

the Natural Sciences and Engineering Research Council of Canada for financial support.

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*Acta Cryst.* (1990). C46, 142–143

## *trans*-Carbonyliodobis(triphenylphosphine)rhodium(I)

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(Received 30 May 1989; accepted 14 August 1989)

**Abstract.**  $[RhI(CO)\{P(C_6H_5)_3\}_2]$ ,  $M_r = 782.41$ , monoclinic,  $P2_1/n$ ,  $a = 9.823$  (2),  $b = 15.340$  (2),  $c = 21.980$  (3) Å,  $\beta = 95.51$  (1)°,  $V = 3296.7$  (8) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.50$  (1),  $D_x = 1.58$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71073$  Å,  $\mu = 15.8$  cm<sup>-1</sup>,  $F(000) = 1552$ ,  $T = 298$  K,  $R = 0.060$  for 4278 absorption-corrected observed reflections. The coordination environment about the Rh atom is square planar with a maximum deviation [0.14 (14) Å] from planarity at the carbonyl C atom. Rh—C(1) = 1.81 (1), Rh—I = 2.683 (1), Rh—P(1) = 2.336 (2) and Rh—P(2) = 2.316 (2) Å.

**Experimental.** The oxidative addition of CH<sub>3</sub>I to  $[Rh(acac)(CO)(PPh_3)]$  gives an equilibrium mixture of  $[Rh(acac)I(CH_3)(CO)(PPh_3)]$  and  $[Rh(acac)I(COCH_3)(PPh_3)]$  which on reacting with PPh<sub>3</sub> in methanol yields a mixture of crystals consisting of ruby-red  $[Rh(acac)I_2(PPh_3)_2]$  (Basson, Leipoldt, Potgieter, Roodt & van der Walt, 1986), orange-yellow  $[Rh(acac)(COCH_3)(OCH_3)(PPh_3)_2]$  and light-yellow  $[RhI(CO)(PPh_3)_2]$ . Crystals of the title compound were selected from the mixture and recrystallized from methanol. Density determined by flotation in NaI solution. Crystal size 0.20 × 0.15 × 0.05 mm, Enraf-Nonius CAD-4F diffractometer, graphite monochromator, Mo K $\alpha$  radiation,  $\omega/2\theta$  scan technique, variable scan width where  $\Delta\omega = (0.5 + 0.34 \times \tan\theta)$ °, scan speed maximum 5.49° min<sup>-1</sup> in  $\omega$  and minimum corresponding to 60 s per reflection, unit-cell parameters from least-squares refinement of 25

reflections with  $7 < \theta < 17^\circ$ , measuring range  $3 < \theta < 25^\circ$ , empirical absorption corrections (North, Phillips & Mathews, 1968) with minimum correction factor 0.94 and maximum 0.99, three standard reflections measured every 3600 s of X-ray exposure time varied by  $\pm 0.1\%$ , all possible reflections with  $(\sin\theta)/\lambda < 0.60$  Å<sup>-1</sup> in the index ranges  $0 < h < 11$ ,  $0 < k < 18$ ,  $-26 < l < 25$ . 5997 unique reflections of which 4278 observed reflections with  $I > 2.0\sigma(I)$  were used in all calculations (*XRAY72*, Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The structure was solved by the heavy-atom method and subjected to anisotropic full-matrix least-squares refinement on  $F$  (380 variables). H atoms were not placed. Neutral-atom scattering factors (Cromer & Mann, 1968) and anomalous-dispersion corrections for Rh and I from *International Tables for X-ray Crystallography* (1962). Final  $R = 0.060$  and  $wR = 0.060$  with unit weights taken,  $\Delta\rho_{\max} = 6.5$  and  $\Delta\rho_{\min} = -4.5$  e Å<sup>-3</sup> within 1 Å from iodine,  $(\Delta/\sigma)_{\max} = 0.196$ . Final atomic coordinates are given in Table 1\* and main geometrical parameters in Table 2, according to the numbering scheme given in Fig. 1.

