

Fig. 3. Molecular arrangement projected down the a axis.

The two benzene rings (D and E) are planar with mean deviations of 0.0053 and 0.0015 Å from the respective least-squares planes. The other two six-membered rings (B and C) and the five-membered ring (A) are nearly planar, the mean deviations from the respective least-squares planes being 0.0149, 0.0173 and 0.0194 Å. A χ^2 test on the least-squares plane through the two N and two O atoms with a mean deviation of 0.039 Å indicates that the Co coordination is slightly distorted from a square planar geometry. The distortion from the coordination expected for square planar dsp^2 hybridization on the Co atom may be attributable to the pure double bond C(1)–C(16). In addition, there are slight bendings of the D and E rings to the same side of the molecular plane about C(9)–C(14) and C(3)–C(8) respectively. Thus the molecule is very slightly twisted and bowed, and the mean deviation is 0.075 Å from the least-squares plane for the whole molecule.

Inspection of the thermal motion ellipsoids drawn with *ORTEP* (Johnson, 1965) suggested that the molecule is librating about a point close to its centroid. The

root-mean-square deviation of the difference between the observed and calculated U_{ij} values is 0.0062 Å² for the rigid-body model of the whole molecule. The molecular arrangement projected down the a axis is shown in Fig. 3. The mean interplanar spacing between the molecules which are related by a centre of symmetry is 3.386 Å, and the distance between the Co atoms of these molecules is 4.7509 (9) Å. Only three intermolecular distances are slightly shorter than the van der Waals contacts: 3.333 (5) Å between C(1) in (x, y, z) and C(8) in $(\bar{x}, \bar{y}, \bar{z})$, 3.332 (4) Å between Co in (x, y, z) and C(2) in $(\bar{x}, \bar{y}, \bar{z})$, and 2.53 (4) Å between H(15) in (x, y, z) and O(1) in $(x, \frac{1}{2} - y, \frac{1}{2} + z)$. The other contacts are normal.

All the calculations were performed on the FACOM 230-60 Computer in the Computer Centre of Kyushu University using the Universal Crystallographic Computation Program System UNICS, Crystallographic Society of Japan, 1967.

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Trichloro- μ -trichloro-tris(tri-*n*-butylphosphine)dirhodium(III)

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Abstract. $\text{Rh}_2(\text{PBu}_3)_3\text{Cl}_6$, $\text{Rh}_2\text{P}_3\text{Cl}_6\text{C}_{36}\text{H}_{81}$, monoclinic, $P2_1/c$, $a = 12.670$ (13), $b = 26.828$ (10), $c = 16.887$ (20) Å, $\beta = 118.98$ (16)°, $Z = 4$, $d_x = 1.306$ (14), $d_m = 1.359$ (3) g cm⁻³, $V = 5021$ Å³. The molecule has a confacial bioctahedral structure with three chlorine bridges, each of which is *trans* to one phosphine and one

terminal chlorine. There are two phosphines on one Rh and one on the other.

Introduction. Binuclear complexes of Rh(III) are known with either two or three halogen bridges (Chatt, Johnson & Shaw, 1964; Allen & Gabuji, 1971;

Brown & Green, 1970; Intille, 1972; Work & Good, 1970; Cotton & Ucko, 1972). For complexes with three halogen bridges, a confacial bioctahedral structure has been assumed and was confirmed by Cotton & Ucko (1972) for Rh_2Cl_3^- . The structure of the title compound was of interest for comparison with the doubly bridged $\text{Rh}_2(\text{PBU}_3)_4\text{Cl}_6$ and to enable interpretation of reactions of both compounds. The compound was prepared by the method of Chatt *et al.* (1964) for the PEt_3 analog and was recrystallized first from ligroin and then from acetone. Red, prismatic crystals were obtained from acetone solution by slow evaporation of the solvent.

