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The Crystal and Molecular Structure of 1-Phenyl-1,3-butanedionato(1,6-dichloro-1,5-cyclooctadiene)rhodium(I)

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$C_{18}H_{19}O_2Cl_2Rh$, monoclinic, $P2_1/c$, $Z = 8$, FW 441·2, $a = 17{\cdot}390$ (3), $b = 12{\cdot}816$ (2), $c = 16{\cdot}523$ (4) Å, $\beta = 109{\cdot}41$ (1)°, $V = 3473$ (1) Å^3, $D_x = 1{\cdot}69$, $D_m = 1{\cdot}65$ (1) g cm^{-3} (flotation), $\lambda(\mathrm{Cu}\ K\bar{\alpha}) = 1{\cdot}5418$ Å (graphite monochromator), $\mu(\mathrm{Cu}\ K\bar{\alpha}) = 108{\cdot}0$ cm^{-1}, final $R = 0{\cdot}030$ for 3522 observed reflexions $[F_o^2 > 3\sigma(F_o^2)]$ in the range $0 < 2\theta \leq 108°$.

Introduction

In a complex study of the chemical and physical properties of 1,3-substituted rhodium chelates (Bouchal, Škramovská, Čoupek, Pokorný & Hrabák, 1972; Ryska, Bouchal & Hrabák, 1973), the determination of the crystal and molecular structure of the symmetrically substituted 1,3-diphenyl-1,3-propanedionato(1,6-dichloro-1,5-cyclooctadiene)rhodium(I) (Ječný & Huml, 1974) was followed by a study of the structure of the asymmetrically substituted title compound.

The lattice parameters were determined by the least-squares method using 15 reflexions from the angle

Table 1. *Final fractional coordinates of non-*H *atoms and their e.s.d.'s* (× 10^4)

	x	*y*	*z*		*x*	*y*	*z*
Rh(1)	1308·7 (2)	3806·2 (3)	5087·8 (2)	Rh(2)	4482·9 (2)	1047·6 (3)	3436·1 (2)
Cl(11)	−358 (1)	3557 (1)	5474 (1)	Cl(21)	6149 (1)	2342 (1)	4186 (1)
Cl(12)	2378 (1)	5901 (1)	5830 (1)	Cl(22)	4537 (1)	−1311 (1)	4142 (1)
O(11)	411 (2)	3194 (2)	4051 (2)	O(21)	4277 (2)	2548 (2)	3739 (2)
O(12)	1746 (2)	4574 (2)	4259 (1)	O(22)	3463 (2)	596 (2)	3710 (2)
C(101)	1800 (3)	5466 (4)	3039 (3)	C(201)	2302 (3)	608 (4)	4122 (3)
C(102)	2371 (4)	6133 (4)	3578 (4)	C(202)	2369 (3)	−466 (4)	4244 (4)
C(103)	2753 (4)	6887 (4)	3247 (4)	C(203)	1737 (4)	−1032 (5)	4378 (4)
C(104)	2580 (4)	6961 (4)	2377 (4)	C(204)	1043 (4)	−531 (5)	4376 (4)
C(105)	2010 (4)	6327 (5)	1839 (4)	C(205)	967 (4)	528 (5)	4232 (4)
C(106)	1619 (4)	5567 (4)	2162 (4)	C(206)	1591 (3)	1092 (4)	4108 (4)
C(107)	724 (3)	4115 (4)	2947 (3)	C(207)	3108 (3)	2237 (4)	4143 (3)
C(108)	1402 (3)	4668 (4)	3448 (3)	C(208)	3007 (3)	1175 (4)	3984 (3)
C(109)	292 (3)	3396 (4)	3268 (3)	C(209)	3726 (3)	2854 (4)	4034 (3)
C(110)	−399 (4)	2788 (5)	2644 (4)	C(210)	3766 (4)	3995 (4)	4258 (4)
C(111)	1090 (3)	2568 (4)	5813 (3)	C(211)	5092 (3)	1663 (4)	2657 (3)
C(112)	1893 (4)	2137 (5)	6425 (4)	C(212)	4894 (4)	1082 (5)	1829 (4)
C(113)	2592 (4)	2869 (5)	6636 (4)	C(213)	4674 (4)	−58 (4)	1900 (4)
C(114)	2459 (3)	3808 (4)	6031 (3)	C(214)	4376 (3)	−269 (4)	2654 (3)
C(115)	2038 (3)	4701 (4)	6126 (3)	C(215)	4908 (3)	−493 (4)	3478 (3)
C(116)	1614 (4)	4912 (5)	6774 (4)	C(216)	5824 (3)	−536 (4)	3785 (4)
C(117)	1018 (4)	4086 (6)	6792 (4)	C(217)	6192 (3)	389 (4)	3509 (4)
C(118)	724 (3)	3462 (4)	5976 (3)	C(218)	5670 (3)	1362 (4)	3429 (3)

