(Acetylacetonato-κ²O,O′)carbonyl-(cyclohexyldiphenylphosphine-κP)-rhodium(I)

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The title compound, $[Rh(C_5H_7O_2)(C_{18}H_{21}P)(CO)]$, has the acetylacetonate-chelated Rh^I atom in a square-planar geometry. Intramolecular C—H···O hydrogen bonds exist between the acetylacetonate group and the cyclohexyl ring, resulting in a buckling of the acetylacetonate skeleton. Molecules are packed in positions of least steric hindrance, with the phosphine ligands positioned above and below the Rh–acetylacetonate backbone.

Related literature

For background literature on the catalytic activity of rhodium–phosphine adducts, see Carraz *et al.* (2000); Moloy & Wegman (1989). Corresponding $[Rh(acac)(CO)(PR_1R_2R_3)]$ complexes, such as $[Rh(acac)(CO)(PPh_3)]$ (Leipoldt *et al.*, 1978), $[Rh(acac)(CO)(PCy_2Ph)]$ (Brink *et al.*, 2007) and $[Rh(acac)(CO)(PCy_3)]$ (Trzeciak *et al.*, 2004) have similar square-planar geometries. For related structures, see Marthinus Janse van Rensburg *et al.* (2006). For comparison of electronic parameters, see Otto & Roodt (2004). For a related palladium compound, see Meij *et al.* (2003). For the related Vaska-type compunds, see Otto *et al.* (2000); Roodt *et al.* (2003). For the synthesis of the starting dirhodium compound, see McCleverty & Wilkinson (1990).
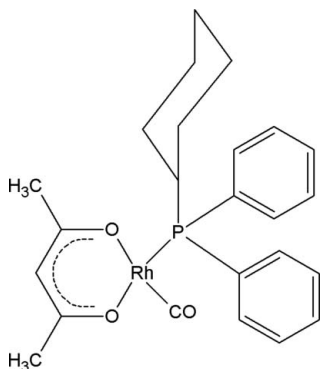
Experimental

Crystal data

$[Rh(C_5H_7O_2)(C_{18}H_{21}P)(CO)]$	$V = 2229.10\,(19)$ Å³
$M_r = 498.34$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 9.4682\,(5)$ Å	$\mu = 0.86$ mm⁻¹
$b = 12.7534\,(6)$ Å	$T = 100\,(2)$ K
$c = 18.4602\,(9)$ Å	$0.42 \times 0.27 \times 0.06$ mm

Data collection

Bruker X8 APEXII diffractometer	12624 measured reflections
Absorption correction: multi-scan	4825 independent reflections
($SADABS$; Bruker, 2004)	4672 reflections with $I > 2\sigma(I)$
$T_{min} = 0.714$, $T_{max} = 0.950$	$R_{int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	H-atom parameters constrained
$wR(F^2) = 0.061$	$\Delta\rho_{max} = 0.56$ e Å⁻³
$S = 1.06$	$\Delta\rho_{min} = -0.62$ e Å⁻³
4825 reflections	Absolute structure: Flack (1983),
258 parameters	2064 Friedel pairs
3 restraints	Flack parameter: −0.02 (2)

Table 1
Selected geometric parameters (Å, °).

C1—Rh1	1.802 (3)	O2—Rh1	2.0764 (18)
P1—Rh1	2.2328 (6)	O3—Rh1	2.044 (2)
C1—Rh1—O3	177.31 (10)	O3—Rh1—O2	88.69 (8)
C1—Rh1—O2	93.72 (10)	C1—Rh1—P1	88.50 (9)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11···O3	1.00	2.39	2.962 (3)	116
C16—H16B···O3	0.99	2.44	3.094 (3)	123

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2345).

metal-organic compounds

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supplementary materials

(Acetylacetonato-*κ^{2}O,O'*)carbonyl(cyclohexyldiphenylphosphine-*κP*)rhodium(I)

