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CARBON COMPOUNDS OF THE TRANSITION METALS X*. THE STRUCTURE OF TETRACYCLOPENTADIENYLHYDRIDOTRIRHODIUM

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The number of compounds which contain clusters of cobalt or rhodium atoms has increased rapidly in recent years. Thus there has been reported a number in which three cobalt atoms are arranged at the corners of an almost equilateral triangle[1-4] whilst in the pure carbonyl, $Co_4(CO)_{12}$, the metal atoms occur at the corners of a tetrahedron[5,6]. Fewer rhodium compounds have been reported but in $Rh_6(CO)_{16}$ an octahedral distribution of rhodium atoms occurs[7]. The structure of one rhodium compound has been reported in which the metal atoms are also arranged at the corners of an almost equilateral triangle[8,9].

We now report the detailed analysis[10] of a second triangular cluster compound, $(C_5H_5)_4Rh_3H$, which is formed in small yield as a by-product during the reaction of $RhCl_3$ with C_5H_5MgBr in benzene-diethylether solution[11]. It is a brownish-black, diamagnetic compound, soluble in organic media and of surprisingly great air-stability and can be heated to 200° without decomposition.

EXPERIMENTAL

Crystal data

Tetracyclopentadienylhydridotrirhodium, $C_{20}H_{21}Rh_3$, mol.wt. 570.1, orthorhombic, $a = 12.82 \pm 0.05$, $b = 14.96 \pm 0.05$, $c = 8.86 \pm 0.04$ Å, $U = 1699$ Å^3, d(measured) $= 2.3$ g·cm^{-3}, d(calculated) $= 2.23$ g·cm^{-3} (based on four molecules per cell), systematic absences $0kl$ when $k+l$ odd, $hk0$ when h odd, spacegroup $Pnma$ (D_{2h}^{16}, No. 62) or $Pn2_1a$ (C_{2v}^{9}, No. 33), $\mu = 27.9$ cm^{-1} for Mo-K_α radiation.

A sample of the material was kindly supplied by Professor E. O. Fischer. Recrystallisation from a mixture of benzene and petrol ether at 5° yielded rather small crystals suitable for analysis. The density was determined by flotation in aqueous potassium iodide; the rather high viscosity of the solution probably accounts for the discrepancy between measured and calculation values.

Unit cell dimensions and intensity data were measured photographically with a precession camera and with Mo-K_α radiation ($\lambda = 0.7107$ Å). For the intensity data a crystal of dimensions $0.5 \times 0.15 \times 0.05$ mm was used with the needle axis, a^*, aligned along the spindle. Eleven levels were recorded: hkn ($n = 0, 1, 2$), hnl ($n = 0, 1, 2, 3$) and $h, l+n, l$ ($n = 0, 1, 2, 3$).

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* For part IX see ref. 18.

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Altogether some 1042 non-zero intensities were estimated together with a further 77 too weak to be estimated. After Lorentz and polarisation corrections had been applied, the inter-level scale factors were determined by the method of Hamilton, Rollett and Sparks[12]. Of all of these reflexions 829 were unique, 56 of which had zero intensity. A correction for absorption was not applied.

Solution of the structure and refinement

The systematic absences do not determine the spacegroup unambiguously. For the lower spacegroup, with $Z=4$, the asymmetric unit is the molecule which would therefore be in a general position. For the holosymmetric spacegroup, however, the molecule must occupy a special position, more probably the mirror plane, though a linear molecule arranged about a centre of symmetry is possible if the hydrogen contribution is ignored. The three-dimensional Patterson synthesis could be interpreted in terms of the spacegroup *Pnma* and the structure was solved and subsequently refined with the symmetry of this spacegroup. The absence of large peaks at $(0, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ excluded the linear structure so that one rhodium atom must lie at a special position on the mirror plane and the other two in general positions related by the mirror plane. One set of peaks could be interpreted by an atom in the general position $(\sim 0, \sim \frac{1}{6}, \sim \frac{5}{6})$ whilst the atom in the special position gave the coordinates $(\pm \frac{19}{240}, \frac{1}{4}, \frac{13}{240}$ or $\frac{133}{240})$ consistent with the observed peaks on Harker lines and sections. The fortuitously special value of the x coordinate of the general position for the first rhodium atom made the decision between these four possibilities difficult. Accordingly we calculated the R-factors $(=\Sigma||F_0|-|F_c||/\Sigma|F_0|)$ for some 39 strong reflexions for each of the four cases *i.e.* with rhodium atom contributions only. The lowest value, 17.5%, was given by the position $(\frac{19}{240}, \frac{1}{4}, \frac{13}{240})$; the values in the other three cases varied between 22.4 and 28.6%. The Fourier synthesis of electron density, calculated with phases based upon the rhodium atom positions which gave this lowest value above, showed peaks which could be interpreted as the twenty carbon atoms of the compound.

