

Structure of [1,3-Bis(4-methoxyphenyl)-1,3-propanedionato](1,6-dichloro-1,5-cyclooctadiene)rhodium(I), $C_{25}H_{25}Cl_2O_4Rh$

BY J. JEČNÝ AND K. HUML

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Praha 6, Czechoslovakia

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Abstract. $M_r = 563.3$, $P2_1/c$, $a = 10.381(7)$, $b = 9.751(7)$, $c = 25.108(17)$ Å, $\beta = 114.94(5)^\circ$, $V = 2305(3)$ Å³, $Z = 4$, $D_m = 1.61(1)$, $D_x = 1.623(2)$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.9916$ mm⁻¹, $F(000) = 1144$, $T = 298$ K, $R = 0.053$ for 2371 independent reflections. The O–Rh–O angle is $88.7(3)^\circ$ and the angle formed by Rh with the centres of the double bonds of the cyclooctadiene molecule is $83.0(4)^\circ$. The cyclooctadiene ring is in a distorted boat-like conformation.

Introduction. The catalytic activity of 1,3-substituted propanedione rhodium(I) chelates is strongly dependent on the character of the substituents of the propanedione ring (Bouchal, Škramovská, Čoupek, Pokorný & Hrabák, 1972). The structure of the title compound has been investigated as part of a systematic study of the correlation between the stereochemistry and catalytic activity of these complexes (Bouchal, Škramovská, Schmidt & Hrabák, 1972; Ječný & Huml, 1974, 1978; Huml & Ječný, 1979).

Experimental. D_m determined by flotation in aqueous CsCl solution. Approximate crystal dimensions $0.25 \times 0.25 \times 0.18$ mm. Syntex $P2_1$ diffractometer, graphite monochromator. Lattice parameters from 15 reflections ($0 \leq 2\theta \leq 26.5^\circ$). No corrections for extinction or absorption applied (max. $\Delta A^* = 0.088$). Max. value of $\sin\theta/\lambda$ reached during the intensity measurement 0.52 Å⁻¹; range of h : -10 to 9 , k : 0 to 10 , l : 0 to 25 . Intensities corrected for the variation of three standard reflections (max. 3%). 2627 independent reflections, 256 unobserved [$I_o < 3\sigma_f$]. Phase problem solved by heavy-atom method. Block-diagonal refinement on F . Difference Fourier map ($\sin\theta/\lambda < 0.4$ Å⁻¹) revealed 19 H in expected positions; other H atoms in calculated positions. Anisotropic refinement led to final $R = 0.053$, $wR = 0.123$, $S = 4.67$. H fixed in calculated positions with $B_{iso} = 6.0$ Å². $w = [\sigma_f^2 + (0.02F)^2]^{-1/2}$, with σ_f^2 based on counting statistics. Max. Δ/σ in final refinement cycle $1/3$. Residual electron density in final difference map within ± 0.35 e Å⁻³ with the exception of four maxima ($1.2, 0.9, 0.45, 0.40$ e Å⁻³) and three minima ($-1.05, -0.45, -0.40$ e Å⁻³) around the Rh atom. Atomic scattering factors from *International*

Tables for X-ray Crystallography (1974). Modified NRC computer programs (Ahmed, Hall, Pippy & Huber, 1966) and PARST83 (Nardelli, 1983) used.

Discussion. The numbering scheme is shown in Fig. 1, and the crystal packing viewed down **b** in Fig. 2. The final positional and thermal parameters are given in Table 1.* Selected interatomic distances and angles are listed in Table 2. The central Rh atom is only slightly displaced from the plane O(1), O(2), M(1), M(2) [$\chi^2 = 10$], where M(1), M(2) are the centres of the double bonds C(60)–C(61) and C(64)–C(65). The angles O(1)–Rh–O(2) and M(1)–Rh–M(2) (Table 2) indicate square-planar dsp^2 hybridization of Rh in which $5s, 4p_x, 4p_y$, and $4d_{x^2-y^2}$ orbitals take part.