Table 2. *Final fractional atomic coordinates of* H *atoms with their e.s.d.'s* ($\times 10^3$) *and bond lengths to the corresponding* C *atoms* (Å)

	x	*y*	*z*	C–H		*x*	*y*	*z*	C–H
H(102)	247 (4)	610 (4)	416 (4)	0·92 (6)	H(202)	284 (4)	−77 (5)	421 (4)	0·93 (7)
H(103)	317 (4)	728 (6)	370 (4)	1·00 (7)	H(203)	188 (4)	−189 (5)	449 (4)	1·13 (7)
H(104)	290 (4)	755 (5)	216 (4)	1·06 (7)	H(204)	61 (3)	−90 (4)	447 (3)	0·94 (5)
H(105)	186 (3)	627 (4)	120 (3)	1·00 (5)	H(205)	44 (4)	87 (5)	420 (4)	1·01 (7)
H(106)	118 (3)	508 (4)	175 (3)	1·04 (5)	H(206)	158 (4)	179 (4)	404 (4)	0·91 (6)
H(107)	54 (2)	424 (3)	230 (3)	1·02 (4)	H(207)	274 (3)	255 (3)	434 (3)	0·91 (5)
H(111)	71 (3)	207 (4)	533 (3)	1·06 (6)	H(211)	500 (3)	238 (4)	256 (3)	0·93 (5)
H(114)	292 (2)	394 (3)	577 (2)	1·05 (4)	H(214)	378 (3)	−50 (4)	252 (3)	1·03 (5)
H(1101)	−34 (5)	217 (7)	270 (5)	0·80 (8)	H(2101)	367 (3)	441 (4)	374 (3)	0·97 (5)
H(1102)	−39 (4)	289 (5)	205 (4)	1·00 (6)	H(2102)	332 (4)	417 (5)	455 (4)	1·06 (7)
H(1103)	−95 (4)	295 (6)	258 (4)	0·95 (8)	H(2103)	433 (4)	417 (6)	459 (5)	0·98 (8)
H(1121)	182 (4)	188 (5)	696 (4)	0·98 (7)	H(2121)	531 (4)	109 (5)	159 (4)	0·94 (7)
H(1122)	209 (5)	170 (7)	613 (5)	0·89 (9)	H(2122)	433 (5)	142 (6)	139 (5)	1·09 (8)
H(1131)	258 (4)	311 (6)	734 (4)	1·20 (7)	H(2131)	518 (3)	−57 (4)	199 (3)	1·07 (6)
H(1132)	311 (4)	241 (6)	668 (4)	1·05 (7)	H(2132)	424 (3)	−33 (4)	144 (3)	0·95 (5)
H(1161)	118 (7)	547 (9)	651 (7)	1·03 (12)	H(2161)	602 (3)	−55 (4)	447 (3)	1·06 (5)
H(1162)	199 (5)	477 (6)	731 (5)	0·92 (8)	H(2162)	601 (3)	−117 (4)	358 (3)	0·97 (6)
H(1171)	136 (6)	371 (7)	726 (6)	0·94 (10)	H(2171)	669 (3)	53 (4)	394 (3)	0·93 (4)
H(1172)	57 (5)	427 (6)	707 (5)	1·05 (8)	H(2172)	623 (3)	13 (4)	283 (4)	1·19 (6)

range $0 < 2\theta \le 26{\cdot}5°$. The intensities of the measured reflexions were corrected for the decrease in intensity of three standard reflexions (10% during the whole measurement), for absorption (spherical sample, ⌀ 0·17 mm), for Lorentz and polarization effects and for coincidence of pulses.