A nearly spherical crystal ground to an average radius of 0.12 mm was mounted with **b** parallel to the ω axis of a Pailred semi-automatic diffractometer equipped with a graphite monochromator and Mo $K\alpha$ radiation. A total of 2030 independent non-zero reflections were measured on layers $h0-20l$. The 200 and 004 reflections were measured after each layer of data was collected and were found to remain constant to $\pm 2\%$. No correction was made for absorption since $\mu = 10.27 \text{ cm}^{-1}$ and the transmission factors varied only from 0.87 to 0.90.

Systematic absences were $0k0$ for k odd and $h0l$ for l odd, which indicated space group $P2_1/c$. A three-dimensional Patterson synthesis revealed the locations of the Rh atoms at $-0.085, 0.15, -0.16$ and $0.025, 0.15, 0.05$. Least-squares refinement and difference Fourier syntheses revealed the positions of the Cl, P, and C atoms. Refinement of the interlayer scale factors, positions, and individual, isotropic temperature factors for all of the non-hydrogen atoms gave an unweighted R value of 0.15. Additional cycles of refinement with anisotropic temperature factors for the Rh, Cl, and P atoms, and with H atoms inserted at the calculated positions on the first two C atoms in each butyl chain, gave a weighted $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o|$ of 0.079. A few γ and δ C atoms failed to refine to reasonable distances and temperature factors. In the final cycle either the position or temperature factors of three such atoms were fixed at reasonable values, with the result that R_w converged to 0.088. In the final cycle the average parameter shifted by 0.17 of its e.s.d. value (maximum 0.93 for U_{iso} for C(111), the α C on the most disordered butyl chain). The weighting scheme employed was $w = 1/\sigma_F^2$, with σ_F determined from counting statistics.

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.*

Table 1. Fractional coordinates and temperature factors

	<i>x</i>	<i>y</i>	<i>z</i>
Rh(1)	-0.0826 (3)	0.1517 (1)	-0.1639 (2)
Rh(2)	0.0088 (3)	0.1470 (1)	0.0481 (2)
Cl(1)	-0.1141 (9)	0.0797 (3)	-0.2478 (7)
Cl(2)	-0.1037 (9)	0.1789 (3)	0.1092 (7)
Cl(3)	0.1759 (10)	0.1882 (3)	0.1530 (7)
Cl(4)	-0.0435 (10)	0.2196 (2)	-0.0644 (7)
Cl(5)	0.1045 (9)	0.1174 (3)	-0.0331 (7)
Cl(6)	-0.1627 (9)	0.1108 (3)	-0.0736 (7)
P(1)	0.0557 (10)	0.0802 (3)	0.1395 (6)
P(2)	-0.2601 (10)	0.1880 (3)	-0.2575 (8)
P(3)	0.0196 (10)	0.1815 (3)	-0.2327 (7)

Anisotropic temperature factors ($\times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh(1)	66 (3)	45 (2)	59 (2)	0 (2)	36 (2)	1 (2)
Rh(2)	59 (3)	54 (2)	57 (2)	-5 (2)	35 (2)	-2 (2)
Cl(1)	92 (9)	49 (5)	82 (9)	-3 (5)	52 (8)	-4 (5)
Cl(2)	88 (9)	58 (6)	93 (10)	-9 (5)	60 (8)	0 (5)
Cl(3)	85 (9)	73 (6)	66 (9)	0 (5)	38 (8)	-10 (5)
Cl(4)	70 (7)	60 (5)	52 (7)	7 (5)	40 (6)	3 (5)
Cl(5)	74 (9)	61 (6)	65 (9)	8 (5)	39 (8)	10 (5)
Cl(6)	84 (9)	68 (6)	67 (8)	6 (5)	45 (7)	-5 (5)
P(1)	88 (10)	76 (7)	30 (7)	-4 (5)	33 (8)	-5 (6)
P(2)	56 (9)	67 (7)	66 (9)	8 (5)	38 (8)	7 (5)
P(3)	59 (9)	69 (6)	54 (9)	5 (5)	33 (8)	3 (6)