The cyclooctadiene ligand has a distorted boat-like conformation. The bonds C(62)–C(63) and C(66)–C(67), and C(60)–C(61) and C(64)–C(65) are crossed with respect to each other, forming angles of $13(1)$ and $-5(1)^\circ$. The bonds C(60)–C(61) and C(64)–C(65) [$1.42(2)$ and $1.36(2)$ Å] are extended compared with the 'normal' C=C double-bond length (1.335 Å).

The weighted mean planes of the phenyl rings C(40–45) and C(50–55) ($\chi^2 = 3.2$ and 3.9) form dihedral angles with the plane of the chelate ring [Rh, O(1), O(2), C(10), C(20), C(30)] of $25.0(3)$ and $154.0(3)^\circ$ and a dihedral angle of $135.6(3)^\circ$ with respect to each other.

The mean value of the phenyl endocyclic angles at the sites of substitution, C(40), C(43), C(50) and C(53), is $117.5(3)^\circ$; at the other phenyl C atoms the mean angle is $121.2(3)^\circ$. The mean values of the C–C bond distances in the C(40–45) and C(50–55) phenyl rings are $1.384(7)$ and $1.387(14)$ Å, respectively.

O(3) and O(4) are displaced from their respective phenyl-ring planes by $0.06(1)$ Å, and the terminal C(70) and C(80) are displaced in the same direction by $0.04(1)$ and $0.29(2)$ Å.

* Lists of structure factors, anisotropic thermal parameters, and calculated H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39911 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses

$$B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B _{eq} (Å ²)
Rh	0.73698 (7)	0.70046 (7)	0.26495 (3)	2.83 (2)
Cl(1)	0.6385 (4)	0.6765 (3)	0.3702 (1)	5.1 (1)
Cl(2)	0.4813 (4)	0.7301 (4)	0.1330 (1)	6.3 (1)
O(1)	0.8542 (6)	0.5606 (6)	0.3275 (3)	3.2 (2)
O(2)	0.7574 (7)	0.5782 (6)	0.2028 (3)	3.3 (2)
O(3)	0.6234 (9)	0.1459 (9)	0.0015 (3)	6.0 (3)
O(4)	1.1222 (8)	0.1189 (8)	0.5237 (3)	5.1 (3)
C(10)	0.806 (1)	0.456 (1)	0.2098 (4)	3.4 (3)
C(20)	0.902 (1)	0.443 (1)	0.3190 (4)	3.1 (3)
C(30)	0.883 (1)	0.390 (1)	0.2651 (4)	2.9 (3)
C(40)	0.971 (1)	0.359 (1)	0.3735 (4)	2.9 (3)
C(41)	1.064 (1)	0.255 (1)	0.3786 (4)	3.1 (3)
C(42)	1.120 (1)	0.175 (1)	0.4293 (4)	3.7 (3)
C(43)	1.080 (1)	0.194 (1)	0.4750 (4)	4.2 (3)
C(44)	0.986 (1)	0.302 (1)	0.4692 (5)	4.4 (4)
C(45)	0.932 (1)	0.380 (1)	0.4198 (4)	3.6 (3)
C(50)	0.773 (1)	0.377 (1)	0.1556 (4)	3.2 (3)
C(51)	0.848 (1)	0.257 (1)	0.1520 (4)	3.6 (3)
C(52)	0.803 (1)	0.182 (1)	0.1034 (4)	3.6 (3)
C(53)	0.682 (1)	0.217 (1)	0.0529 (5)	4.4 (4)
C(54)	0.610 (1)	0.334 (1)	0.0545 (4)	5.0 (4)
C(55)	0.655 (1)	0.416 (1)	0.1052 (4)	3.9 (3)
C(60)	0.657 (1)	0.793 (1)	0.3216 (5)	4.0 (4)
C(61)	0.794 (1)	0.844 (1)	0.3339 (5)	4.0 (4)
C(62)	0.819 (1)	0.985 (1)	0.3129 (6)	5.8 (5)
C(63)	0.754 (2)	1.004 (1)	0.2489 (6)	6.3 (6)
C(64)	0.696 (1)	0.875 (1)	0.2116 (5)	4.6 (4)
C(65)	0.571 (1)	0.814 (1)	0.2011 (5)	3.9 (4)
C(66)	0.468 (1)	0.861 (1)	0.2240 (5)	5.7 (5)
C(67)	0.524 (1)	0.874 (1)	0.2880 (5)	5.4 (4)
C(70)	1.222 (1)	0.012 (1)	0.5321 (6)	5.6 (5)
C(80)	0.677 (1)	0.011 (1)	-0.0014 (6)	6.6 (5)