The structure was determined by the heavy-atom method. All 84 atoms (two independent molecules) lie in general positions and their coordinates and temperature factors (anisotropic for non-H, isotropic for H) were refined by a block-diagonal least-squares procedure. The refinement was completed when none of the shifts of the refined parameters of non-H atoms and H atoms exceeded $\frac{1}{4}$ and $\frac{1}{3}$ of their e.s.d.'s, respectively.

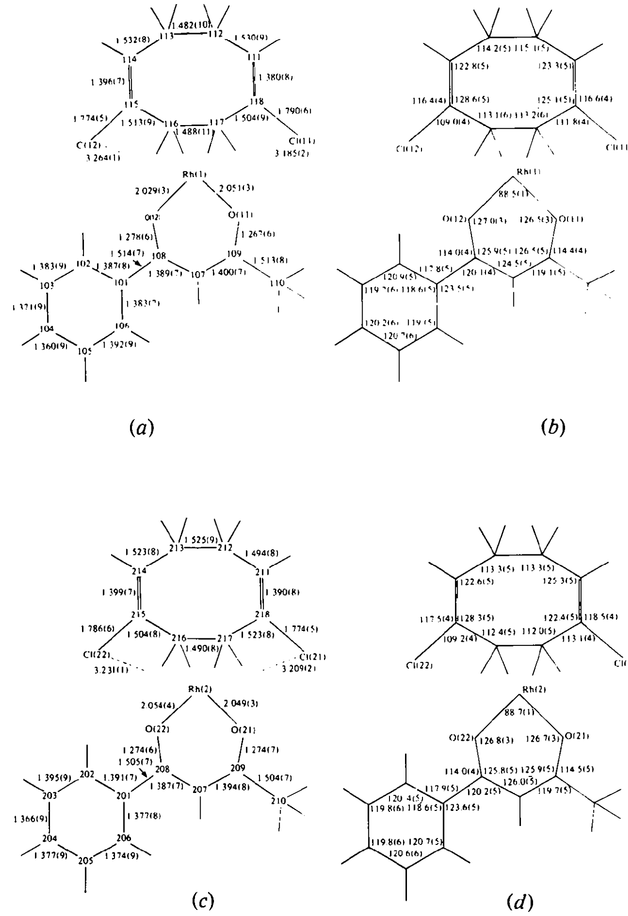

Fig. 2. The bond lengths (Å) and valence angles (°) of (*a*), (*b*) the first and (*c*), (*d*) the second independent molecule. The C atoms are marked by their numbers only or are without labels. H atoms are without labels. For additional values see Tables 2 and 3.

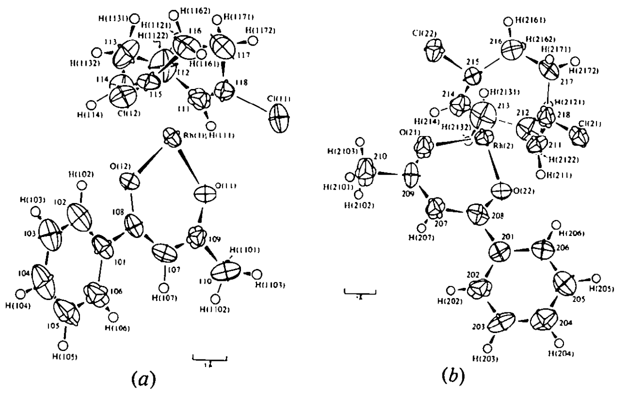

Fig. 1. The molecular structure and atomic numbering scheme for (*a*) the first and (*b*) the second independent molecule. The thermal ellipsoids are at 50% probability. H atoms are represented by artificially small spheres, C atoms are marked by their numbers only. The views are approximately down the *b* axis (first molecule) and the *c* axis (second molecule).

