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Structure of (η-1,5-Cyclooctadiene)[1–3-η-(*exo*-4-methyl-1,2,3,4-tetraphenylcyclobutenyl)]rhodium(I)

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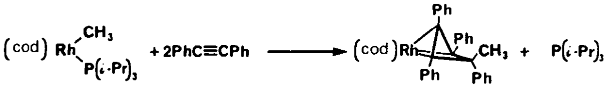
Abstract. $[Rh(C_8H_{12})(C_{29}H_{23})]$, $M_r = 582\cdot60$, tetragonal, $P4_2/n$, $a = 23\cdot807\,(2)$, $c = 9\cdot8849\,(9)$ Å, $V = 5602\cdot4\,(13)$ Å^3, $Z = 8$, $D_m = 1\cdot37$, $D_x = 1\cdot381$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0\cdot71073$ Å, $\mu = 6\cdot218$ cm^{-1}, $F(000) = 1208$, $T = 293$ K, $R = 0\cdot0254$ for 2612 observed reflections with $F_o^2 \geq 3\sigma(F_o^2)$. The structure consists of an Rh$^{\text{I}}$ atom coordinated by the four vinylic C atoms of the 1,5-cyclooctadiene ligand and by the three allylic C atoms of the cyclobutenyl ring. The methyl group of the 4-methyl-1,2,3,4-tetraphenylcyclobutenyl ligand is in the *exo* position.

Introduction. In the course of studying the insertion of acetylenes into rhodium–methyl bonds, the title compound (1) was obtained according to the equation:



(cod = 1,5-cyclooctadiene)

(1)

The crystal-structure determination was undertaken as part of a study to determine the mechanism by which (1) is formed.

Experimental. Orange crystals provided by Dr S. M. Fine (Fine, 1986); D_m measured by flotation method in aqueous KI solution; sample crystal was $0\cdot15 \times 0\cdot15 \times 0\cdot30$ mm. Crystal was mounted on glass fiber in air using polyacrylate cement. Precession photographs, tetragonal; Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Lattice parameters from setting angles of 24 reflections, $24 \leq 2\theta \leq 26°$; data collected 4144, $2\theta \leq 45°$, $0 \leq h \leq 25$, $0 \leq k \leq 25$, $0 \leq l \leq 10$; scan speed $\leq 6\cdot7°$ min^{-1}, θ–2θ scan, variation in three intensity standards $< 1\cdot3\%$; Lorentz and polarization correction applied (Frenz, 1985); negligible absorption, ψ-scan variation $\pm 1\cdot3\%$, 3663 unique reflections, 2612 with $F_o^2 \geq 3\sigma(F_o^2)$. Structure solved by Patterson methods and ΔF syntheses; full-matrix least-squares refinement for 364 parameters with anisotropic temperature factors for all non-H atoms, all H atoms were located in a ΔF map, H atoms were assigned idealized coordinates (C–H $0\cdot95$ Å) and isotropic thermal parameters $B(\text{H}) = 1\cdot3 \times B_{\text{eq}}(\text{C})$. Function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [\sigma_o^2(F_o^2) + (pF_o^2)^2]$, $p = 0\cdot03$; $R = 2\cdot54\%$, $wR = 3\cdot29\%$, GOF $= 1\cdot419$, max. shift/e.s.d. $< 0\cdot00$; highest peak in final ΔF map $0\cdot246$ e Å^{-3}; atomic scattering factors, f' and f'' terms for all non-H atoms were taken from *International Tables for X-ray Crystallography* (1974). All computations were carried out on a Microvax II computer using the *SDP* system of programs (Frenz, 1985).

Discussion. The structure of the title compound is shown in Fig. 1 (*ORTEP*). Positional parameters of the non-H atoms and the equivalent values of the anisotropic temperature factors are given in Table 1,[*] selected bond lengths, angles and torsion angles in Table 2.