The structure was then improved by six cycles of conventional full-matrix least-squares refinement with individual isotropic temperature factors and individual level scale factors after which the R-factor was 11.1%.

At this stage twenty hydrogen atoms were introduced into the model so that the carbon–hydrogen distance was 1.09 Å and the vector bisected the ring angle at the carbon atom. After another three cycles of least-squares refinement with anisotropic refinement of the rhodium atoms and isotropic treatment for the carbon atoms the R-factor was 7.0% for the 1042 non-zero reflexions and 8.0% for the 1119 reflexions including zero-intensity reflexions.

Finally all the reflexions were put on a common scale which then contained only the unique reflexions. This final set of reflexions contained 829 unique terms of which 56 were of zero intensity. It was observed that the bond-lengths in the ring parallel to the rhodium triangle appeared to be less uniform than in the other three rings, although because of the mirror symmetry in this ring only three lengths are determined. We examined the possibility of a disordered ring system but the difference electron density observed in the plane of the ring showed no regions of pronounced density in the regions between the atoms. We also attempted to test for false minima in the region of the solution by inserting a symmetrical ring in place of the one found. Refinement of this structure produced the same model as previously. An examination of the electron density in the plane of the rhodium atoms did not lead to an unambiguous location of the twentyfirst hydrogen atom. Refinement was then terminated with a further three cycles of full-matrix least-squares using the unique data. The maximum shift in any parameter was no greater than one tenth of the corresponding standard deviation and the final R-factors were 6.8% and 7.9%. In the final refinement* the following weighting scheme was used:

$$w = 0.03 \text{ if } F_0 < 2 \text{ electron}$$

$$w = 1.00/(1 + 0.0001\ F_0^2 + 0.1\ F_0) \text{ if } 2 \leqslant F_0 \leqslant 128 \text{ electron}$$

$$w = 0.30/(1 + 0.0001\ F_0^2 + 0.1\ F_0) \text{ if } F_0 > 128 \text{ electron.}$$

TABLE 1

ATOMIC PARAMETERS

Atom	x/a	y/b	z/c	B (Å^2)
Rh1	0.0163(1)	0.8407(1)	0.1774(2)	
Rh2	−0.0765(1)	0.7500	−0.0537(2)	
C11	0.0150(19)	0.9845(19)	0.2170(28)	5.2(5)
C12	−0.0891(19)	0.9555(19)	0.2391(31)	6.0(6)
C13	−0.0870(17)	0.8931(17)	0.3616(26)	4.5(5)
C14	0.0146(19)	0.8887(20)	0.4117(30)	5.6(6)
C15	0.0800(17)	0.9418(17)	0.3317(24)	4.6(4)
C1	0.0750(16)	0.7963(14)	−0.1285(22)	3.9(4)
C2	0.1310(17)	0.8288(16)	0.0108(25)	4.6(5)
C3	0.1597(22)	0.7500	0.0921(34)	4.0(6)
C21	−0.1743(18)	0.7978(16)	−0.2460(28)	4.9(5)
C22	−0.2249(15)	0.8263(16)	−0.1100(23)	4.1(4)
C23	−0.2495(21)	0.7500	−0.0301(33)	3.7(6)
H11	0.0401	0.0313	0.1262	5.0
H12	−0.1578	0.9709	0.1727	5.0
H13	−0.1497	0.8510	0.4098	5.0
H14	0.0401	0.8484	0.5050	5.0
H15	0.1627	0.9511	0.3641	5.0
H1	0.0398	0.8416	−0.2102	5.0
H2	0.1492	0.8988	0.0480	5.0
H3	0.1965	0.7500	0.2018	5.0
H21	−0.1415	0.8400	−0.3335	5.0
H22	−0.2386	0.8961	−0.0702	5.0
H23	−0.2868	0.7500	0.0776	5.0

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.

The anisotropic temperature coefficients for the rhodium atoms are:

Rh1: $b_{11} = 0.00482(8)$ $b_{22} = 0.00375(8)$ $b_{33} = 0.00829(17)$
$b_{12} = -0.00034(8)$ $b_{13} = -0.00018(11)$ $b_{23} = -0.00017(11)$
Rh2: $b_{11} = 0.00338(10)$ $b_{22} = 0.00445(13)$ $b_{33} = 0.00716(23)$
$b_{12} = 0.00000$ $b_{13} = -0.00015(15)$ $b_{23} = 0.00000$

The expression for the temperature factor used was

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

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* Atomic scattering factors were taken from ref. 14a (for carbon), ref. 14b (for hydrogen) and ref. 14c (for rhodium, with dispersion correction given in ref. 14b).