Table 3. *Some intramolecular distances* (Å) *and angles* (°) *with their e.s.d.'s*

(For others see Fig. 2 and Table 4)

Rh(1)···C(111)	2·098 (5)	Rh(2)···C(211)	2·075 (6)
···C(112)	2·999 (7)	···C(212)	2·970 (6)
···C(113)	3·029 (7)	···C(213)	3·019 (6)
···C(114)	2·088 (5)	···C(214)	2·096 (5)
···C(115)	2·102 (5)	···C(215)	2·101 (5)
···C(116)	3·012 (6)	···C(216)	3·000 (6)
···C(117)	3·042 (7)	···C(217)	3·053 (6)
···C(118)	2·092 (5)	···C(218)	2·107 (5)
···M(11)*	1·978 (8)	···M(21)*	1·972 (8)
···M(12)*	1·975 (7)	···M(22)*	1·979 (7)
···Cl(11)	3·185 (2)	···Cl(21)	3·209 (2)
···Cl(12)	3·264 (1)	···Cl(22)	3·231 (1)
O(11)···O(12)	2·847 (5)	O(21)···O(22)	2·868 (5)
···H(1101)	2·539 (80)	···H(2103)	2·493 (74)
···Cl(11)	3·103 (4)	···Cl(21)	3·101 (4)
O(12)···C(102)	2·693 (7)	O(22)···C(202)	2·715 (7)
···H(102)	2·365 (59)	···H(202)	2·352 (64)
···Cl(12)	2·990 (3)	···Cl(22)	3·014 (4)
C(112)···C(116)	3·662 (9)	C(212)···C(216)	3·726 (9)
C(113)···C(117)	3·234 (10)	C(213)···C(217)	3·114 (9)
M(11)···M(12)*	2·755 (11)	M(21)···M(22)*	2·753 (10)
M(11)···Rh(1)···M(12)*	88·4 (3)	M(21)···Rh(2)···M(22)*	88·3 (3)

* M(11), M(12) and M(21), M(22) are the centres of the double bonds in the cyclooctadiene ring of the first and second independent molecule, respectively.

The conventional R factor reached the final value 0·030. The resulting difference map exhibited four maxima of electron density 0·5 e Å^{-3}, distributed almost symmetrically around the two rhodium atoms at distances 1·12–1·24 Å. Final fractional coordinates of the non-H and H atoms are given in Tables 1 and 2 respectively.* The conformations and atomic numbering schemes are shown in Fig. 1.

Table 4. *The shortest intermolecular distances* (Å) *with their e.s.d.'s*

Symmetry code

None	x,	y,	z	(iv)	x,	$y-1$,	z
(i)	$-x$,	$1-y$,	$1-z$	(v)	x,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$
(ii)	$1-x$,	$-y$,	$1-z$	(vi)	$1-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}+z$
(iii)	$1-x$,	$1-y$,	$1-z$				

Cl(11)···Cl(12^{i})	3·526 (2)	Cl(12)···H(104^{v})	2·88 (6)
Cl(12)···Cl(21^{iii})	3·418 (2)	H(1103)···H(1161^{i})	2·63 (14)
Cl(21)···Cl(22^{ii})	3·605 (2)	H(114)···H(2122^{v})	2·37 (9)
Cl(22)···H(103^{iv})	2·88 (8)	H(2101)···H(2131^{vi})	2·66 (8)

Table 5. *Weighted mean planes*

Atoms with asterisks were omitted from the calculation of the plane. The second line contains deviations of atoms from the plane (Å).