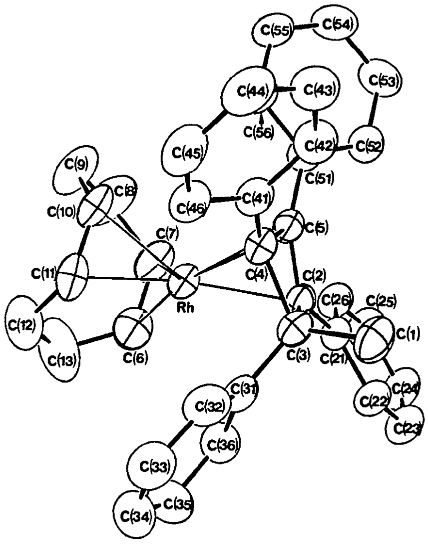


Fig. 1. *ORTEP* (Johnson, 1965) drawing and numbering scheme for (1). The ellipsoids are scaled to represent 50% of the probability surface. H atoms are omitted for clarity.

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[*] Tables of H-atom coordinates, anisotropic temperature factors, distances and angles in the phenyl rings, least-squares planes and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44235 (29 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. *Final fractional atomic coordinates and equivalent isotropic thermal parameters for* (1) *with e.s.d.'s in parentheses*

	x	y	z	B_{eq}(Å^2)*
Rh	0·03183 (1)	0·20660 (1)	−0·01726 (3)	2·928 (6)
C(1)	−0·0698 (2)	0·2181 (2)	0·3121 (4)	4·37 (9)
C(2)	−0·0295 (1)	0·2600 (1)	0·0872 (3)	2·93 (7)
C(3)	−0·0243 (2)	0·2148 (1)	0·2003 (3)	3·17 (8)
C(4)	−0·0408 (1)	0·1738 (1)	0·0831 (3)	2·97 (7)
C(5)	−0·0583 (1)	0·2206 (1)	0·0022 (3)	2·95 (7)
C(6)	0·1008 (2)	0·2576 (2)	−0·0934 (4)	4·60 (9)
C(7)	0·0587 (2)	0·2558 (2)	−0·1883 (4)	4·23 (9)
C(8)	0·0604 (3)	0·2210 (2)	−0·3154 (5)	7·4 (1)
C(9)	0·0550 (2)	0·1590 (2)	−0·2985 (4)	5·8 (1)
C(10)	0·0481 (2)	0·1381 (2)	−0·1551 (4)	4·15 (9)
C(11)	0·0904 (2)	0·1403 (2)	−0·0605 (4)	4·40 (9)
C(12)	0·1492 (2)	0·1630 (2)	−0·0886 (5)	6·7 (1)
C(13)	0·1541 (2)	0·2239 (2)	−0·1014 (7)	8·4 (2)
C(21)	−0·0296 (1)	0·3218 (1)	0·0959 (3)	2·91 (7)
C(22)	−0·0234 (2)	0·3487 (1)	0·2201 (4)	3·53 (8)
C(23)	−0·0245 (2)	0·4070 (2)	0·2281 (4)	4·46 (9)
C(24)	−0·0321 (2)	0·4389 (2)	0·1143 (4)	4·8 (1)
C(25)	−0·0384 (2)	0·4129 (2)	−0·0094 (4)	4·57 (9)
C(26)	−0·0372 (2)	0·3548 (2)	−0·0180 (4)	3·68 (8)
C(31)	0·0337 (2)	0·2038 (1)	0·2591 (3)	3·26 (8)
C(32)	0·0459 (2)	0·1522 (2)	0·3180 (4)	4·19 (9)
C(33)	0·0987 (2)	0·1401 (2)	0·3673 (4)	5·0 (1)
C(34)	0·1398 (2)	0·1804 (2)	0·3641 (4)	5·3 (1)
C(35)	0·1286 (2)	0·2324 (2)	0·3094 (4)	5·2 (1)
C(36)	0·0756 (2)	0·2439 (2)	0·2561 (4)	3·99 (9)
C(41)	−0·0659 (1)	0·1170 (1)	0·0917 (3)	3·07 (8)
C(42)	−0·1243 (2)	0·1113 (2)	0·0876 (4)	3·93 (9)
C(43)	−0·1493 (2)	0·0589 (2)	0·0988 (4)	4·41 (9)
C(44)	−0·1169 (2)	0·0113 (2)	0·1139 (4)	4·43 (9)
C(45)	−0·0592 (2)	0·0166 (2)	0·1181 (4)	4·24 (9)
C(46)	−0·0338 (2)	0·0688 (1)	0·1069 (3)	3·54 (8)
C(51)	−0·0975 (1)	0·2237 (1)	−0·1134 (3)	3·00 (8)
C(52)	−0·1379 (2)	0·2654 (2)	−0·1207 (4)	4·15 (9)
C(53)	−0·1760 (2)	0·2661 (2)	−0·2266 (5)	5·1 (1)
C(54)	−0·1739 (2)	0·2258 (2)	−0·3263 (4)	5·2 (1)
C(55)	−0·1340 (2)	0·1840 (2)	−0·3192 (4)	5·0 (1)
C(56)	−0·0967 (2)	0·1827 (2)	−0·2127 (4)	4·24 (9)