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Comment

This work is part of an ongoing investigation aimed at determing the steric and electronic effects induced by various phosphine ligands on a rhodium(I) metal centre. Previous work illustrating the catalytic importance of the rhodium(I) square-planar moieties has been conducted on rhodium mono- and di-phosphine complexes containing the symmetrical bidentate ligand, acac (acac = acetylacetonate) (Moloy *et al.*, 1989). Symmetrical di-phosphine ligands result in the producton of acetaldehyde, whereas unsymmetrical di-phosphine ligands are more stable and efficient catalysts for the carbonylation of methanol to acetic acid (Carraz *et al.*, 2000). The title compound, [Rh(acac)(CO)(PCyPh$_2$)] (Cy = cyclohexyl, Ph = phenyl), (Fig. 1), forms part of our study on complexes of the type [Rh(β-diketone)(CO)(P$R_1R_2R_3$)] (R_1, R_2 and R_3 = cyclohexyl or phenyl).

Slight distortion of the square-planar coordination sphere is observed as illustrated by a 5.04 (4)° deviation from the square plane. The Rh(I) atom deviates by 0.0596 (2) Å from the plane defined by the four coordinate atoms O2, O3, P1 and C1. The acetylacetonate ligand exhibits a bite angle of 88.72 (7)° and the C1—Rh—P1 bond angle is 88.51 (8)°. The carbonyl ligand is nearly linear (Rh1—C1—O1 = 179.2 (3)°). Intramolecular C—H⋯O interaction (Table 2) results in twisting of the the acetylacetonate backbone as indicated by the C2—O2—O3—C4 torsion angle (3.1 (2)°).

The steric demand of the cyclohexyldiphenyl phosphine ligand is quantified by the effective cone angle (θ$_E$), calculated using the actual Rh—P bond distance (Otto *et al.*, 2000). The θ$_E$ value of 151° agrees with the value determined by Meij *et al.* (2003) for the *trans*-[PdCl$_2$(PCyPh$_2$)$_2$] complex (151 and 155°). The value of the effective cone angle of the title compound fits the sequence of 163° for [Rh(acac)(CO)(PCy$_2$Ph)] (Brink *et al.*, 2007) and of 145 and 170° for the corresponding Vaska-type rhodium complexes *trans*- [Rh(CO)(Cl)(PPh$_3$)$_2$] and *trans*-[Rh(CO)(Cl)(PCy$_3$)$_2$] (Roodt *et al.*, 2003). In Table 3, the title compound is compared with other closely related Rh(I) phosphine complexes from literature containing the acetylacetonate bidentate ligand.

Experimental

[RhCl(CO)$_2$]$_2$ was prepared according to McCleverty and Wilkinson (1990). [Rh(acac)(CO)$_2$] was synthesized by mixing a solution of acetylacetonate (85.0 mg, 0.849 mmol) in dimethylformamide (DMF) and [RhCl(CO)$_2$]$_2$ (121.5 mg, 0.313 mmol) in DMF. Upon addition of ice-water, the complex precipitated and was filtered off. Ligand substitution on the complex [Rh(acac)(CO)$_2$] was performed by dissolving (80.0 mg, 0.310 mmol) in acetone followed by slow addition of PCyPh$_2$ (95.5 mg, 0.356 mmol). Crystals of (I) were obtained by slow evaporation of the reaction mixture. Spectroscopic analysis: ^{31}P{H} NMR (CDCl$_3$, 121.495 MHz, p.p.m.): 53.3 [d, ^{1}J(Rh—P) = 171.3 Hz]; IR υ(CO): 1971.2 cm^{-1}; (CH$_2$Cl$_2$) υ(CO): 1959.3 cm^{-1}.

Refinement

The methyl, methine and aromatic H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.95–0.98Å and U_{iso}(H) = 1.5Ueq(C) and 1.2Ueq(C), respectively. The methyl protons were located in a difference Fourier map and the group was refined as a rigid rotor. Residual electron density due to disorder resulted in large thermal vibrations on the periphery. Phenyl carbons, C31 to C36, were restrained as planar atoms. The anisotropic displacement parameters for C13 were restrained.
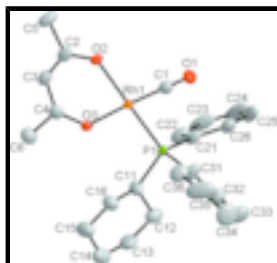
Figures

