the carbonyl O atom (2·87 Å) and the ether O atom (2·78 Å) of the methoxycarbonyl group.

The Pd—O(3) bond length, 2·116 (3) Å, is comparable with the largest values observed in complexes with bridging acetate ligands; in this case it could be related to the short length of the opposite Pd—C bond, 1·984 (4) Å, in agreement with a rather strong *trans* effect of the σ-bonded C atom. Presumably, the same effect is responsible for a partial shift of the electron charge from O(3) to the O(3)—C(3) bond, and from the C(3)=O(4) double bond to O(4), as indicated by the short O—C lengths of 1·285 (4) and 1·232 (4) Å, respectively. The possible interaction of O(4) with the metal orbitals out of the coordination plane cannot be excluded even though it should be very weak, whereas the completely full d_{z^2} axial orbital could exert a strong repulsive effect. No perturbation is observed in the geometry of the methoxycarbonyl ligand [C(1)—O(1), 1·194 (5) and C(1)—O(2), 1·353 (4) Å].

The mean Pd—P and P—C bond lengths, 2·339 (1) and 1·831 (3) Å, and the mean C—C(P-bonded)—C bond angle, 119·27 (7)°, agree with usual values.

The last two values are in good agreement with the molecular geometries of substituted benzene derivatives discussed by Domenicano, Vaciago & Coulson (1975).

The phenyl groups are located, as in other complexes, in such a way that a H atom is directed towards the central metal atom; in this structure, however, all of the observed $\mathrm{Pd}\cdots\mathrm{H}$ distances are greater than 3·0 Å, a value corresponding to the sum of the van der Waals radii.

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(1,6-Dichloro-1,5-cyclooctadiene)(2,4-pentanedionato)rhodium(I)

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Abstract. $[\mathrm{Rh(C_8H_{10}Cl_2)(C_5H_7O_2)}]$, $\mathrm{C_{13}H_{17}Cl_2O_2Rh}$, monoclinic, $P2_1/c$, a = 14·96 (2), b = 11·83 (2), c = 18·22 (2) Å, β = 116·1 (2)°, V = 2896 Å^3, Z = 8, M_r = 379·1, m.p. 406–407 K, D_m = 1·70, D_x = 1·77 Mg m^{-3}, μ(Mo $K\alpha$) = 1·532 mm^{-1}. The structure has been solved by the heavy-atom method and refined to R = 0·087 for 3808 observed reflexions. The structure contains two independent molecules.

Introduction. As part of a systematic study of the correlation between the stereochemistry and catalytic activity of 1,3-substituted Rh chelates (Ječný & Huml, 1974, 1978), the structure of the title compound has been investigated.

A yellow crystal (0·5 × 0·37 × 0·17 mm) was prepared in the laboratory of Dr Hrabák at this Institute. A series of Weissenberg photographs revealed Laue symmetry $2/m$, an initial unit cell and the systematic absences $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$, the latter giving the space group as $P2_1/c$. Least-squares-refined unit-cell parameters were obtained from reflexions measured on a Hilger & Watts Y230/FA126 four-circle automatic off-line diffractometer. Intensities were collected to $\sin\theta_{\max}/\lambda$ = 0·61 Å^{-1} [λ(Mo $K\alpha$) = 0·71069 Å, Zr filter, variable θ–2θ scan, room temperature, b parallel to φ diffractometer axis]. During the measurement the crystal showed a 10% decrease in intensity of the reference reflexion 040, probably due to

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Table 1. *Fractional coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å^2) *with e.s.d.'s for nonhydrogen atoms*