* $B_{eq} = \frac{4}{3}[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table 2. *Selected bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *for* (1)

Rh—C(2)	2·194 (3)	C(2)—C(21)	1·474 (4)
Rh—C(4)	2·141 (3)	C(5)—C(4)	1·433 (4)
Rh—C(5)	2·179 (3)	C(5)—C(51)	1·478 (4)
Rh—C(6)	2·176 (3)	C(4)—C(41)	1·481 (4)
Rh—C(7)	2·154 (3)		
Rh—C(10)	2·160 (3)	C(6)—C(7)	1·374 (5)
Rh—C(11)	2·149 (3)	C(7)—C(8)	1·506 (5)
		C(8)—C(9)	1·491 (5)
C(1)—C(3)	1·549 (4)	C(9)—C(10)	1·511 (5)
C(3)—C(2)	1·556 (4)	C(10)—C(11)	1·375 (5)
C(3)—C(4)	1·565 (4)	C(11)—C(12)	1·524 (5)
C(3)—C(31)	1·522 (4)	C(12)—C(13)	1·460 (6)
C(2)—C(5)	1·435 (4)	C(13)—C(6)	1·505 (5)
C(2)—Rh—C(4)	57·02 (11)	C(3)—C(2)—C(5)	90·4 (2)
C(2)—Rh—C(5)	38·30 (10)	C(3)—C(2)—C(21)	130·4 (3)
C(2)—Rh—C(6)	109·98 (13)	C(5)—C(2)—C(21)	133·3 (3)
C(2)—Rh—C(7)	104·58 (13)	C(1)—C(3)—C(2)	115·0 (3)
C(2)—Rh—C(10)	148·64 (13)	C(1)—C(3)—C(4)	112·6 (3)
C(2)—Rh—C(11)	161·97 (13)	C(1)—C(3)—C(31)	111·8 (3)
C(4)—Rh—C(5)	38·73 (11)	C(2)—C(3)—C(4)	83·1 (2)
C(4)—Rh—C(6)	166·66 (13)	C(2)—C(3)—C(31)	117·7 (3)
C(4)—Rh—C(7)	143·31 (14)	C(4)—C(3)—C(31)	113·7 (2)
C(4)—Rh—C(10)	99·35 (13)	C(3)—C(4)—C(5)	90·1 (2)
C(4)—Rh—C(11)	110·41 (13)	C(3)—C(4)—C(41)	129·0 (3)
C(5)—Rh—C(6)	133·48 (13)	C(5)—C(4)—C(41)	128·6 (3)
C(5)—Rh—C(7)	106·16 (14)	C(4)—C(5)—C(2)	92·4 (2)
C(5)—Rh—C(10)	110·35 (13)	C(4)—C(5)—C(51)	130·9 (3)
C(5)—Rh—C(11)	140·22 (13)	C(2)—C(5)—C(51)	136·3 (3)
C(6)—Rh—C(7)	36·99 (14)	C(6)—C(7)—C(8)	124·5 (4)
C(6)—Rh—C(10)	93·85 (14)	C(7)—C(8)—C(9)	116·7 (3)
C(6)—Rh—C(11)	81·43 (14)	C(8)—C(9)—C(10)	116·1 (3)
C(7)—Rh—C(10)	82·08 (13)	C(9)—C(10)—C(11)	123·1 (4)
C(7)—Rh—C(11)	92·91 (15)	C(10)—C(11)—C(12)	124·1 (4)
C(10)—Rh—C(11)	37·22 (13)	C(11)—C(12)—C(13)	116·2 (3)
		C(12)—C(13)—C(6)	117·1 (4)
		C(13)—C(6)—C(7)	124·3 (4)
C(1)—C(3)—C(2)—C(5)	−97·2 (3)	C(2)—C(3)—C(4)—C(5)	−14·5 (2)
C(1)—C(3)—C(4)—C(5)	99·7 (3)	C(3)—C(2)—C(5)—C(4)	−15·8 (3)