Fig. 1. View of (I), with atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity. For the C atoms in rings; the first digit indicates ring number and the second digit indicates the position of the atom in the ring.
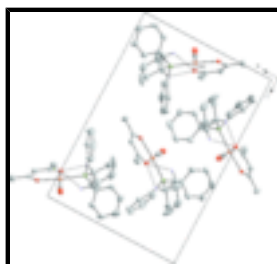

Fig. 2. Unit cell view, showing the intermolecular H-bonding. The interaction is indicated with dashed lines. [Symmetry operators: (Rh1) *x*, *y*, *z*]

(Acetylacetonato-κ^2*O*,*O*')carbonyl(cyclohexyldiphenylphosphine- κ*P*)rhodium(I)

Crystal data

[Rh(C$_5$H$_7$O$_2$)(C$_{18}$H$_{21}$P)(CO)]	F_{000} = 1024
M_r = 498.34	D_x = 1.485 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 7313 reflections
a = 9.4682 (5) Å	θ = 2.4–28.3º
b = 12.7534 (6) Å	μ = 0.86 mm^{-1}
c = 18.4602 (9) Å	T = 100 (2) K
V = 2229.10 (19) Å^3	Plate, yellow
Z = 4	0.42 × 0.27 × 0.06 mm

Data collection

Bruker X8 APEXII 4K KappaCCD diffractometer	4825 independent reflections

Radiation source: sealed tube	4672 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.023$
Detector resolution: 512 pixels mm^{-1}	$\theta_{max} = 27°$
ω and φ scans	$\theta_{min} = 2.2°$
Absorption correction: multi-scan SADABS (Bruker, 2004)	$h = -11 \rightarrow 12$
$T_{min} = 0.714$, $T_{max} = 0.950$	$k = -16 \rightarrow 16$
12624 measured reflections	$l = -23 \rightarrow 12$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0301P)^2 + 1.123P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.024$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.061$	$\Delta\rho_{max} = 0.56$ e Å^{-3}
$S = 1.06$	$\Delta\rho_{min} = -0.62$ e Å^{-3}
4825 reflections	Extinction correction: none
258 parameters	Absolute structure: Flack (1983), 2064 Friedel pairs
3 restraints	Flack parameter: −0.02 (2)

Special details

Experimental. The intensity data was collected on a Bruker X8 Apex II 4 K Kappa CCD diffractometer using an exposure time of 10 s/frame. A total of 566 frames were collected with a frame width of 0.5° covering up to $\theta = 27.00°$ with 99.0% completeness accomplized.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.2396 (3)	0.5478 (2)	0.07028 (15)	0.0204 (6)
O1	0.3520 (2)	0.56474 (19)	0.04995 (13)	0.0321 (5)
P1	0.07950 (8)	0.66367 (5)	0.17222 (3)	0.01498 (14)
O2	0.0442 (2)	0.38392 (14)	0.04299 (9)	0.0194 (4)
O3	−0.1404 (2)	0.50184 (14)	0.13645 (10)	0.0200 (4)
C2	−0.0620 (4)	0.32317 (19)	0.04253 (13)	0.0192 (5)
C4	−0.2233 (3)	0.4269 (2)	0.11987 (14)	0.0184 (6)
C3	−0.1889 (3)	0.3388 (2)	0.07867 (14)	0.0212 (6)
H3	−0.258	0.2851	0.075	0.025*
C5	−0.0467 (4)	0.2258 (2)	−0.00365 (16)	0.0288 (7)
H5A	−0.0188	0.2459	−0.0529	0.043*
H5B	−0.1371	0.1884	−0.0053	0.043*
H5C	0.0257	0.1801	0.0173	0.043*