TABLE 2

MOLECULAR GEOMETRY

Interatomic distances and estimated standard deviations (Å)

Rh1–Rh1′	2.715(3)	C11–C12	1.42(4)
Rh1–Rh2	2.730(2)	C11–C15	1.46(3)
Rh1–C11	2.18(3)	C12–C13	1.43(3)
Rh1–C12	2.25(3)	C13–C14	1.38(3)
Rh1–C13	2.24(2)	C14–C15	1.35(3)
Rh1–C14	2.20(3)	C21–C21′	1.43(5)
Rh1–C15	2.20(2)	C21–C22	1.43(3)
Rh1–C1	2.89(2)	C22–C23	1.38(3)
Rh1–C2	2.09(2)	C1–C1′	1.39(4)
Rh1–C3	2.41(2)	C1–C2	1.51(3)
Rh2–C21	2.23(2)	C2–C3	1.43(3)
Rh2–C22	2.27(2)		
Rh2–C23	2.23(3)		
Rh2–C1	2.17(2)		
Rh2–C2	2.96(2)		
Rh2–C3	3.29(3)		

Intramolecular angles and estimated standard deviations (°)

Rh1′–Rh1–Rh2	60.2(1)	C21′–C21–C22	107.3(21)
Rh1–Rh2–Rh1′	59.7(1)	C21–C22–C23	106.7(21)
C15–C11–C12	107.8(22)	C22–C23–C22′	111.7(21)
C11–C12–C13	106.7(22)	C1′–C1–C2	108.8(20)
C12–C13–C14	107.0(22)	C1–C2–C3	105.6(20)
C13–C14–C15	112.9(24)	C2–C3–C2′	111.1(20)
C14–C15–C11	105.5(20)		

Best least-squares planes through atomic positions

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

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{bmatrix} \begin{bmatrix} x\ a \\ y\ b \\ z\ c \end{bmatrix}$$

(*i*) Plane defined by Rh1, Rh1′, Rh2:
$-0.8646X + 0.5025Z - 0.6087 = 0$

(*ii*) Plane defined by C11, C12, C13, C14, C15:
$0.1712X - 0.7544Y - 0.6338Z + 12.3107 = 0$
Distances of atoms from the plane (Å):
C11 0.012 C14 −0.001
C12 −0.013 C15 −0.007
C13 0.008 Rh1 1.860

(*iii*) Plane defined by C1, C2, C3, C1′, C2′:
$0.8714X - 0.4905Z - 1.4014 = 0$
Distances of atoms from the plane (Å):
C1 −0.005 C2 0.014 C3 −0.018

(*iv*) Plane defined by C21, C22, C23, C21′, C22′:
$-0.8895X - 0.4570Z - 2.9903 = 0$
Distances of atoms from the plane (Å):
C21 −0.007 C22 0.019 C23 −0.025 Rh2 1.901

Plane (*ii*) forms an angle of 62.6°, plane (*iii*) an angle of 179.2° and plane (*iv*) an angle of 57.4° with plane (*i*).

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

These coefficients were chosen so that the weighting analysis showed a uniform distribution of weighted differences when sampled in increasing values of $\sin \theta/\lambda$ or F_0.

The final atomic coordinates and estimated standard deviations as obtained from the final cycle of the least-squares analysis are listed in Table 1 and details of molecular geometry in Table 2. A drawing of the molecule, projected onto the plane of the rhodium atoms, together with the numbering scheme used is shown in Fig. 1.

