

## The Structure of Hydridotetracyclopentadienyltrirrhodium

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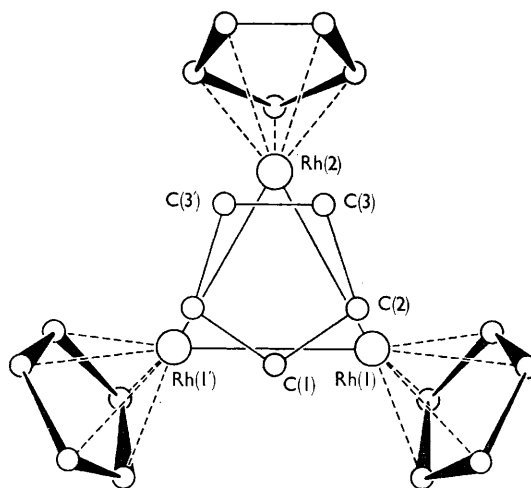
THE isolation of a byproduct, formed in low yield during the reaction of  $\text{RhCl}_3$  with  $\text{cpMgBr}$  in benzene-diethyl ether, has been briefly reported.<sup>1</sup> At that time the formula  $\text{Rh}_3\text{C}_{20}\text{H}_{20-21}$  was put forward for the brownish-black, diamagnetic compound which is soluble in organic media, is air stable, and can be heated to  $200^\circ$  without decomposition.

The parent molecular ion occurred in the mass spectrum† at  $m/e$  570, together with isotopic contributions corresponding to the carbon content, which determined the formula as  $\text{C}_{20}\text{H}_{21}\text{Rh}_3$ . The main fragmentation pattern consists of peaks at 504, 502, and 500, presumably associated with the ion  $\text{cp}_3\text{Rh}_3^+$ , at 233 ( $\text{cp}_3\text{Rh}^+$ ), and at 168 ( $\text{cpRh}^+$ ). In addition a number of small peaks occur in the region 309–335 which may be associated with  $\text{Rh}_3^+$  residues.

*Crystal data.*  $\text{C}_{20}\text{H}_{21}\text{Rh}_3$ ,  $M = 570.1$ , orthorhombic,  $a = 12.82$ ,  $b = 14.96$ ,  $c = 8.86$  Å,  $U = 1699$  Å<sup>3</sup>,  $D_m = 2.3$  g.cm.<sup>-3</sup> by flotation in aqueous potassium mercuric iodide,  $Z = 4$ ,  $D_c = 2.23$  g.cm.<sup>-3</sup>. Space group by systematic absences either  $Pnma$  or  $Pn2_1a$ . With the former space group the molecular symmetry must be either  $m$  or, if the hydrogen atoms are ignored, possibly  $\bar{1}$  but in this latter case the rhodium atoms would be linear. The alternative space group imposes no constraint on the molecular geometry. The structure was solved with three-dimensional intensity data collected by the precession method with molybdenum- $K_\alpha$  radiation. The three-dimensional Patterson synthesis was entirely consistent with the space group  $Pnma$  and was interpreted in terms of a triangle of metal atoms perpendicular to the mirror plane of the space group. The remaining light atoms were located from successive Fourier approximations to the electron density. The structure was then refined by least-squares methods ( $R = 6.8\%$  for 773 non-zero observations,  $7.9\%$  for 829 unique reflexions).

The structure consists of an almost equilateral triangle of rhodium atoms with mean edge  $2.72$  Å. One  $\pi$ -cyclopentadienyl group is attached to each rhodium atom in a manner similar to that found in tris-( $\pi$ -cyclopentadienylcarbonyl)rhodium (II).<sup>2,3</sup> The metal-ring-plane distances,  $1.86$  and  $1.90$  Å,

are in close agreement with the values found for (II),  $1.90$  and  $1.91$  Å, and in  $\text{cp}_2(\text{CO})_3\text{Rh}_2$ ,  $1.90$  and  $1.91$  Å.<sup>4</sup> The fourth five-membered ring lies very nearly parallel to the rhodium triangle on the opposite side to the three  $\pi$ -cyclopentadienyl groups. The normals to the metal plane and the fourth ring-plane are inclined at less than  $1^\circ$ . All the five-membered rings are planar with maximum displacements from the respective mean planes of  $0.01_3$ ,  $0.02_5$ , and  $0.01_8$  Å. The Figure shows a projection of the molecule on to the plane of the metal triangle. The staggered arrangement of the fourth ring with respect to the rhodium atoms is clearly shown.