C6	−0.3723 (3)	0.4384 (3)	0.14649 (17)	0.0264 (7)
H6A	−0.3726	0.4778	0.1921	0.04*
H6B	−0.4133	0.3688	0.1545	0.04*
H6C	−0.4283	0.476	0.1102	0.04*
C31	0.1614 (4)	0.7821 (2)	0.13684 (15)	0.0265 (7)
C21	0.1791 (3)	0.6308 (2)	0.25351 (14)	0.0189 (6)
C11	−0.0933 (3)	0.7092 (3)	0.20456 (16)	0.0270 (7)
H11	−0.1385	0.6428	0.2215	0.032*
C16	−0.1869 (3)	0.7417 (2)	0.14486 (15)	0.0236 (6)
H16A	−0.146	0.8046	0.1214	0.028*
H16B	−0.1894	0.685	0.1082	0.028*
C12	−0.1011 (4)	0.7767 (3)	0.26998 (19)	0.0344 (6)
H12A	−0.0491	0.7422	0.3099	0.041*
H12B	−0.0538	0.8442	0.2596	0.041*
C14	−0.3460 (4)	0.8275 (3)	0.2347 (2)	0.0372 (8)
H14A	−0.444	0.8203	0.2528	0.045*
H14B	−0.3308	0.9024	0.2229	0.045*
C15	−0.3322 (4)	0.7656 (3)	0.1672 (2)	0.0430 (9)
H15A	−0.3837	0.6987	0.1736	0.052*
H15B	−0.379	0.8046	0.1275	0.052*
C13	−0.2474 (4)	0.7977 (3)	0.29391 (19)	0.0344 (6)
H13A	−0.2456	0.8549	0.3302	0.041*
H13B	−0.2845	0.7342	0.3182	0.041*
C22	0.1109 (4)	0.5767 (2)	0.30957 (15)	0.0260 (7)
H22	0.0128	0.5618	0.3061	0.031*
C23	0.1872 (5)	0.5446 (2)	0.37068 (16)	0.0373 (9)
H23	0.1403	0.509	0.4089	0.045*
C26	0.3233 (4)	0.6486 (2)	0.25875 (17)	0.0261 (7)
H26	0.3717	0.6823	0.2201	0.031*
C24	0.3293 (5)	0.5644 (3)	0.37565 (19)	0.0471 (11)
H24	0.3807	0.5419	0.417	0.056*
C25	0.3979 (4)	0.6174 (2)	0.3202 (2)	0.0393 (9)
H25	0.4959	0.6324	0.3241	0.047*
C32	0.1993 (3)	0.8649 (2)	0.18374 (15)	0.0223 (6)
H32	0.1853	0.858	0.2345	0.027*
C34	0.2447 (4)	0.9782 (3)	0.08060 (18)	0.0388 (8)
H34	0.261	1.0468	0.0623	0.047*
C36	0.1472 (4)	0.8045 (3)	0.06191 (16)	0.0278 (7)
H36	0.0974	0.7577	0.031	0.033*
C33	0.2576 (4)	0.9577 (2)	0.15549 (18)	0.0350 (8)
H33	0.305	1.0058	0.1863	0.042*
C35	0.2078 (5)	0.8969 (3)	0.03382 (18)	0.0434 (10)
H35	0.2235	0.9038	−0.0168	0.052*
Rh1	0.06207 (2)	0.522795 (15)	0.100971 (10)	0.01435 (6)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