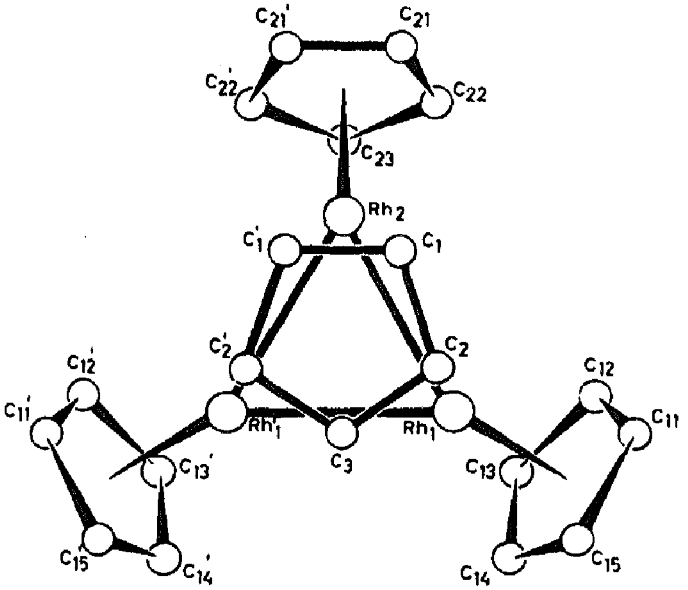

Fig. 1. Projection of the molecule onto the rhodium plane showing numbering scheme.

DISCUSSION

The structure consists of discrete molecules in which one π-cyclopentadienyl group is attached to each rhodium atom. The rhodium atoms forms a triangle and although the crystallographic symmetry requires that the triangle be only strictly isosceles, the experimentally determined values of the bond lengths, 2.71_5 and 2.73_0 Å, with estimated standard deviations of 0.003 Å (a value which excludes the contribution from the uncertainty in the unit cell determination) are in accord with an equilateral-triangular arrangement.

The π-cyclopentadienyl groups are accurately coplanar with maximum deviation of any atom from the "best" least-squares planes of 0.02 Å. These groups are symmetrically displaced to one side of the rhodium triangle so that the angles made between the normals to the least-square planes and that of the rhodium triangle are 62.6° (for that attached to Rh1) and 57.4° for that attached to Rh2. This part of the molecule very strongly resembles the structure of $(C_5H_5)_3Rh_3(CO)_3$ (ref. 9) where the corresponding angles are 57.7° and 59.8°. The Rh–ring plane distances are correspondingly 1.86 and 1.90 Å and these can be compared with 1.91 and 1.90 Å in $(C_5H_5)_3Rh_3(CO)_3$ and 1.90 and 1.91 Å in $(C_5H_5)_2Rh_2(CO)_3$ (ref. 13). The corresponding sets of average Rh–C distances are 2.21, 2.24, 2.24, 2.24, 2.25 and 2.27 Å. There is however one major difference between the present compound and that of the tricarbonyl complex, namely the Rh–Rh distance is almost 0.1 Å larger in the present analysis.

TABLE 3

CLOSEST INTERMOLECULAR APPROACHES (Å)

Rh1···H11(V)	3.38	C3···H23(II)	3.01
Rh1···H23(II)	3.59	C23···H14(II)	3.08
Rh2···H11(III)	3.37	C23···H3(II)	2.99
C1···C21(VIII)	3.40	H11···H11(V)	2.63
C1···C22(VIII)	3.49	H11···H1(V)	2.28
C2···C21(VIII)	3.46	H12···H15(V)	2.34
C1···H11(V)	2.97	H15···H22(VIII)	2.37
C2···H13(VIII)	2.92	H3···H23(II)	1.97
C3···H13(II)	2.87		

The Roman numerals contained in parentheses indicate that the contact is made to an atom related, by one of the operations listed below, to the one whose coordinates (x, y, z) are tabulated in Table 1.

I	$x,$	$y,$	z	V	$-x,$	$-y,$	$-z$
II	$\frac{1}{2}+x,$	$\frac{1}{2}-y,$	$\frac{1}{2}-z$	VI	$\frac{1}{2}-x,$	$\frac{1}{2}+y,$	$\frac{1}{2}+z$
III	$-x,$	$\frac{1}{2}+y,$	$-z$	VII	$x,$	$\frac{1}{2}-y,$	z
IV	$\frac{1}{2}-x,$	$-y,$	$\frac{1}{2}+z$	VIII	$\frac{1}{2}+x,$	$y,$	$\frac{1}{2}-z$

