2. A sketch of the molecule is given in Fig. 1.

DISCUSSION

The structure consists of a triangle of rhodium atoms which by symmetry is strictly isosceles though the deviation from equilateral is not significant. The cyclo-

TABLE 2

MOLECULAR GEOMETRY

Interatomic distances and estimated standard deviations (Å)

Rh 1–Rh 1′	2.622 (3)	Rh 1–C 10	2.00 (2)	C 4–C 5	1.30 (4)
Rh 1–Rh 2	2.617 (3)	Rh 2–C 1	2.30 (2)	C 4–C 8	1.41 (4)
Rh 1–C 4	2.28 (3)	Rh 2–C 2	2.19 (3)	C 5–C 6	1.42 (4)
Rh 1–C 5	2.28 (3)	Rh 2–C 3	2.25 (4)	C 6–C 7	1.30 (4)
Rh 1–C 6	2.24 (3)	Rh 2–C 10	2.01 (2)	C 7–C 8	1.42 (5)
Rh 1–C 7	2.23 (3)	C 1–C 1′	1.41 (4)	C 9–O 1	1.18 (4)
Rh 1–C 8	2.16 (4)	C 1–C 2	1.39 (4)	C 10–O 2	1.15 (3)
Rh 1–C 9	1.99 (2)	C 2–C 3	1.41 (4)		

Intramolecular angles and estimated standard deviations (°)

Rh 1–Rh 1′–Rh 2	60.0 (1)	C 5–C 4–C 8	105.4 (29)	C 4–C 8–C 7	108.2 (31)
Rh 1–Rh 2–Rh 1′	60.0 (1)	O 2–C 10–Rh 1	140.7 (22)	Rh 1′–C 9–Rh 1	82.4 (9)
C 1′–C 1–C 2	106.4 (29)	C 4–C 5–C 6	111.1 (29)	Rh 1–C 10–Rh 2	81.4 (9)
C 1–C 2–C 3	112.3 (28)	C 5–C 6–C 7	108.3 (31)	Rh 2–C 10–O 2	137.8 (22)
C 2–C 3–C 2′	102.3 (29)	C 6–C 7–C 8	106.7 (30)		

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 defined by C 1, C 1′, C 2, C 2′, C 3:
$0.4706X+0.8824Z+0.4437=0$
Distances of atoms from the plane (Å):
C 1, −0.010; C 2, 0.024; C 3, −0.029.

(*ii*) Plane defined by C 4, C 5, C 6, C 7, C 8:
$0.5509X+0.7123Y-0.4349Z+0.2394=0$
Distances of atoms from the plane (Å):
C 4, 0.014; C 5, 0.001; C 6, −0.017; C 7, 0.025; C 8, −0.023.

(*iii*) Plane defined by Rh 1, Rh 1′, Rh 2:
$0.9993X+0.0381Z-2.6272=0$

(*iv*) Plane defined by C 9, C 10, C 10′:
$0.9991X+0.0416Z-3.9098=0$

(*v*) Plane defined by O 1, O 2, O 2′:
$0.9989+0.0467Z-4.8506=0$

Atoms which are related by the plane of symmetry to those listed in Table 1 are marked with a prime.

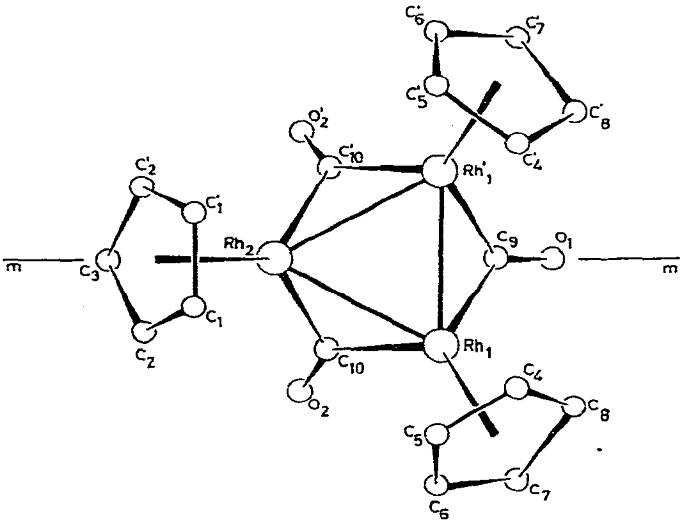

Fig. 1. View of the molecule along the idealised three-fold axis.

pentadienyl rings are planar within experimental error, exhibit the usual π-bonded geometry with respect to the rhodium atoms *i.e.* the Rh–C_{ring} distances are identical, and are all displaced to the same side of the rhodium triangle. The three carbonyl bridging groups occur on the opposite side of the triangle. The structure found contains an idealised 3-fold axis of symmetry. The normals to the cyclopentadienyl ring planes make angles of 57.7 and 59.9° with the normal to the rhodium triangle. The carbonyl groups are similarly symmetrically disposed. The planes defined by the three carbon atoms and the three oxygen atoms of the carbonyl groups make angles of 0.0 and 0.5° with the rhodium plane.

The average Rh–C distances found are 2.24 and 2.00 Å for Rh–ring and Rh–carbonyl respectively. These are in close agreement with the values 2.26 and 2.01 Å found in $Rh_2(C_5H_5)_2(CO)_3$[11]. The values for the Rh–CO distance fall between the previously determined values of 1.87[11] and 1.86[12] for terminal groups and 2.17 Å[12] for triple-bridging groups.

The Rh–Rh distances, average 2.62 Å, are shorter than those found, to our knowledge, in any other comparable rhodium complex. Thus in $Rh_6(CO)_{16}$[12] the mean value is 2.78, in $Rh_3C_{20}H_{21}$[13] 2.72, in $Rh_2(C_5H_5)_2(CO)_3$[11] 2.68 whilst in the metal the value is 2.69 Å[14]. At the present it seems therefore that the triangular arrangement, the bridging carbonyls or the cyclopentadienyl rings cannot, by themselves, be the reason for the short distance.

The mass spectrum of the sample proved to be complicated. In addition to the parent molecular ion at *m/e* 588, with associative fragments corresponding to loss of successive CO groups, there were frequent groups of peaks which corresponded roughly to ejection of single carbon atoms together with a variable number of protons. The peak of greatest *m/e* value, which was more intense than the parent molecular ion, occurred at *m/e* 728 and corresponds to the species $Rh_4(C_5H_5)_4(CO)_2^+$ which presumably arises through thermal decomposition of the trimer on the probe. Evidence for a similar decomposition has been reported in the case of the cobalt trimer by King[6].

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SUMMARY

The structure of tris(cyclopentadienylcarbonylrhodium) in the solid state has been determined by X-ray diffraction methods. The crystals are monoclinic with $a = 7.06$, $b = 12.92$, $c = 9.47$ Å and $\beta = 94°45'$. The structure consists of a triangular arrangement of rhodium atoms with π-cyclopentadienyl groups displaced to one side of the triangle and bridging carbonyl groups on the other. The Rh–Rh distance is 2.62 Å, Rh–C(ring) 2.24 Å and Rh–C(carbonyl) 2.00 Å.

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