C1	0.0230 (16)	0.0182 (14)	0.0201 (13)	0.0012 (10)	−0.0019 (12)	−0.0027 (10)
O1	0.0224 (13)	0.0363 (13)	0.0375 (12)	−0.0007 (9)	0.0068 (10)	−0.0054 (10)
P1	0.0197 (4)	0.0144 (3)	0.0109 (3)	−0.0002 (3)	−0.0014 (3)	−0.0011 (2)
O2	0.0264 (12)	0.0162 (9)	0.0155 (8)	−0.0010 (9)	0.0038 (9)	−0.0021 (7)
O3	0.0222 (11)	0.0178 (11)	0.0199 (9)	−0.0002 (7)	0.0036 (8)	−0.0021 (7)
C2	0.0292 (15)	0.0164 (12)	0.0120 (11)	−0.0011 (13)	−0.0025 (13)	0.0023 (9)
C4	0.0209 (15)	0.0191 (12)	0.0152 (13)	0.0002 (11)	−0.0003 (10)	0.0050 (10)
C3	0.0267 (16)	0.0167 (12)	0.0202 (13)	−0.0051 (12)	−0.0016 (12)	0.0002 (10)
C5	0.043 (2)	0.0180 (14)	0.0250 (13)	−0.0045 (14)	0.0063 (15)	−0.0072 (11)
C6	0.0235 (16)	0.0287 (16)	0.0268 (15)	−0.0007 (13)	0.0037 (12)	0.0043 (12)
C31	0.046 (2)	0.0160 (13)	0.0173 (13)	−0.0047 (13)	−0.0026 (14)	0.0035 (11)
C21	0.0291 (16)	0.0155 (13)	0.0120 (11)	−0.0003 (11)	−0.0047 (12)	−0.0002 (10)
C11	0.0209 (18)	0.0337 (16)	0.0264 (14)	0.0049 (12)	−0.0039 (12)	−0.0160 (13)
C16	0.0217 (16)	0.0277 (15)	0.0215 (13)	0.0030 (12)	−0.0002 (12)	−0.0003 (11)
C12	0.0340 (15)	0.0293 (12)	0.0400 (13)	0.0005 (10)	0.0058 (11)	−0.0135 (10)
C14	0.0270 (19)	0.0256 (17)	0.059 (2)	−0.0020 (13)	0.0096 (17)	0.0005 (16)
C15	0.032 (2)	0.041 (2)	0.055 (2)	0.0136 (16)	−0.0134 (18)	−0.0221 (18)
C13	0.0340 (15)	0.0293 (12)	0.0400 (13)	0.0005 (10)	0.0058 (11)	−0.0135 (10)
C22	0.042 (2)	0.0177 (14)	0.0183 (13)	−0.0026 (12)	−0.0014 (13)	0.0004 (11)
C23	0.078 (3)	0.0185 (15)	0.0153 (12)	0.0046 (16)	−0.0058 (17)	0.0013 (11)
C26	0.0294 (18)	0.0163 (14)	0.0325 (16)	−0.0016 (12)	−0.0064 (14)	−0.0008 (12)
C24	0.084 (3)	0.0221 (16)	0.0351 (18)	0.0128 (19)	−0.038 (2)	−0.0035 (14)
C25	0.042 (2)	0.0219 (15)	0.054 (2)	0.0050 (14)	−0.0323 (18)	−0.0090 (15)
C32	0.0242 (16)	0.0227 (14)	0.0200 (13)	−0.0049 (12)	−0.0014 (12)	0.0034 (11)
C34	0.046 (2)	0.0363 (17)	0.0337 (17)	−0.0129 (18)	0.0090 (15)	0.0143 (16)
C36	0.038 (2)	0.0290 (16)	0.0167 (14)	−0.0021 (14)	0.0033 (13)	−0.0016 (12)
C33	0.053 (2)	0.0193 (15)	0.0332 (17)	−0.0011 (14)	0.0033 (16)	0.0041 (13)
C35	0.080 (3)	0.0309 (18)	0.0194 (15)	0.0161 (19)	0.0104 (18)	0.0101 (13)
Rh1	0.01800 (10)	0.01415 (9)	0.01091 (8)	0.00045 (8)	0.00012 (9)	−0.00112 (8)

Geometric parameters (Å, °)

C1—O1	1.149 (4)	C16—H16A	0.99
C1—Rh1	1.802 (3)	C16—H16B	0.99
P1—C31	1.819 (3)	C12—C13	1.479 (5)
P1—C21	1.821 (3)	C12—H12A	0.99
P1—C11	1.836 (3)	C12—H12B	0.99
P1—Rh1	2.2328 (6)	C14—C15	1.480 (5)
O2—C2	1.269 (4)	C14—C13	1.487 (5)
O2—Rh1	2.0764 (18)	C14—H14A	0.99
O3—C4	1.274 (3)	C14—H14B	0.99
O3—Rh1	2.044 (2)	C15—H15A	0.99
C2—C3	1.388 (4)	C15—H15B	0.99
C2—C5	1.513 (4)	C13—H13A	0.99
C4—O3	1.274 (3)	C13—H13B	0.99
C4—O3	1.274 (3)	C22—C23	1.401 (4)
C4—C3	1.395 (4)	C22—H22	0.95
C4—C6	1.501 (4)	C23—C24	1.372 (6)
C3—H3	0.95	C23—H23	0.95