	Molecule *A*				Molecule *B*			
	x	*y*	*z*	*B*	*x*	*y*	*z*	*B*
Rh	4049 (1)	2564 (1)	4146 (1)	2·47 (2)	8184 (1)	2065 (1)	4570 (1)	2·44 (2)
Cl(1)	2413 (3)	1415 (3)	2486 (3)	4·7 (1)	9398 (3)	3885 (4)	5982 (2)	4·2 (1)
Cl(2)	3456 (4)	2955 (4)	5651 (3)	4·7 (1)	8711 (3)	1984 (3)	3004 (2)	3·7 (1)
O(1)	4637 (7)	1375 (8)	3668 (6)	3·8 (3)	8680 (7)	1444 (8)	5732 (5)	3·2 (2)
O(2)	5164 (6)	2243 (8)	5282 (5)	3·9 (3)	8298 (7)	485 (7)	4159 (5)	2·9 (2)
C(1)	5410 (9)	786 (10)	4062 (9)	2·2 (3)	8988 (8)	471 (11)	5952 (8)	3·3 (3)
C(2)	6024 (10)	821 (11)	4906 (7)	2·2 (3)	9037 (10)	−416 (11)	5462 (9)	3·1 (3)
C(3)	5840 (10)	1501 (11)	5439 (8)	3·2 (3)	8689 (9)	−368 (11)	4627 (8)	3·0 (3)
C(4)	5677 (13)	−31 (14)	3555 (12)	4·0 (4)	9400 (13)	260 (15)	6893 (10)	4·0 (4)
C(5)	6609 (13)	1481 (15)	6370 (10)	3·9 (4)	8751 (13)	−1439 (12)	4175 (10)	5·4 (7)
C(6)	1840 (10)	3179 (15)	3184 (13)	4·6 (5)	8519 (11)	4587 (11)	4372 (9)	2·4 (3)
C(7)	2087 (13)	3167 (17)	4086 (13)	4·7 (5)	8694 (14)	3972 (13)	3737 (11)	4·0 (4)
C(8)	3159 (11)	3349 (10)	4618 (9)	3·7 (5)	8183 (10)	2830 (11)	3522 (8)	2·8 (3)
C(9)	3785 (11)	4153 (11)	4525 (9)	3·3 (3)	7213 (9)	2573 (11)	3370 (6)	1·9 (3)
C(10)	3408 (13)	5056 (12)	3849 (11)	4·2 (4)	6460 (11)	3451 (14)	3365 (10)	4·6 (5)
C(11)	3531 (12)	4630 (11)	3107 (10)	3·3 (4)	6516 (10)	3671 (11)	4203 (8)	3·2 (4)
C(12)	3458 (11)	3341 (12)	2988 (8)	4·1 (4)	7499 (9)	3354 (11)	4906 (8)	2·2 (3)
C(13)	2715 (10)	2696 (10)	3065 (9)	4·5 (5)	8409 (11)	3756 (12)	4977 (8)	4·4 (5)

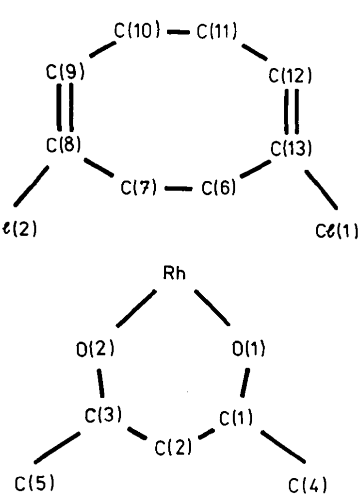

Fig. 1. The numbering scheme of the molecules.

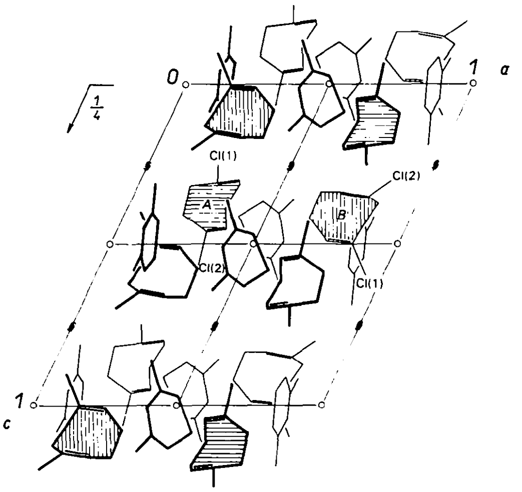

Fig. 2. Projection of the structure along the *b* axis. The top of the cyclooctadiene ring is hatched.