The geometry of (1) is based upon four-coordinated Rh^I, with the Rh atom at the center of a rectangle defined by the midpoints of the cyclooctadiene olefin bonds, C(6,7) and C(10,11), and the allylic carbon atoms C(2) and C(4). The average Rh to cyclooctadiene carbon bond length of 2·160 (12) Å is in the range found in (cod)$_2$Rh$_2$(μ-Cl)$_2$ (Ibers & Snyder, 1962) of 2·12 (3) Å, (cod)Rh(η^3-cyclooctadienyl) (Pickardt & Stühler, 1980) of 2·23 (13) Å, and (cod)Rh(η^3-benzyl) (Stühler & Pickardt, 1981) of 2·15 (3) Å. The rhodium to η^3-cyclobutenyl carbon bond lengths are rather asymmetric; the Rh—C(4) distance is 2·141 (3) Å, the Rh—C(2) distance is 2·194 (3) Å, and the Rh—C(5) distance is 2·179 (3) Å, which average to 2·17 (3) Å. These distances are in the range found in related rhodium allyls, (cod)Rh(η^3-cyclooctadienyl) of 2·17 (7) Å (Pickardt & Stühler, 1980), (cod)Rh(η^3-benzyl) of 2·21 (8) Å (Stühler & Pickardt, 1981), and of 2·25 (8) Å (Ebbinghaus, Madigan, Osterberg & Nathan, 1988) in {[(CH$_3$)$_3$C]$_2$PCH$_2$CH$_2$P[C(CH$_3$)$_3$]$_2$}-Rh(η^3-benzyl).

The bond parameters in the cyclobutenyl portion of (1) are similar to those found in two other cyclobutenyl–metal complexes, CpNi[η^3-C$_4$(CH$_3$)$_4$(Cp)] (Oberhansli & Dahl, 1965) and CpRu(Cl)$_2$(C$_4$H$_4$-OCH$_3$) (Albers, Liles, Robinson, Shaver & Singleton, 1986). In particular, the angles at the allylic C atoms are near 90° and the angle at the alicyclic C atom is near 80° in all three structures. The allylic carbon—carbon bond lengths, C(2)—C(5) and C(4)—C(5), in (1) are *ca* 0·1 Å shorter than the C(2)—C(3) and C(3)—C(4) bonds. This is expected since the former are based upon *sp*^{2}-hybridized C atoms and the latter are based upon *sp*^{3}-hybridized C atoms. The fold angle, defined by the intersection of the planes defined by C(2,4,5) and C(2,3,4) is 21·2 (5)°. The equivalent dihedral angle in CpNi[C$_4$(CH$_3$)$_4$(Cp)] is 25°.