C5—H5A	0.98	C26—C25	1.394 (4)
C5—H5B	0.98	C26—H26	0.95
C5—H5C	0.98	C24—C25	1.387 (6)
C6—H6A	0.98	C24—H24	0.95
C6—H6B	0.98	C25—H25	0.95
C6—H6C	0.98	C32—C33	1.406 (4)
C31—C32	1.412 (4)	C32—H32	0.95
C31—C36	1.419 (4)	C34—C35	1.393 (5)
C21—C26	1.388 (5)	C34—C33	1.412 (5)
C21—C22	1.402 (4)	C34—H34	0.95
C11—C16	1.473 (4)	C36—C35	1.410 (5)
C11—C12	1.485 (4)	C36—H36	0.95
C11—H11	1	C33—H33	0.95
C16—C15	1.469 (5)	C35—H35	0.95
O1—C1—Rh1	179.0 (3)	C15—C14—C13	115.3 (3)
C31—P1—C21	105.44 (14)	C15—C14—H14A	108.5
C31—P1—C11	103.52 (16)	C13—C14—H14A	108.5
C21—P1—C11	105.45 (14)	C15—C14—H14B	108.5
C31—P1—Rh1	119.22 (10)	C13—C14—H14B	108.5
C21—P1—Rh1	109.80 (9)	H14A—C14—H14B	107.5
C11—P1—Rh1	112.35 (10)	C16—C15—C14	115.5 (3)
C2—O2—Rh1	126.06 (18)	C16—C15—H15A	108.4
C4—O3—Rh1	126.78 (18)	C14—C15—H15A	108.4
O2—C2—C3	126.5 (2)	C16—C15—H15B	108.4
O2—C2—C5	115.4 (3)	C14—C15—H15B	108.4
C3—C2—C5	118.2 (3)	H15A—C15—H15B	107.5
O3—C4—C3	126.3 (3)	C12—C13—C14	114.5 (3)
O3—C4—C6	115.3 (3)	C12—C13—H13A	108.6
C3—C4—C6	118.5 (3)	C14—C13—H13A	108.6
C2—C3—C4	125.4 (3)	C12—C13—H13B	108.6
C2—C3—H3	117.3	C14—C13—H13B	108.6
C4—C3—H3	117.3	H13A—C13—H13B	107.6
C2—C5—H5A	109.5	C23—C22—C21	120.0 (3)
C2—C5—H5B	109.5	C23—C22—H22	120
H5A—C5—H5B	109.5	C21—C22—H22	120
C2—C5—H5C	109.5	C24—C23—C22	120.4 (3)
H5A—C5—H5C	109.5	C24—C23—H23	119.8
H5B—C5—H5C	109.5	C22—C23—H23	119.8
C4—C6—H6A	109.5	C21—C26—C25	120.6 (3)
C4—C6—H6B	109.5	C21—C26—H26	119.7
H6A—C6—H6B	109.5	C25—C26—H26	119.7
C4—C6—H6C	109.5	C23—C24—C25	119.9 (3)
H6A—C6—H6C	109.5	C23—C24—H24	120
H6B—C6—H6C	109.5	C25—C24—H24	120
C32—C31—C36	118.1 (3)	C24—C25—C26	120.1 (3)
C32—C31—P1	120.6 (2)	C24—C25—H25	119.9
C36—C31—P1	118.5 (2)	C26—C25—H25	119.9
C26—C21—C22	118.9 (3)	C33—C32—C31	120.1 (3)
C26—C21—P1	122.0 (2)	C33—C32—H32	119.9