	<i>x</i>	<i>y</i>	<i>x</i>	U_{iso}
C(111)	0.176 (3)	0.045 (1)	0.145 (2)	0.06 (1)
C(211)	0.310 (3)	0.067 (1)	0.195 (3)	0.12 (1)
C(311)	-0.327 (11)	0.094 (3)	0.279 (5)	0.15
C(411)	0.389 (19)	0.153 (3)	0.297 (10)	0.20
C(121)	-0.057 (3)	0.036 (1)	0.107 (3)	0.08 (1)
C(221)	-0.170 (4)	0.048 (1)	0.108 (3)	0.10 (1)
C(321)	-0.242 (8)	0.000 (3)	0.099 (6)	0.15
C(421)	-0.360	0.014	0.101	0.120
C(131)	0.089 (3)	0.097 (1)	0.250 (2)	0.08 (1)
C(231)	0.114 (4)	0.054 (1)	0.314 (3)	0.09 (1)
C(331)	0.124 (4)	0.065 (1)	0.403 (3)	0.12 (1)
C(431)	0.148 (4)	0.012 (2)	0.462 (4)	0.14 (2)
C(112)	-0.344 (3)	0.157 (1)	-0.366 (2)	0.07 (1)
C(212)	-0.409 (4)	0.109 (1)	-0.370 (3)	0.11 (1)
C(312)	-0.446 (7)	0.069 (2)	-0.447 (6)	0.22 (3)
C(412)	-0.499 (6)	0.101 (2)	-0.513 (5)	0.21 (3)
C(122)	-0.246 (3)	0.254 (1)	-0.282 (2)	0.06 (1)
C(222)	-0.374 (3)	0.277 (1)	-0.348 (2)	0.08 (1)
C(322)	-0.367 (4)	0.332 (1)	-0.352 (3)	0.10 (1)
C(422)	-0.496 (5)	0.354 (2)	-0.412 (3)	0.14 (2)
C(132)	-0.372 (3)	0.189 (1)	-0.218 (3)	0.09 (1)
C(232)	-0.347 (3)	0.222 (1)	-0.139 (2)	0.08 (1)
C(332)	-0.459 (6)	0.228 (2)	-0.130 (4)	0.17 (2)
C(432)	-0.516 (7)	0.269 (3)	-0.149 (5)	0.23 (3)
C(113)	0.147 (3)	0.143 (1)	-0.209 (2)	0.06 (1)
C(213)	0.224 (3)	0.157 (1)	-0.251 (3)	0.08 (1)
C(313)	0.329 (4)	0.124 (2)	-0.238 (3)	0.12 (2)
C(413)	0.271 (6)	0.080 (2)	-0.297 (5)	0.12 (2)
C(123)	-0.056 (3)	0.180 (1)	-0.354 (2)	0.06 (1)
C(223)	-0.079 (3)	0.144 (1)	-0.414 (2)	0.09 (1)
C(323)	-0.139 (4)	0.162 (1)	-0.512 (3)	0.10 (1)
C(423)	-0.166 (5)	0.115 (2)	-0.577 (4)	0.17 (2)
C(133)	0.085 (3)	0.244 (1)	-0.188 (2)	0.06 (1)
C(233)	0.189 (3)	0.244 (1)	-0.095 (2)	0.07 (1)
C(333)	0.209 (5)	0.297 (1)	-0.049 (4)	0.12 (2)
C(433)	0.313 (5)	0.246 (2)	0.041 (4)	0.15 (2)

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31347 (13 pp., 1 microfiche). Copies may be obtained from The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. The coordination about the two Rh atoms and the atom numbering scheme are shown in Fig. 1. Each carbon chain n on P atom m is numbered from $1nm$ to $4nm$ starting from the P atoms, so that C(321)

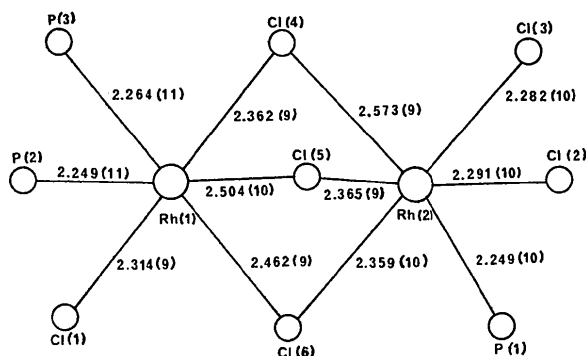


Fig. 1. View of molecular skeleton. For clarity, the butyl groups are not shown.