chemical decomposition. 5102 independent measurements gave 3808 reflexions* classified as observed (net count higher than 30 pulses, or net count higher than 5% of the background). Lorentz and polarization corrections were applied but not those for absorption and extinction. The coordinates of the Rh and Cl atoms were obtained from a three-dimensional Patterson synthesis. Repeated Fourier syntheses based on the Rh atoms and a subsequent difference synthesis revealed all the non-H atoms. During the least-squares refinement (Ahmed, Hall, Pippy & Huber, 1966), H atoms were fixed in calculated positions (with $B = 4{\cdot}0$ Å^2), as they showed unrealistic shifts. The function minimized was $\sum w\Delta^2$, where $\Delta = ||F_o| - |F_c||$. The weighting scheme, chosen to ensure reasonable constancy of $w\Delta^2$ with respect to $|F_o|$ and sin θ, was $w = w_1 w_2$, where $w_1 = 1$ for $|F_o| \leq 80$, and $(80/F_o)^2$ otherwise; $w_2 = 1$ for $\sin^2\theta > 0{\cdot}04$, and $\sin^4\theta/0{\cdot}0016$ otherwise. The scattering factors and the correction for the anomalous scattering of Rh were taken from *International Tables for X-ray Crystallography* (1962). The final atomic coordinates are given in Table 1.

Discussion. The numbering scheme is shown in Fig. 1. Some interatomic distances and angles are listed in Table 2. Equations of weighted mean planes and corre-

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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 34590 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Some intramolecular distances* (Å) *and angles* (°) *with their e.s.d.'s*

	Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*
Rh–Cl(1)	3·24 (1)	3·23 (1)	C(11)–C(12)	1·54 (2)	1·51 (2)
Rh–Cl(2)	3·26 (1)	3·28 (1)	C(12)–C(13)	1·40 (2)	1·39 (2)
Rh–O(1)	2·05 (1)	2·05 (1)	*M*–*M**	2·75	2·77
Rh–O(2)	2·04 (1)	2·05 (1)			
Rh–C(6)	3·07 (2)	3·07 (1)	O(1)–Rh–O(2)	89·5 (4)	90·0 (4)
Rh–C(7)	2·97 (2)	3·00 (2)	Rh–O(1)–C(1)	126 (1)	126 (1)
Rh–C(8)	2·09 (2)	2·11 (1)	O(1)–C(1)–C(2)	127 (1)	127 (1)
Rh–C(9)	2·10 (1)	2·11 (1)	O(1)–C(1)–C(4)	115 (1)	114 (1)
Rh–C(10)	3·07 (1)	3·03 (2)	C(2)–C(1)–C(4)	118 (1)	118 (1)
Rh–C(11)	2·98 (1)	2·97 (1)	C(1)–C(2)–C(3)	124 (1)	125 (1)
Rh–C(12)	2·11 (1)	2·08 (1)	C(2)–C(3)–O(2)	129 (1)	127 (1)
Rh–C(13)	2·10 (2)	2·11 (1)	C(2)–C(3)–C(5)	118 (1)	118 (1)
Cl(1)–C(13)	1·79 (1)	1·78 (1)	O(2)–C(3)–C(5)	112 (1)	114 (1)
Cl(2)–C(8)	1·79 (2)	1·78 (1)	C(3)–O(2)–Rh	125 (1)	124 (1)
O(1)–C(1)	1·27 (2)	1·24 (2)	C(6)–C(7)–C(8)	113 (2)	113 (1)
O(2)–C(3)	1·27 (2)	1·28 (2)	C(7)–C(8)–C(9)	128 (2)	128 (1)
C(1)–C(2)	1·40 (2)	1·40 (2)	C(7)–C(8)–Cl(2)	110 (1)	110 (1)
C(1)–C(4)	1·51 (2)	1·57 (2)	C(9)–C(8)–Cl(2)	116 (1)	116 (1)
C(3)–C(2)	1·38 (2)	1·38 (2)	C(8)–C(9)–C(10)	123 (1)	124 (1)
C(3)–C(5)	1·58 (2)	1·54 (2)	C(9)–C(10)–C(11)	110 (1)	113 (1)
C(6)–C(7)	1·52 (3)	1·48 (2)	C(10)–C(11)–C(12)	115 (1)	114 (1)
C(6)–C(13)	1·53 (2)	1·54 (2)	C(11)–C(12)–C(13)	122 (1)	123 (1)
C(7)–C(8)	1·48 (3)	1·52 (2)	C(12)–C(13)–C(6)	125 (1)	124 (1)
C(8)–C(9)	1·40 (2)	1·39 (2)	C(12)–C(13)–Cl(1)	114 (1)	117 (1)
C(9)–C(10)	1·54 (2)	1·53 (2)	C(6)–C(13)–Cl(1)	113 (1)	112 (1)
C(10)–C(11)	1·53 (2)	1·52 (2)	C(13)–C(6)–C(7)	110 (2)	111 (1)

