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Tetrachloro- μ -dichloro-tetrakis(tri-*n*-butylphosphine)dirhodium(III)

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Abstract. $\text{Rh}_2(\text{PBu}_3)_4\text{Cl}_6$, $\text{Rh}_2\text{P}_4\text{Cl}_6\text{C}_{48}\text{H}_{108}$, is monoclinic, $C2/c$, $a = 15.70(5)$, $b = 20.11(5)$, $c = 20.91(6)$ Å, $\beta = 102.3(3)^\circ$, $Z = 4$, $d_x = 1.24$, $d_m = 1.264$ g cm $^{-3}$, $V = 6450$ Å 3 . The two Rh atoms, each with octahedral coordination, lie on a twofold axis. The two phosphines on one Rh are *cis* to each other and *trans* to the bridging chlorines, while the two phosphines on the other Rh are *trans* to each other.

Introduction. Several different molecular structures have been proposed (Brown & Green, 1970; Allen & Gabuji, 1971; Intille, 1972) for complexes of the type $\text{Rh}_2(\text{PR}_3)_4\text{Cl}_6$. Our single-crystal X-ray study establishes the correct structure when *R* is *n*-butyl. The compound was prepared by the method of Chatt, Johnson & Shaw (1964) and recrystallized from ligroin and then several times from acetone. Nearly spherical red prismatic crystals were obtained from an acetone solution by slow evaporation of the solvent.

Experimental. A crystal of average radius 0.24 mm was mounted with the *b* axis parallel to the axis of rotation and the multiple-film equi-inclination Weissenberg method with Mo $K\alpha$ radiation was used to collect intensity data, which were estimated visually by comparison with a standard strip. Al foil was inserted between the films to give sufficient attenuation. Spots from adjacent layers, when present, were partially blocked by the layer-line screen, and so were easily distinguishable and provided no problems in indexing. In total, 1086 independent non-zero reflections were measured on layers $k = 0$ to $k = 10$, scaled according to exposure time, and checked by comparison with a $0kl$ photograph for another crystal. Correction was made for spot-shape extension (Phillips, 1956) but not for absorption, since $\mu = 8.5$ cm $^{-1}$ and the transmission factors varied only from 0.78 to 0.84.

Systematic absences were hkl for $h+k$ odd and $h0l$ for l odd, which indicated space groups Cc or $C2/c$ and the latter was chosen when statistical tests (Howells, Phillips & Rogers, 1950) indicated a centrosymmetric space group. A three-dimensional Patterson synthesis revealed the locations of the Rh atoms in the fourfold special positions on the twofold axis at $0, 0.19, \frac{1}{4}$ and $0, 0.37, \frac{1}{4}$. Least-squares refinement and difference Fourier syntheses revealed the positions of the Cl, P, and C atoms. Refinement of the inter-layer scale factors, positions, and individual, isotropic tem-

perature factors for all of the non-hydrogen atoms gave an unweighted *R* value of 0.122. Additional cycles of refinement with anisotropic temperature factors for the Rh, Cl, and P atoms gave a weighted residual $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o|$ of 0.104. At this point considerable correlation was observed between inter-layer scale factors and anisotropic temperature factors. This problem was eliminated in the final refinement by fixing the U_{22} temperature factors for the P and Cl atoms at their isotropic values.

The δ carbons on three of the butyl chains showed evidence of disorder between two sites and could not be refined. These three carbon atoms were included as six half atoms in fixed atomic positions. The final weighted residual was 0.098. In the final cycle the average parameter shifted by 0.04 of its e.s.d. value [maximum 0.24 for the shift/e.s.d. of the y/b parameter of C(33)]. The weighting scheme employed was $w = (2F_{\min} + F_o + 2F_o^2/F_{\max})^{-1}$, with $F_{\min} = 26.41$ and $F_{\max} = 719.4$. Neutral atom scattering factors (Cromer & Mann, 1968) were used, except for Rh^{3+} , and were corrected for anomalous dispersion (Cromer & Liberman, 1970). The atomic coordinates and thermal parameters are given in Table 1.*

* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30441 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

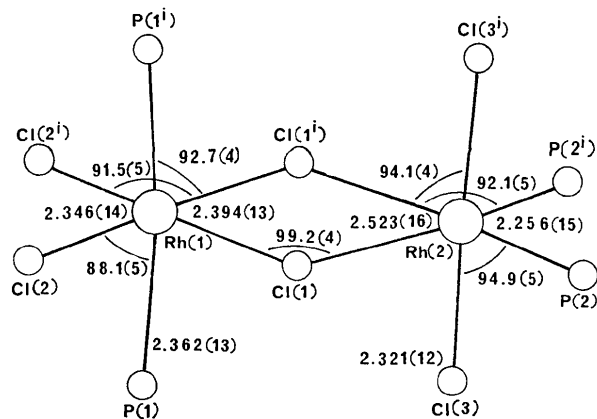


Fig. 1. View of molecular skeleton perpendicular to the twofold axis. For clarity, the butyl groups are not shown.