Plane									χ^2
1	O(11)	O(12)	M(11)	M(12)	Rh(1)*	Cl(11)*	Cl(12)*	C(110)*	155·7
	0·024 (5)	−0·023 (5)	−0·057 (8)	0·054 (7)	−0·076 (1)	−1·778 (3)	−1·358 (2)	0·170 (10)	
2	O(21)	O(22)	M(21)	M(22)	Rh(2)*	Cl(21)*	Cl(22)*	C(210)*	54·4
	−0·016 (5)	0·015 (5)	0·033 (7)	−0·031 (7)	−0·088 (1)	−1·658 (2)	−1·565 (2)	−0·066 (10)	
3	C(111)	C(114)	C(115)	C(118)					50·6
	0·028 (8)	−0·026 (8)	0·024 (7)	−0·027 (8)					
4	C(211)	C(214)	C(215)	C(218)					100·4
	−0·044 (9)	0·039 (8)	−0·041 (8)	0·040 (8)					
5	C(111)	C(112)	C(117)	C(118)	Rh(1)*	Cl(11)*	H(111)*		12·7
	−0·018 (8)	0·013 (11)	−0·015 (11)	0·017 (8)	1·913 (1)	−0·716 (3)	−0·352 (88)		
6	C(113)	C(114)	C(115)	C(116)	Rh(1)*	Cl(12)*	H(114)*		4·59
	−0·007 (10)	0·011 (8)	−0·010 (8)	0·008 (10)	1·917 (1)	−0·866 (2)	−0·459 (39)		
7	C(211)	C(212)	C(217)	C(218)	Rh(2)*	Cl(21)*	H(211)*		1·16
	0·006 (9)	−0·004 (10)	0·003 (9)	−0·005 (8)	−1·905 (1)	0·734 (3)	0·436 (81)		
8	C(213)	C(214)	C(215)	C(216)	Rh(2)*	Cl(22)*	H(214)*		2·85
	0·004 (9)	−0·007 (7)	0·008 (7)	−0·004 (8)	−1·924 (1)	0·785 (2)	0·294 (74)		
9	O(11)	O(12)	C(107)	C(108)	C(109)	Rh(1)*	C(110)*		110·6
	−0·019 (5)	0·017 (5)	−0·003 (8)	−0·045 (7)	0·052 (8)	−0·146 (1)	0·194 (10)		
10	O(21)	O(22)	C(207)	C(208)	C(209)	Rh(2)*	C(210)*		13·6
	0·007 (5)	−0·005 (5)	0·006 (8)	0·011 (7)	−0·021 (8)	−0·063 (1)	−0·060 (10)		
11	C(101)	C(102)	C(103)	C(104)	C(105)	C(106)	C(108)*		4·30
	−0·004 (8)	0·000 (9)	0·010 (10)	−0·015 (10)	0·008 (10)	0·002 (9)	−0·001 (8)		
12	C(201)	C(202)	C(203)	C(204)	C(205)	C(206)	C(208)*		5·20
	−0·010 (7)	0·011 (9)	−0·001 (9)	−0·009 (9)	0·007 (9)	0·004 (8)	−0·002 (7)		

Some dihedral angles (°) between the planes

First molecule		Second molecule		First molecule		Second molecule	
Planes	Angle	Planes	Angle	Planes	Angle	Planes	Angle
1–3	94·3	2–4	95·3	3–5	59·0	4–7	59·0
1–5	89·4	2–7	86·8	3–6	58·1	4–8	57·8
1–6	93·7	2–8	89·1	1–9	3·2	2–10	1·2
				9–11	11·9	10–12	23·6

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33612 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion

The position of the central Rh atom with respect to the O atoms of the chelate ring and the C atoms of the cyclooctadiene ring [very similar to that described by Tucker, Scutcher & Russell (1975) and by Ječný & Huml (1974) in related complexes] indicates square-planar dsp^2 hybridization of Rh, in which the $5s$, $4p_x$, $4p_y$ and $4d_{x^2-y^2}$ orbitals take part. The bond lengths in the chelate rings indicate strong conjugation close to a pseudoaromatic six-membered system. (Bond lengths and angles are shown in Fig. 2.) Such a configuration, which results in an O–Rh–O angle of practically 90°, is the cause of an increase in the valence angles at the C and O atoms compared with the 'normal' value 120° in the aromatic ring. An interesting consequence of such a configuration is the fact that both oxygen atoms in the chelate ring become situated at a short non-bonding distance (Table 3), which leads to steric stress in the ring. This stress gives rise to torsional deformations of the chelate ring: O(11)···O(12) against C(108)···C(109) 3·0°, O(21)···O(22) against C(208)···C(209) 1·1°. However, this torsional deformation may also be affected by short non-bonding distances O(12)···C(102), O(12)···Cl(12), O(11)···Cl(11), or O(22)···C(202), O(22)···Cl(22), O(21)···Cl(21) (Table 3). Shortest intermolecular distances are given in Table 4.

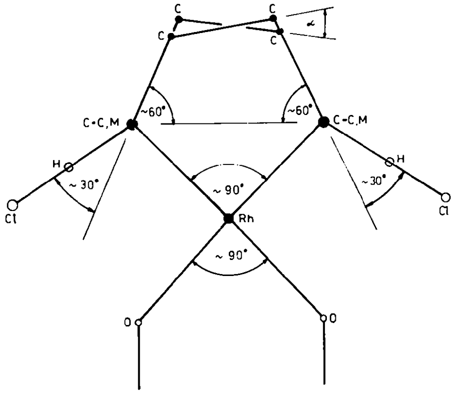

Fig. 3. Schematic representation of the conformation of the cyclooctadiene ring viewed approximately perpendicular to the plane O, Rh, O.

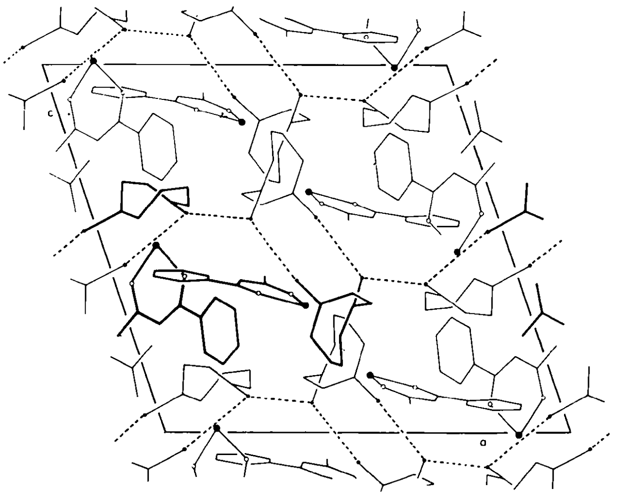

Fig. 4. The structure viewed along b, H atoms omitted. The dashed lines denote the intermolecular Cl···Cl contacts. Large filled circles: Rh, small filled circles: Cl, small open circles: O.

The view that the phenyl ring is partly conjugated with the chelate ring, as indicated for a related symmetrically substituted complex (Ječný & Huml, 1974), though supported in this case by the smaller dihedral angle of the mean planes of both rings, is on the other hand opposed by the unshortened bonds C(101)–C(108) or C(201)–C(208).

The cyclooctadiene ligands have a boat-like conformation [Fig. 1(*a*,*b*)]. While the C atoms participating in the double bonds lie virtually in the plane (Table 5), the second sets of four atoms are distinctly nonplanar. The bonds C(112)–C(113) and C(116)–C(117), or C(212)–C(213) and C(216)–C(217), are crossed with respect to each other making an angle of 14·8° in the first and 21·6° in the second independent molecule (angle α in Fig. 3).

Taking into account the van der Waals radius, 1·8 Å, of Cl atoms, the only intermolecular contacts in the structure are the shortened (3·605 Å) and greatly shortened (3·526 and 3·418 Å) contacts between the Cl atoms of adjacent molecules (Zefirov & Zorkij, 1976). Since no further short intermolecular contacts appear in the structure, one is justified in assuming that the Cl···Cl contacts are predominantly responsible for the 'packing' of the structure (Fig. 4).

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