The fourth C_5 ring is uniquely bonded to the metal atoms since it lies parallel, the angle between the least-squares plane of the ring and the metal atom plane is 0.8°, with the rhodium triangle and 2.00 Å from it. This ring also has *m* symmetry and is staggered with respect to the rhodium triangle. As referred to in the experimental section there was no evidence in the analysis for a disordered arrangement of the C_5 ring. Because of the *m* symmetry only three C–C distances are determined. The values are 1.39, 1.51 and 1.43 Å and it is necessary to enquire if these values are significantly different. At the same time we also ask if the variations found in the other rings are significant and whether there is any evidence for the fourth ring being different from the others. Firstly we note that the average C–C distances for the three separately determined rings, *i.e.* those attached to Rh1, Rh2 and the fourth ring, are 1.40_8, 1.41_0 and 1.45 Å respectively. The maximum deviations from these average values observed in any ring is 0.05, 0.03 and 0.06 Å respectively and these are 2 σ, 1 σ and 2 σ respectively. The observed variations all lie within two standard deviations and any individual variation is therefore not significant. The standard errors of the mean values for the three rings are 0.01_8, 0.01_5 and 0.01_5 Å respectively and so the observed values of 1.45 and 1.41 Å for the mean distances may just be significant. It might be imagined that the bonding of a five-fold symmetric ring onto a three-fold symmetric system would produce distortion in both systems. We have seen that the values for all the rings lie within the rather large estimated standard deviations associated with the determination of carbon atom positions in a structure containing three rhodium atoms; we also note that the rhodium triangle, for which the positions of the metal atoms are much more precisely determined, shows no significant distortion from 3-fold symmetry.

The present complex and the tricarbonyl complex are formally isoelectronic since in place of the three CO groups we have one C_5H_5 ring and one additional hydrogen atom. Although the position of this twentyfirst hydrogen atom was not determined from the X-ray analysis, the mass spectrum[10] clearly establishes the overall formula. Further the NMR spectrum shows an absorption at high field ($\tau = 22.47$) split into a quartet. These observations are consistent with the hydrogen atom being bound to all three rhodium atoms, at least in a time-averaged sense. A possible position is that where the three-fold axis cuts the metal triangle. The Rh–triangle centre distance is 1.57 Å. La Placa and Ibers have reported[15] a Rh–H distance initially as 1.72 Å which they subsequently[16] revised to 1.60 Å, both ±0.12 Å. The Rh–centre distance is thus in harmony with this revised figure and in keeping with the Re–H distance of 1.68 Å determined by neutron diffraction methods[17].

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SUMMARY

The structure of tetracyclopentadienylhydridotrirhodium has been determined by X-ray analysis of the solid. The black crystals belong to the orthorhombic system with spacegroup *Pnma* and $a = 12.82$, $b = 14.96$ and $c = 8.86$ Å. The rhodium atoms are arranged in an almost equilateral triangle with mean edge 2.72 Å. Three π-cyclopentadienyl groups, one attached to each rhodium atom, are displaced to one side of the rhodium triangle and the fourth cyclopentadienyl group lies parallel to the triangle on the opposite side to the other three. The mean rhodium–carbon distance of the three rings is 2.23 Å. The shortest rhodium–carbon distance to the fourth ring is 2.09 Å. NMR measurements are consistent with the hydridic proton being situated near the centre of the rhodium triangle.

REFERENCES

1 R. B. King, *Inorg. Chem.*, 5 (1966) 2227.
2 R. B. King and F. T. Korenowski, *Chem. Commun.*, (1966) 771.
3 C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 6 (1967) 1229.
4 P. W. Sutton and L. F. Dahl, *J. Amer. Chem. Soc.*, 89 (1967) 261.
5 P. Corradini, *J. Chem. Phys.*, 31 (1959) 1676.
6 C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, 88 (1966) 1821.
7 E. R. Corey, L. F. Dahl and W. Beck, *J. Amer. Chem. Soc.*, 85 (1963) 1202.
8 O. S. Mills and E. F. Paulus, *Chem. Commun.*, (1966) 815.
9 O. S. Mills and E. F. Paulus, *J. Organometal. Chem.*, 10 (1967) 331.
10 E. O. Fischer, O. S. Mills, E. F. Paulus and H. Wawersik, *Chem. Commun.*, (1967) 643.
11 E. O. Fischer and H. Wawersik, *Chem. Ber.*, in press.
12 W. C. Hamilton, J. S. Rollett and R. A. Sparks, *Acta Crystallogr.*, 18 (1965) 129.
13 O. S. Mills and J. P. Nice, *J. Organometal. Chem.*, 10 (1967) 337.
14 (a) J. Berghuis, I. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry and A. L. Veenendaal, *Acta Crystallogr.*, 8 (1955) 478;
(b) C. H. MacGillavry and G. D. Rieck, *International Tables for X-ray Crystallography*, Vol. III, Kynoch Press, Birmingham, 1962;
(c) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, 26 (1957) 293.

15 S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, 85 (1963) 3501.
16 S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, 18 (1965) 511.
17 S. C. Abrahams, A. P. Ginsberg and K. Knox. *Inorg. Chem.*, 3 (1964) 558.
18 O. S. Mills and E. F. Paulus, *J. Organometal. Chem.*, 10 (1967) 337.