C22—C21—P1	118.9 (2)	C31—C32—H32	119.9
C16—C11—C12	114.6 (3)	C35—C34—C33	119.4 (3)
C16—C11—P1	112.4 (2)	C35—C34—H34	120.3
C12—C11—P1	119.5 (2)	C33—C34—H34	120.3
C16—C11—H11	102.4	C35—C36—C31	119.2 (3)
C12—C11—H11	102.4	C35—C36—H36	120.4
P1—C11—H11	102.4	C31—C36—H36	120.4
C15—C16—C11	114.3 (3)	C32—C33—C34	119.0 (3)
C15—C16—H16A	108.7	C32—C33—H33	120.5
C11—C16—H16A	108.7	C34—C33—H33	120.5
C15—C16—H16B	108.7	C34—C35—C36	119.7 (3)
C11—C16—H16B	108.7	C34—C35—H35	120.1
H16A—C16—H16B	107.6	C36—C35—H35	120.1
C13—C12—C11	113.3 (3)	C1—Rh1—O3	177.31 (10)
C13—C12—H12A	108.9	C1—Rh1—O2	93.72 (10)
C11—C12—H12A	108.9	O3—Rh1—O2	88.69 (8)
C13—C12—H12B	108.9	C1—Rh1—P1	88.50 (9)
C11—C12—H12B	108.9	O3—Rh1—P1	89.18 (5)
H12A—C12—H12B	107.7	O2—Rh1—P1	174.94 (5)
Rh1—O2—C2—C3	2.2 (4)	C11—C16—C15—C14	42.9 (4)
Rh1—O2—C2—C5	−179.09 (18)	C13—C14—C15—C16	−40.8 (5)
Rh1—O3—C4—C3	5.7 (4)	C11—C12—C13—C14	−45.8 (4)
Rh1—O3—C4—C6	−172.64 (18)	C15—C14—C13—C12	42.3 (4)
O2—C2—C3—C4	2.6 (5)	C26—C21—C22—C23	2.2 (4)
C5—C2—C3—C4	−176.1 (3)	P1—C21—C22—C23	176.0 (2)
O3—C4—C3—C2	−6.9 (5)	C21—C22—C23—C24	−1.0 (4)
C6—C4—C3—C2	171.3 (3)	C22—C21—C26—C25	−2.9 (4)
C21—P1—C31—C32	−43.6 (3)	P1—C21—C26—C25	−176.5 (2)
C11—P1—C31—C32	66.9 (3)	C22—C23—C24—C25	0.6 (5)
Rh1—P1—C31—C32	−167.5 (2)	C23—C24—C25—C26	−1.3 (5)
C21—P1—C31—C36	155.6 (3)	C21—C26—C25—C24	2.5 (5)
C11—P1—C31—C36	−93.9 (3)	C36—C31—C32—C33	−16.8 (5)
Rh1—P1—C31—C36	31.8 (3)	P1—C31—C32—C33	−177.6 (3)
C31—P1—C21—C26	−34.9 (3)	C32—C31—C36—C35	17.6 (5)
C11—P1—C21—C26	−144.0 (2)	P1—C31—C36—C35	178.9 (3)
Rh1—P1—C21—C26	94.7 (2)	C31—C32—C33—C34	16.1 (5)
C31—P1—C21—C22	151.5 (2)	C35—C34—C33—C32	−16.1 (6)
C11—P1—C21—C22	42.4 (3)	C33—C34—C35—C36	17.2 (6)
Rh1—P1—C21—C22	−78.9 (2)	C31—C36—C35—C34	−18.1 (6)
C31—P1—C11—C16	68.1 (2)	C4—O3—Rh1—O2	−1.2 (2)
C21—P1—C11—C16	178.6 (2)	C4—O3—Rh1—P1	−176.6 (2)
Rh1—P1—C11—C16	−61.8 (2)	C2—O2—Rh1—C1	178.6 (2)
C31—P1—C11—C12	−70.5 (3)	C2—O2—Rh1—O3	−2.6 (2)
C21—P1—C11—C12	40.0 (3)	C31—P1—Rh1—C1	42.38 (16)
Rh1—P1—C11—C12	159.6 (2)	C21—P1—Rh1—C1	−79.31 (14)
C12—C11—C16—C15	−46.9 (4)	C11—Rh1—Rh1—C1	163.68 (15)
P1—C11—C16—C15	172.4 (2)	C31—P1—Rh1—O3	−136.25 (14)
C16—C11—C12—C13	48.4 (4)	C21—P1—Rh1—O3	102.06 (12)
P1—C11—C12—C13	−173.9 (3)	C11—P1—Rh1—O3	−14.95 (13)

Hydrogen-bond geometry (Å, °)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C11—H11$\cdots$O3	1	2.39	2.962 (3)	116
C16—H16B$\cdots$O3	0.99	2.44	3.094 (3)	123

Table 3

Comparative spectroscopic (cm^{-1}, p.p.m., Hz) and geometrical parameters (Å) for selected [Rh(acac)(CO)(P-Lig)] complexes.