\* Lists of anisotropic thermal parameters, structure factors and least-squares-plane deviations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52207 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^2$ )

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
Rh	8662 (1)	2279 (1)	411 (1)	3.68 (6)
I	6930 (1)	2897 (1)	1180 (1)	5.90 (6)
P(1)	7463 (2)	2991 (2)	-414 (1)	3.8 (1)
P(2)	10037 (2)	1769 (2)	1251 (1)	3.8 (1)
O(1)	10473 (8)	1451 (6)	-413 (4)	8.3 (6)
C(1)	9777 (8)	1795 (7)	-103 (4)	5.2 (6)
C(111)*	5744 (8)	2592 (6)	-668 (4)	4.5 (5)
C(112)	5079 (10)	2879 (8)	-1224 (4)	6.2 (7)
C(113)	3732 (11)	2608 (7)	-1386 (5)	7.5 (8)
C(114)	3082 (10)	2035 (9)	-1027 (5)	6.8 (7)
C(115)	3759 (10)	1735 (7)	-480 (5)	5.8 (6)
C(116)	5093 (10)	2020 (6)	-298 (4)	5.0 (6)
C(121)	8320 (9)	2956 (7)	-1125 (4)	4.5 (5)
C(122)	8299 (10)	2174 (8)	-1449 (4)	5.9 (6)
C(123)	9077 (13)	2106 (9)	-1955 (5)	7.6 (8)
C(124)	9812 (12)	2807 (10)	-2136 (5)	7.7 (8)
C(125)	9829 (13)	3572 (9)	-1806 (6)	8.1 (9)
C(126)	9049 (12)	3677 (7)	-1306 (5)	6.4 (7)
C(131)	7261 (10)	4148 (6)	-275 (4)	4.7 (5)
C(132)	8214 (13)	4554 (8)	132 (6)	7.9 (8)
C(133)	8116 (17)	5468 (9)	256 (8)	10.5 (12)
C(134)	7101 (19)	5946 (9)	-36 (8)	10.1 (12)
C(135)	6119 (17)	5541 (10)	-437 (7)	9.5 (11)
C(136)	6186 (13)	4635 (8)	-563 (5)	7.2 (8)
C(211)	9308 (9)	1001 (6)	1771 (4)	4.3 (5)
C(212)	10078 (11)	735 (7)	2310 (4)	5.3 (6)
C(213)	9531 (13)	114 (8)	2679 (5)	6.7 (7)
C(214)	8221 (14)	-218 (8)	2525 (5)	7.8 (8)
C(215)	7470 (13)	41 (9)	1988 (7)	8.7 (9)
C(216)	8030 (11)	652 (8)	1598 (5)	6.6 (7)
C(221)	11600 (8)	1180 (6)	1117 (3)	4.1 (5)
C(222)	11472 (10)	429 (6)	771 (5)	5.4 (6)
C(223)	12632 (12)	-61 (7)	669 (5)	6.6 (7)
C(224)	13944 (12)	216 (8)	899 (6)	6.7 (7)
C(225)	14077 (12)	965 (9)	1254 (6)	7.7 (8)
C(226)	12889 (10)	1463 (9)	1359 (5)	6.0 (6)
C(231)	10613 (9)	2717 (6)	1696 (4)	4.5 (5)
C(232)	11391 (11)	3332 (7)	1413 (4)	5.8 (6)
C(233)	11786 (14)	4107 (8)	1727 (7)	8.0 (9)
C(234)	11368 (19)	4271 (8)	2302 (7)	7.5 (8)
C(235)	10588 (12)	3665 (7)	2576 (5)	6.5 (7)
C(236)	10211 (9)	2887 (6)	2275 (4)	5.0 (6)

\*C(abc) labelling: *a* refers to P-atom number and *b* to phenyl-ring numbers (Fig. 1) bonded to it.