FIGURE

View of molecule projected on to the rhodium plane. Interatomic distances and estimated standard deviations.

Rh(1)–Rh(1')	2.715(3) (Å)
Rh(1)–Rh(2)	2.730(2)
C(1)–C(2)	1.43(3)
C(2)–C(3)	1.51(3)
C(3)–C(3')	1.39(4)

The Rh–Rh distances are significantly longer than those found in the only other  $\text{Rh}_3$  system yet reported (II),  $2.62$  Å. At the same time they are significantly shorter than those in the  $\text{Rh}_6$  system

† We thank Dr. J. M. Wilson for the mass spectrum measurement.

found in  $\text{Rh}_6(\text{CO})_{16}$ .<sup>5</sup> The separation between the rhodium triangle and the fourth five-membered ring is 2.00 Å. The C-C distances in this fourth ring have a higher mean value (1.45 against 1.41 Å) and show a greater variation between bond lengths than those for the other rings. However tempting it may be to speculate upon the reasons for this variation, we must affirm that the least-squares estimates of standard deviations indicate that the variations lie within three standard deviations for any individual value.

The infrared spectrum, measured in a KBr disc, shows the characteristics of a  $\pi$ -cyclopentadienyl complex and an additional intensive absorption at 1333  $\text{cm}^{-1}$ . The vibration of the rhodium triangle, measured in a Nujol mull, appears at 206  $\text{cm}^{-1}$ . The ring-proton resonances, measured in  $\text{C}_6\text{D}_6$  solution,<sup>†</sup> occur in the n.m.r. spectrum at  $\tau = 4.75$  and 5.9 in the ratio of  $\sim 3.1 : 1$ . Because of spin-spin coupling with the  $^{103}\text{Rh}$  nuclear spin, the signal from the three  $\pi$ -cyclopentadienyl rings is split into a doublet

( $J = 0.3$  c./sec.) and that due to the fourth ring into a quartet ( $J = 0.8$  c./sec.)

In the final calculations of the crystal structure analysis, twenty hydrogen atoms were included at positions co-planar with the four five-membered rings. The position of the last remaining hydrogen atom was not observed in the X-ray analysis. When the fourth ring is excluded, the molecule has idealized three-fold symmetry. That the time-averaged position of this last hydrogen atom lies on this three-fold axis is shown by the n.m.r. spectrum which shows a high-field resonance, at  $\tau 22.47$ , split into a quartet ( $J = 26.5$  c./sec.). Each rhodium atom is 1.57 Å from the centre of the rhodium triangle and it may be possible for the hydrogen atom to be accommodated in, or close to, this plane (compare Re-H 1.68 Å<sup>6</sup>). Finally we observe that although the structure contains an idealized five-fold symmetric system fused to a three-fold one, there is scant evidence for any distortion in the three-fold portion.

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<sup>1</sup> E. O. Fischer and H. Wawersik, *J. Organometallic Chem.*, 1966, 5, 559.

<sup>2</sup> O. S. Mills and E. F. Paulus, *Chem. Comm.*, 1966, 815.

<sup>3</sup> O. S. Mills and E. F. Paulus, *J. Organometallic Chem.*, 1967, 10, in the press.

<sup>4</sup> O. S. Mills and J. P. Nice, *J. Organometallic Chem.*, 1967, 9, in the press.

<sup>5</sup> E. R. Corey, L. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, 1963, 85, 1202.

<sup>6</sup> S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, 1964, 3, 558.