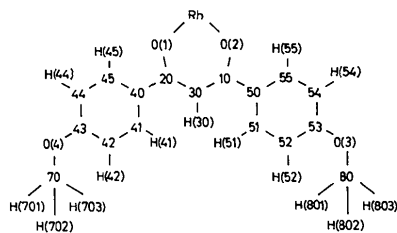
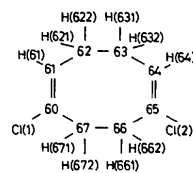


Fig. 1. Atomic numbering scheme.

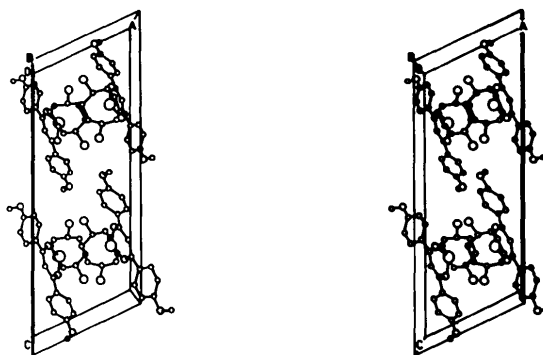


Fig. 2. Stereoview of the crystal packing along *b* (Motherwell & Clegg, 1978).

Table 2. Selected intramolecular distances (Å) and angles (°) with e.s.d.'s in parentheses

Rh—Cl(1)	3.219 (4)	C(10)—C(30)	1.43 (1)
Rh—Cl(2)	3.270 (4)	C(10)—C(50)	1.47 (1)
Rh—O(1)	2.049 (6)	C(20)—C(30)	1.38 (1)
Rh—O(2)	2.045 (7)	C(20)—C(40)	1.49 (1)
Rh—C(60)	2.13 (1)	C(60)—C(61)	1.42 (2)
Rh—C(61)	2.11 (1)	C(60)—C(67)	1.51 (2)
Rh—C(64)	2.10 (1)	C(61)—C(62)	1.53 (2)
Rh—C(65)	2.11 (1)	C(62)—C(63)	1.47 (2)
Cl(1)—C(60)	1.73 (1)	C(63)—C(64)	1.53 (2)
Cl(1)...O(1)	3.08 (1)	C(64)—C(65)	1.36 (2)
Cl(2)—C(65)	1.76 (1)	C(65)—C(66)	1.48 (2)
Cl(2)...O(2)	3.04 (1)	C(66)—C(67)	1.47 (2)
O(1)—C(20)	1.31 (1)		
O(2)—C(10)	1.28 (1)		
O(3)—C(53)	1.36 (1)		
O(3)—C(80)	1.44 (2)		
O(4)—C(43)	1.33 (1)		
O(4)—C(70)	1.42 (2)		
O(1)—Rh—O(2)	88.7 (3)	C(10)—C(30)—C(20)	125 (1)
M(1)—Rh—M(2)*	89.1 (2)	C(67)—C(60)—C(61)	123 (1)
Rh—O(1)—C(20)	127.3 (6)	C(60)—C(61)—C(62)	123 (1)
Rh—O(2)—C(10)	127.0 (6)	C(61)—C(62)—C(63)	115 (1)
C(53)—O(3)—C(80)	119 (1)	C(62)—C(63)—C(64)	116 (1)
C(43)—O(4)—C(70)	119 (1)	C(63)—C(64)—C(65)	125 (1)
O(2)—C(10)—C(30)	125 (1)	C(64)—C(65)—C(66)	125 (1)
C(30)—C(10)—C(50)	119 (1)	C(65)—C(66)—C(67)	116 (1)
O(1)—C(20)—C(30)	125 (1)	C(66)—C(67)—C(60)	114 (1)
C(30)—C(20)—C(40)	121 (1)		

* M(1) and M(2) are the centres of bonds C(60)—C(61) and C(64)—C(65), respectively.

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