Table 2. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

Rh—I	2.683 (1)	P(1)—C(121)	1.847 (9)
Rh—P(1)	2.336 (2)	P(1)—C(131)	1.814 (9)
Rh—P(2)	2.316 (2)	P(2)—C(211)	1.835 (9)
Rh—C(1)	1.81 (1)	P(2)—C(221)	1.829 (9)
O(1)—C(1)	1.14 (1)	P(2)—C(231)	1.813 (9)
P(1)—C(111)	1.832 (9)		
P(1)—Rh—P(2)	171.28 (9)	Rh—P(1)—C(111)	117.5 (3)
C(1)—Rh—I	176.3 (3)	Rh—P(2)—C(211)	118.7 (3)
Rh—C(1)—O(1)	176.6 (10)	Rh—P(2)—C(221)	118.3 (3)
P(1)—Rh—C(1)	89.9 (3)	Rh—P(2)—C(231)	106.7 (3)
P(2)—Rh—C(1)	91.0 (3)	P(1)—C(121)—C(122)	118.2 (7)
P(1)—Rh—I	91.19 (6)	P(1)—C(131)—C(132)	118.2 (8)
P(2)—Rh—I	88.54 (6)	P(1)—C(111)—C(112)	120.0 (7)
Rh—P(1)—C(121)	114.0 (3)	P(2)—C(211)—C(212)	120.1 (7)
Rh—P(1)—C(131)	112.5 (3)	P(2)—C(221)—C(222)	117.9 (7)
		P(2)—C(231)—C(232)	117.2 (7)

**Related literature.** The present structure determination was undertaken to characterize the substitution behaviour with triphenylphosphine of the reaction products of the above-mentioned Rh<sup>III</sup>-alkyl and -acetyl complexes: this structure determination accentuates the presence of a reductive elimination step along the mechanistic route presently being studied in our laboratory.

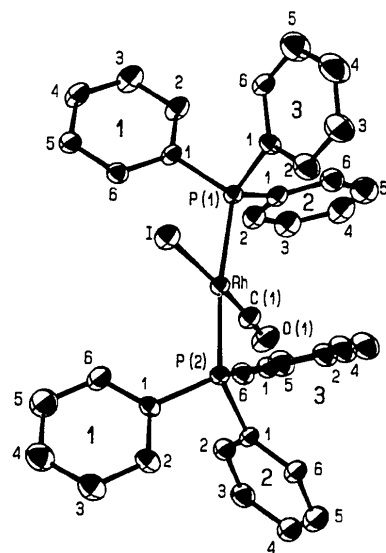


Fig. 1. Perspective view and atom labelling of the molecule.

The Rh—P distances are longer than those of [Rh(LL')(CO)(PPh<sub>3</sub>)] complexes (Botha, Basson & Leipoldt, 1987) but comparable to those of *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (Rheingold & Geib, 1987). Relevant Rh—I bond distances are to be found in the fumaronitrile complex [RhI{*trans*-H(NC)C=C(CN)-H}{P(OPh)<sub>3</sub>}(*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>NC)<sub>2</sub>] (Gaughan & Ibers, 1975) and those tabulated for Rh<sup>III</sup> complexes (Collman, Christian, Current, Denisevich, Halbert, Schmittou & Hodgson, 1976).

The authors gratefully thank the Foundation for Research and Development and the Central Research Fund of the University of the Orange Free State for financial support.

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## (1Z,3E,5E,7Z)-1,2,3,4,5,6,7,8-Octaphenyl-octa-1,3,5,7-tetraene and 3,4-Diphenylisocoumarin

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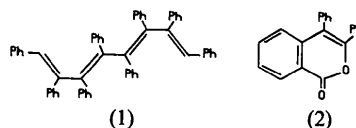
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(Received 22 May 1989; accepted 13 July 1989)

**Abstract.** (1) 1,2,3,4,5,6,7,8-Octaphenyl-Z,E,E,Z-octa-1,3,5,7-tetraene,  $C_{56}H_{42}$ ,  $M_r = 714.90$ , monoclinic,  $C2/c$ ,  $a = 23.649$  (7),  $b = 10.613$  (3),  $c = 17.015$  (5) Å,  $\beta = 99.17$  (2)°,  $V = 4216$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.126$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.61$  cm<sup>-1</sup>,  $F(000) = 1512$ ,  $T = 296$  K,  $R_F = 6.37\%$  for 1372 reflections and 205 parameters. The molecule contains crystallographic  $C_2$  symmetry. The central C—C bond is unusually long, 1.644 (8) Å, reflecting the steric crowding of the phenyl rings attached to the 1 and 2' positions; the H(15)—H(21a) contact is particularly short, 2.19 Å. The absence of conjugation is further demonstrated by these distances in the octa-1,3,5,7-tetraene framework: C(1)—C(2) 1.348 (7), C(2)—C(3) 1.487 (6) and C(3)—C(4) 1.346 (7) Å. (2) 3,4-Diphenylisocoumarin,  $C_{21}H_{14}O_2$ ,  $M_r = 298.37$ , monoclinic,  $P2_1/n$ ,  $a = 10.950$  (4),  $b = 7.913$  (3),  $c = 17.850$  (10) Å,  $\beta = 93.12$  (4)°,  $V = 1544$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.284$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.76$  cm<sup>-1</sup>,  $F(000) = 624$ ,  $T = 296$  K,  $R_F = 5.71\%$  for 1873 reflections and 240 parameters. The fused six-membered rings are, as expected, nearly coplanar; the dihedral angle is 5.3°. The C—C double bond in the lactone ring is 1.350 (3) Å.