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Structure of (α–2-η-Benzyl)(*P*,*P*,*P*′,*P*′-tetra-*tert*-butylethylenebisphosphine)rhodium(I)

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Abstract. $[Rh(C_7H_7)(C_{18}H_{40}P_2)]$, $M_r = 512\cdot50$, triclinic, $P\bar{1}$, $a = 9\cdot5973\,(8)$, $b = 10\cdot4471\,(15)$, $c = 14\cdot3667\,(15)$ Å, $\alpha = 88\cdot46\,(1)$, $\beta = 83\cdot92\,(1)$, $\gamma = 67\cdot95\,(1)^\circ$, $V = 1327\cdot5\,(3)$ Å^3, $Z = 2$, $D_m = 1\cdot29$, $D_x = 1\cdot283$ g cm^{-3}, Mo $K\alpha$ ($\lambda = 0\cdot7107$ Å), $\mu = 7\cdot59$ cm^{-1}, $F(000) = 544$, $T = 295$ K, $R = 0\cdot022$, $wR = 0\cdot033$ for 3152 independent reflections with $F_o > 3\sigma(F_o)$. The Rh atom is in a distorted square-planar environment in which two coordination sites are occupied by an allylic bond to the benzyl ligand. The benzyl ligand is unsymmetrically bound: the Rh—C(6) and Rh—C(7) distances are 2·371 (2) and 2·162 (2) Å, respectively. The non-allylic portion of the ligand exhibits the expected bond-length alternation.

Introduction. The title compound, $[(\eta^3\text{-}C_6H_5CH_2)\text{-}Rh\{(\{(CH_3)_3C\}_2P)_2C_2H_4\}]$, is the product of the reaction of $[(\mu\text{-}Cl)Rh\{(\{(CH_3)_3C\}_2P)_2C_2H_4\}]_2$ and benzyllithium. The fluxional nature of the product in solution is confirmed by the equivalence of the two *ortho* and *meta* C atoms in the ^{13}C NMR spectrum (Del Paggio, 1986; Del Paggio, Andersen & Muetterties, 1987). In this crystal structure determination, the title compound is shown to be an approximately square-planar complex. The diene-like bond-length alternation between those C atoms not involved in allylic bonding is consistent with a simple resonance model of ligand bonding and is typical of η^3-benzyl complexes (Cotton & LaPrade, 1968; Behrens & Weiss, 1975; Becker & Stille, 1978; Sonada, Bailey & Maitlis, 1979).

Experimental. The complex $[(\eta^3\text{-}C_6H_5CH_2)Rh\text{-}\{(\{(CH_3)_3C\}_2P)_2C_2H_4\}]$, prepared as described previously (Del Paggio, 1986; Del Paggio, Andersen & Muetterties, 1987), was crystallized from pentane. The density was measured by flotation in $CH_3CN/H_2O/KI$. An orange parallelepiped crystal measuring $0\cdot45 \times 0\cdot25 \times 0\cdot15$ mm was mounted in a 0·3 mm quartz capillary under argon. Data were collected on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Accurate cell dimensions and orientation matrix were obtained by centering 24 reflections (12 Friedel pairs) with $27 \le 2\theta \le 30^\circ$. 3791 reflections were collected, of which 3463 were independent and 3152 were observed based on $I > 3\sigma(I)$. The θ–2θ scan mode was used ($3 \le 2\theta \le 45^\circ$) and the index ranges were $0 \le h \le 10$, $-11 \le k \le 11$, and $-15 \le l \le 15$. Intensity checks every 2 h on three standard reflections indicated no significant decay. ψ scans on four reflections yielded an average maximum variation in intensity of 3·2%; thus, no absorption correction was applied.

The data were reduced and the structure solved using the *Enraf–Nonius Structure Determination Package* (Frenz, 1985). The structure was refined in space group $P\bar{1}$; initial positions of the Rh and two P atoms were determined from a three-dimensional Patterson map. H atoms (not refined) were included at idealized positions with a C—H distance of 0·95 Å and with isotropic thermal parameters set at 1·3 times those of the corresponding C atom. Full-matrix least-squares refinement of positional and anisotropic thermal parameters of non-H atoms converged at $R = 0\cdot022$, $wR = 0\cdot033$ and $S = 1\cdot813$. A secondary-extinction parameter was not included in final refinements. The function mini-

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