* *M*, *M* are the centres of the double bonds in the cyclooctadiene ring.

Table 3. *Weighted mean planes*

Equations are given in the form $pX + qY + rZ - s = 0$, where X,Y,Z are coordinates in Å related to the *a*, *b*, and c^* directions. Atoms denoted by asterisks were omitted from the calculations of the planes. Deviations of atoms from the planes are in Å; χ^2 is a test of the planarity.

Plane	*p*	*q*	*r*	*s*
1*A*	−6972	−7040	1351	31242
1*B*	9600	2317	1570	−99719
2*A*	−5962	6780	−4300	−20
2*B*	−2037	8721	−4450	−4586
3*A*	5224	−6181	−5874	−63370
3*B*	1554	1719	−9728	−35760
4*A*	−1278	1009	−9867	−48055
4*B*	3425	−7747	−5316	−48395

Some dihedral angles (°) between the planes

	1 ∧ 2	2 ∧ 3	2 ∧ 4	3 ∧ 4
Molecule *A*	96·9	61·4	55·3	63·2
Molecule *B*	93·6	56·6	59·4	64·1

	Rh	O(1)	O(2)	C(1)	C(2)	C(3)	C(4)*	C(5)*	χ^2
1*A*	0·000 (1)	0·01 (1)	−0·01 (1)	0·00 (1)	−0·02 (1)	−0·03 (1)	0·00 (2)	−0·03 (2)	5·64
1*B*	0·001 (1)	−0·05 (1)	−0·06 (1)	0·01 (1)	0·09 (2)	0·03 (2)	0·06 (2)	0·06 (2)	88·10
	C(6)	C(7)	C(10)	C(11)	Rh*				
2*A*	0·19 (2)	−0·24 (2)	0·15 (2)	−0·13 (2)	−2·486 (1)				327·70
2*B*	0·13 (1)	−0·20 (2)	0·15 (2)	−0·11 (1)	−2·485 (1)				400·28
	C(7)	C(8)	C(9)	C(10)	Cl(2)*				
3*A*	0·01 (2)	−0·01 (1)	0·01 (2)	−0·01 (2)	−0·92 (1)				2·70
3*B*	−0·01 (2)	0·01 (1)	−0·01 (1)	0·01 (2)	0·849 (4)				1·51
	C(6)	C(11)	C(12)	C(13)	Cl(1)*				
4*A*	0·02 (2)	−0·01 (1)	0·03 (1)	−0·02 (1)	0·755 (4)				8·07
4*B*	0·00 (1)	0·00 (1)	−0·01 (1)	0·01 (1)	−0·753 (4)				0·82

sponding dihedral angles are summarized in Table 3. A projection along **b** is shown in Fig. 2. The chelate ring of the first molecule (*A*) is planar, but the Rh atom of the second molecule (*B*) is slightly shifted away from the corresponding ring in the direction of the Cl atoms, similarly to the structure of (1,6-dichloro-1,5-cyclooctadiene)(1,3-diphenyl-1,3-propanedionato)rhodium(I) (Ječný & Huml, 1974).