**Experimental.** (1) Pale yellow crystals from acetone (0.16 × 0.26 × 0.37 mm); Nicolet R3m diffractometer with graphite monochromator,  $\omega$  scans; lattice parameters from least-squares fit of 25 reflections ( $18 \leq 2\theta \leq 22^\circ$ );  $2\theta_{\max} = 42^\circ$ , no observed data beyond  $42^\circ$ , ( $h = \pm 24$ ,  $k = +11$ ,  $l = +18$ ), standard reflections  $\bar{6}04$ ,  $131$ ,  $80\bar{4}$  ( $\leq 2\%$ ). 2508 reflections collected, 2252 independent ( $R_{\text{int}} = 2.5\%$ ), 1372 observed with  $F_o \geq 3\sigma(F_o)$ , 880 unobserved reflections, no absorption correction. Direct-methods structure solution (SOLV); least-squares refinement on 205 parameters; all non-H atoms anisotropic, H atoms idealized and updated (C—H = 0.96 Å,  $U = 1.2U$  of attached C), all phenyl rings constrained to rigid, planar hexagons (C—C = 1.395 Å).  $R_F = 6.37\%$ ,  $wR_F = 7.00\%$ ,  $S = 1.52$ ,  $w^{-1} = \sigma^2(F_o) + gF_o^2$ ,  $g = 0.001$ ;  $(\Delta/\sigma)_{\max} = 0.074$ ;  $\Delta\rho_{\max} = 0.20$ ,  $\Delta\rho_{\min} =$

$-0.20$  e Å<sup>-3</sup>; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); SHELXTL (5.1) computer program (Sheldrick, 1984). Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1. Bond lengths and angles are given in Table 3. Phenyl-ring framework torsion angles are given in Table 5. Fig. 1 shows the molecular labeling scheme. A unit-cell packing diagram is shown in Fig. 3.



(2) Orange crystals from diethyl ether (0.40 × 0.30 × 0.37 mm); Wyckoff scans; lattice parameters from least-squares fit of 25 reflections ( $20 \leq 2\theta \leq 25^\circ$ );  $2\theta_{\max} = 50^\circ$ ,  $h = \pm 14$ ,  $k = +10$ ,  $l = +22$ , standard reflections  $\bar{5}13$ ,  $241$ ,  $317$  ( $\leq 1\%$ ). 3036 reflections collected, 2716 independent ( $R_{\text{int}} = 1.90\%$ ), 1873 observed with  $F_o \geq 3\sigma(F_o)$ , 843 unobserved reflections, no absorption correction. Direct-methods structure solution (SOLV), least-squares refinement on 240 parameters; all non-H atoms anisotropic, H atoms located and refined isotropically, phenyl rings constrained to rigid, planar hexagons.  $R_F = 5.71\%$ ,  $wR_F = 6.05\%$ ,  $S = 1.29$ ,  $w^{-1} = \sigma^2(F_o) + gF_o^2$ ,  $g = 0.001$ ;  $(\Delta/\sigma)_{\max} = 0.044$ ;  $\Delta\rho_{\max} = 0.228$ ,  $\Delta\rho_{\min} = -0.162$  e Å<sup>-3</sup>; atomic scattering factors and software as above.

Atomic coordinates and equivalent isotropic thermal parameters are given in Table 2. Bond lengths and angles are given in Table 4.† Interplanar angles are given in Table 6. Fig. 2 shows the molecular structure and numbering scheme. A unit-cell packing diagram is shown in Fig. 4.

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52126 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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