is the third or γ carbon in the second chain on P(1). The heavy atoms form a distorted confacial bioctahedron. The arrangement of P and terminal Cl is consistent with the labilizing effect of the phosphine groups, since each bridge Cl is *trans* to only one P. The

distribution of phosphines on the two Rh atoms is also consistent with the structure of $\text{Rh}_2(\text{PBu}_3)_4\text{Cl}_6$ (Muir, Muir & Rivera, 1974), which can be obtained from the title compound by the cleavage of one bridge by PBu_3 (Muir & Fernandez, 1975).

Important interatomic distances are shown in Fig. 1 and important angles are given in Table 2. The average values for the different types of Rh-Cl and Rh-P bond lengths are comparable to those from related compounds and are in agreement with a *trans* influence for P greater than for Cl.

The relatively large temperature factors for the γ and δ C atoms are not unexpected for a compound with long aliphatic chains. Average bond lengths (\AA) with their respective average e.s.d.'s are: P-C $^\alpha$, 1.80 (3); C $^\alpha$ -C $^\beta$, 1.52 (4); C $^\beta$ -C $^\gamma$, 1.53 (5); C $^\gamma$ -C $^\delta$, 1.51 (6). Average bond angles ($^\circ$) with their average e.s.d.'s are: Rh-P-C $^\alpha$, 114 (1); C $^\alpha$ -P-C $^\alpha$, 104 (1); P-C $^\alpha$ -C $^\beta$, 117 (2); C $^\alpha$ -C $^\beta$ -C $^\gamma$, 113 (3); C $^\beta$ -C $^\gamma$ -C $^\delta$, 109 (5). The average for all C-C bonds was 1.52 (5) \AA and for all C-C-C angles, 111 (4) $^\circ$. The Rh(1)-Rh(2) distance is 3.187 (4) \AA .

Table 2. *Interatomic angles* ($^\circ$)

	Rh (1)	Rh (2)
Cl(4) -Rh-Cl(5)	82.7 (3)	81.2 (3)
Cl(4) -Rh-Cl(6)	84.9 (3)	82.5 (3)
Cl(5) -Rh-Cl(6)	77.8 (3)	82.6 (3)
Cl(4) -Rh-Cl(1)	173.8 (3)	
Cl(4) -Rh-P(1)		176.1 (4)
Cl(5) -Rh-P(2)	167.3 (4)	
Cl(5) -Rh-Cl(2)		172.7 (4)
Cl(6) -Rh-P(3)	170.2 (4)	
Cl(6) -Rh-Cl(3)		173.0 (3)
Cl(4) -Rh-P(2)	87.7 (4)	
Cl(4) -Rh-P(3)	96.8 (3)	
Cl(4) -Rh-Cl(2)		93.2 (3)
Cl(4) -Rh-Cl(3)		91.0 (3)
Cl(5) -Rh-Cl(1)	92.4 (3)	
Cl(5) -Rh-P(3)	92.9 (4)	
Cl(5) -Rh-Cl(3)		93.9 (4)
Cl(5) -Rh-P(1)		95.2 (3)
Cl(6) -Rh-Cl(1)	90.3 (3)	
Cl(6) -Rh-P(2)	93.2 (4)	
Cl(6) -Rh-Cl(2)		92.0 (2)
Cl(6) -Rh-P(1)		95.4 (3)
P(2) -Rh-Cl(1)	96.6 (4)	
P(3) -Rh-P(2)	96.5 (4)	
P(3) -Rh-Cl(1)	87.3 (3)	
Cl(3) -Rh-Cl(2)		90.9 (4)
P(1) -Rh-Cl(2)		90.2 (4)
P(1) -Rh-Cl(3)		90.9 (4)
Rh(1) -Cl(4) -Rh(2)	80.3 (2)	
Rh(1) -Cl(5) -Rh(2)	81.7 (3)	
Rh(1) -Cl(6) -Rh(2)	82.7 (3)	

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