P-Lig	υ(CO)	δ^{31}P	^{1}J(Rh-P)	Rh-P	C1-O1	notes
PPh$_3$	1983	46	177.4	2.244 (2)	1.153 (11)	(i,iv)
PCyPh$_2$	1959	53.3	171.3	2.2327 (6)	1.149 (4)	(ii)
PCy$_2$Ph	1949	58.8	168.3	2.2425 (9)	1.151 (3)	(iii)
PCy$_3$	1945	58	170.0	2.2613 (10)	1.169 (4)	(iv)

Notes: (i) Leipoldt *et al.* (1978); (ii) This work; (iii) Brink *et al.* (2007); (iv) Trzeciak *et al.* (2004).
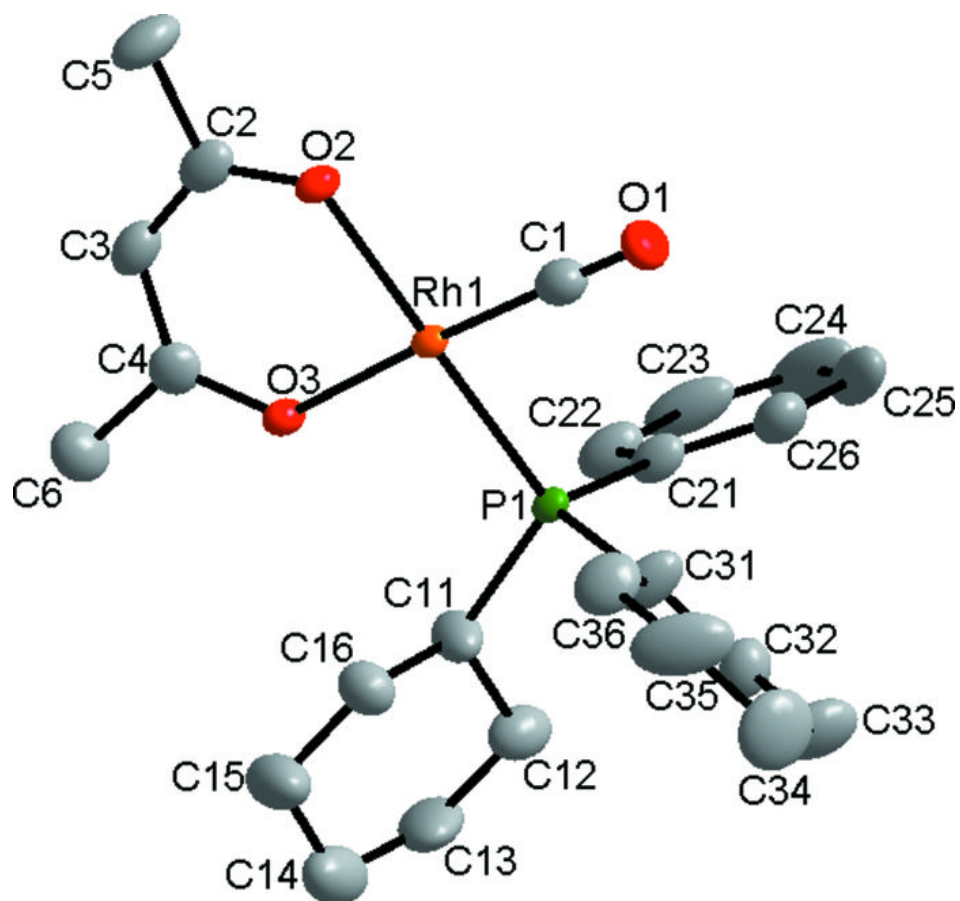
Fig. 1

Fig. 2