Table 1. Fractional coordinates and temperature factors

	x	y	z
Rh(1)	0	0.1866 (4)	0.2500
Rh(2)	0	0.3728 (4)	0.2500
Cl(1)	0.0951 (6)	0.2755 (8)	0.2347 (5)
Cl(2)	0.1029 (8)	0.1068 (8)	0.2348 (6)
Cl(3)	-0.0713 (8)	0.3760 (7)	0.1407 (6)
P(1)	-0.0615 (9)	0.1791 (8)	0.1369 (7)
P(2)	0.1039 (8)	0.4467 (9)	0.2386 (6)

Anisotropic temperature factors ($\times 10^3$)						
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh(1)	17 (3)	33 (9)	35 (4)	0	14 (2)	0
Rh(2)	20 (3)	76 (9)	25 (3)	0	4 (2)	0
Cl(1)	59 (7)	54†	82 (9)	-8 (8)	9 (6)	-32 (8)
Cl(2)	70 (9)	69†	96 (11)	-4 (9)	16 (8)	22 (8)
Cl(3)	68 (9)	69†	77 (11)	-15 (8)	1 (8)	-1 (8)
P(1)	80 (10)	61†	63 (11)	-10 (8)	11 (9)	0 (8)
P(2)	52 (8)	58†	78 (10)	-1 (9)	10 (7)	13 (8)

	x	y	z	U_{1so}
C(11)	-0.004 (3)	0.214 (3)	0.084 (2)	0.07 (1)
C(21)	0.086 (3)	0.186 (3)	0.083 (2)	0.08 (1)
C(31)	0.135 (5)	0.219 (4)	0.042 (4)	0.17 (3)
C(41)	0.112 (5)	0.208 (5)	-0.024 (5)	0.21 (4)
C(12)	-0.079 (3)	0.093 (2)	0.108 (2)	0.06 (1)
C(22)	-0.112 (3)	0.085 (2)	0.031 (2)	0.06 (1)
C(32)	-0.125 (3)	0.008 (3)	0.018 (2)	0.08 (2)
C(42)	-0.171 (4)	0.005 (4)	-0.060 (3)	0.15 (3)
C(13)	-0.176 (2)	0.223 (3)	0.111 (2)	0.07 (1)
C(23)	-0.246 (3)	0.189 (3)	0.131 (3)	0.11 (2)
C(33)	-0.339 (4)	0.233 (3)	0.102 (3)	0.14 (2)
C(431)	-0.415	0.189	0.113	0.11‡
C(432)	-0.349	0.240	0.025	0.11‡
C(14)	0.096 (3)	0.485 (3)	0.156 (2)	0.09 (2)
C(24)	0.124 (3)	0.430 (3)	0.113 (2)	0.10 (2)
C(34)	0.104 (4)	0.450 (3)	0.036 (3)	0.13 (2)
C(441)	0.132	0.512	0.024	0.13‡
C(442)	0.125	0.390	-0.006	0.13‡
C(15)	0.212 (3)	0.407 (2)	0.264 (2)	0.06 (1)
C(25)	0.292 (3)	0.456 (2)	0.257 (2)	0.08 (2)
C(35)	0.388 (4)	0.419 (3)	0.260 (3)	0.12 (2)
C(451)	0.415	0.379	0.322	0.14‡
C(452)	0.374	0.378	0.198	0.14‡
C(16)	0.107 (3)	0.521 (3)	0.287 (2)	0.09 (2)
C(26)	0.141 (3)	0.586 (2)	0.269 (2)	0.06 (1)
C(36)	0.150 (4)	0.642 (3)	0.324 (3)	0.10 (2)
C(46)	0.159 (5)	0.713 (5)	0.298 (4)	0.20 (3)

† U_{22} fixed at the isotropic value.

‡ Disorder is represented by two atoms of site occupation factors 0.5 with fixed positions and U .

Discussion. The coordination about the two Rh atoms and the atom numbering scheme are shown in Fig. 1. Each carbon chain n is numbered from $1n$ to $4n$ starting from the P atom, so that C(32) is the third or γ carbon in the second chain. Chains one to three are on P(1) and four to six on P(2). The heavy atoms all lie very close to one or both of the planes ($-0.1708x - 0.9853z + 4.8423 = 0$) and ($0.9722x - 0.2341z + 2.2780 = 0$). The Rh atoms, bridge Cl atoms, Cl(2), Cl(2¹), P(2) and P(2¹) are within 0.058 Å of the first plane and the Rh atoms, Cl(3), Cl(3¹), P(1), and P(1¹) are within

0.093 Å of the second plane. The angle between the planes is 86.3°. The distance Rh(1)-Rh(2) is 3.745(15) Å.

The structure is in accord with the large dipole moment (Chatt *et al.*, 1964) and with the n.m.r. data of Allen & Gabuji (1971).

The differences between the various Rh-P and Rh-Cl bond lengths are all in agreement with a *trans* effect for P larger than that for Cl. The distances from Rh(2) to Cl(1) and Cl(1¹), which are *trans* to P(2) and P(2¹), are greater than any of the distances from Rh to those Cl atoms which are *trans* to Cl. Similarly, P(2), which is *trans* to a Cl, is closer to Rh(2) than is P(1), which is *trans* to a P, to Rh(1). The labilizing effect of P(2) and P(2¹) on the bonds between Rh(2) and the bridge Cl atoms has been observed (Muir & Fernandez, 1974) in kinetic studies in which unsymmetrical cleavage occurs with amines.

The disorder in some of the butyl chains and relatively large e.s.d. values and temperature factors for γ and δ carbon atoms are not unreasonable for a compound with long aliphatic chains. Average bond lengths (Å) with their respective average e.s.d.'s are: P-C(α) 1.84(2); C(α)-C(β) 1.53(3); C(β)-C(γ) 1.60(3); C(γ)-C(δ) 1.52(3). Average bond angles (°) with their average e.s.d.'s are: Rh-P-C(α) 114.3(7); C(α)-P-C(α) 104.2(9); P-C(α)-C(β) 115(1); C(α)-C(β)-C(γ) 112(2); C(β)-C(γ)-C(δ) 110(2). The average for all C-C bonds was 1.54(7) Å and for all C-C-C angles was 110(4)°.

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