The angle O(1)—Rh—O(2) = 89·5 (4)° for molecule *A* [90·0 (4)° for molecule *B*] and the Rh angle formed with the centres of the double bonds C(8)=C(9) and C(12)=C(13) is 88·1 (6)° for molecule *A* [88·5 (5)° for molecule *B*] – close to 90° (*cf.* Ibers & Snyder, 1962). This indicates that the prevailing orbitals that participate in the hybridization of the Rh orbitals are $4p_x$, $4p_y$ and $4d$ of suitable symmetry. The angle between the double bond C(8)=C(9) and the normal to the chelate ring is 3°. The corresponding double bond in molecule *B* shows an angle of 2°. The angle between the chelate ring of molecule *A* and the double bond C(12)=C(13) is 12°; similarly in molecule *B* we found 8°. The bonds C(6)—C(7) and C(10)—C(11) are not coplanar but are crossed with respect to each other, forming an angle of 27·4° in molecule *A* and 23·2° in molecule *B*. The half-normal probability plot (De Camp, 1973; Hamilton & Abrahams, 1972) applied to the intramolecular distances of all the nonhydrogen atoms is significantly nonlinear; in particular, this is due to the longer non-valence distances between the chelate ring and the cyclooctadiene ring. This indicates differences between both independent molecules. Thermal-motion analysis (Schomaker & Trueblood, 1968) gives negative eigenvalues for the **L** tensors. This can be interpreted as non-rigid behaviour of the molecules. No intermolecular contacts involving nonhydrogen atoms shorter than 3·4 Å were found.

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Cyclooctynebis(triphenylphosphine)platinum(0)–0·5 Benzene

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Abstract. $C_{44}H_{42}P_2Pt.\frac{1}{2}C_6H_6$, $[Pt(C_8H_{12})(C_{18}H_{15}P)_2].\frac{1}{2}C_6H_6$, $M_r = 866·9$, triclinic, $P\bar{1}$, $a = 11·334$ (5), $b = 15·931$ (6), $c = 12·021$ (6) Å, $\alpha = 97·77$ (5), $\beta = 113·66$ (4), $\gamma = 90·80$ (3)°, $V = 1964$ (2) Å^3, $Z = 2$, $D_c = 1·466$ Mg m^{-3}. Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 7·8$ mm^{-1}. The structure is based on 2579 diffractometric intensities refined to R 0·093. Two P and two acetylenic C atoms define a plane about the zero-valent Pt atom. The conformation of the cyclooctyne ring is such that the C—C—C≡C—C—C unit is planar to within ±0·06 Å; the remaining two ring C atoms are displaced from this plane in the same direction by 0·85 (5) and 1·14 (5) Å.

Introduction. Haase & Krebs (1971) have shown that gaseous cyclooctyne adopts a conformation in which the C—C—C≡C—C—C unit is planar and the remaining two C atoms lie 0·571 Å from this plane in opposite directions. We have examined the title compound by X-ray diffraction to see whether this conformation persists when cyclooctyne is complexed to $[Pt(PPh_3)_2]$. An X-ray study of $[Pt(C_8H_{12})(Ph_3P)_2]$ has been mentioned by Robertson & Whimp (1975) but no details were given.

A sample of the title compound was kindly provided by Professor C. W. Rees (Gilchrist, Graveling & Rees, 1968). A suitable crystal was obtained from benzene solution only after many recrystallizations. It was a white plate 0·2 × 0·2 × 0·1 mm. Preliminary Weissenberg and precession photographs indicated triclinic symmetry. Final cell dimensions and the intensities of all independent reflexions with θ(Cu $K\alpha$) ≤ 57° were measured with Ni-filtered Cu radiation on a Hilger & Watts Y290 diffractometer. Integrated intensities were

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