Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

(Acetylacetonato)carbonyl(dicyclohexylphenylphosphine)rhodium(I)

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Received 3 November 2006
Accepted 20 November 2006

In the title complex, [Rh(acac)(CO)(PCy_2Ph)] (acac = acetylacetonate, Cy = cyclohexyl) or [Rh($C_5H_7O_2$)(CO)($C_{18}H_{27}P$)], the Rh atom is coordinated by one P [Rh—P = 2.2424 (9) Å], two O [Rh—O = 2.0783 (17) and 2.0411 (18) Å] and one C [Rh—C = 1.797 (3) Å] atoms in a slightly distorted square-planar geometry. The bite angle O—Rh—O is 88.20 (6)° and the calculated effective cone angle (θ_E) for the dicyclohexylphenyl phosphine is 163°.

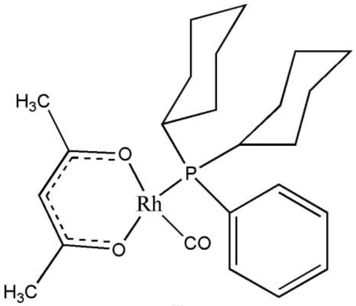
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
R factor = 0.027
wR factor = 0.070
Data-to-parameter ratio = 18.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Acetylacetonate has two O-donor atoms with equivalent σ-electron donor capabilities. The high symmetry of dicarbonyl(acetylacetonate)rhodium(I) complexes promotes easy carbonyl displacement of either carbonyl group with a variety of phosphines, phosphites and arsines (Bonati & Wilkinson, 1964).



(I)

The title compound, [Rh(acac)(CO)(PCy_2Ph)] (acac = acetylacetonate, Cy = cyclohexyl), (I) (Fig. 1), forms a part of our study on complexes of the type [Rh(β-diketone)(CO)($PR_1R_2R_3$)] (R_1, R_2 and R_3 = cyclohexyl or phenyl). The Rh atoms in (I) have a slightly distorted square-planar coordination, illustrated by P1—Rh1—C1 and O2—Rh1—O3 angles of 89.34 (7) and 88.20 (7)° (Table 1), respectively, deviating from the ideal 90° bite angle. The intramolecular C—H···O hydrogen bond (Table 2) influences the molecular conformation, while the weak intermolecular C—H···O interaction (Table 2) link the molecules into centrosymmetric dimers with a distance between the two rhodium centers of 6.135 (1) Å (Fig. 2).

The Tolman cone angle (θ_T) is the most widely used method for determining ligand steric behavior at a metal center, as described by Tolman (1977) and Otto *et al.* (2000). Actual Rh—P bond distances were used for the present study, with a van der Waals radius of 1.20 Å for H. The effective cone angle (θ_E) of 163° calculated for (I) fits the sequence of 145 and 170°

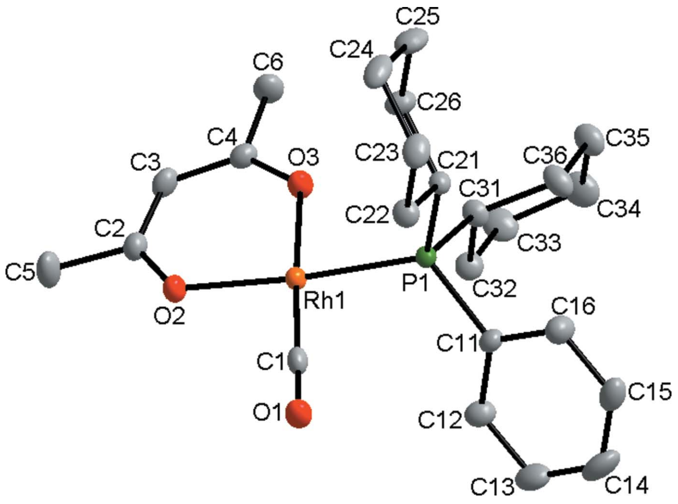


Figure 1
Molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. For the C atoms in rings, the first digit indicates ring number and the second digit indicates the position of the atom in the ring.

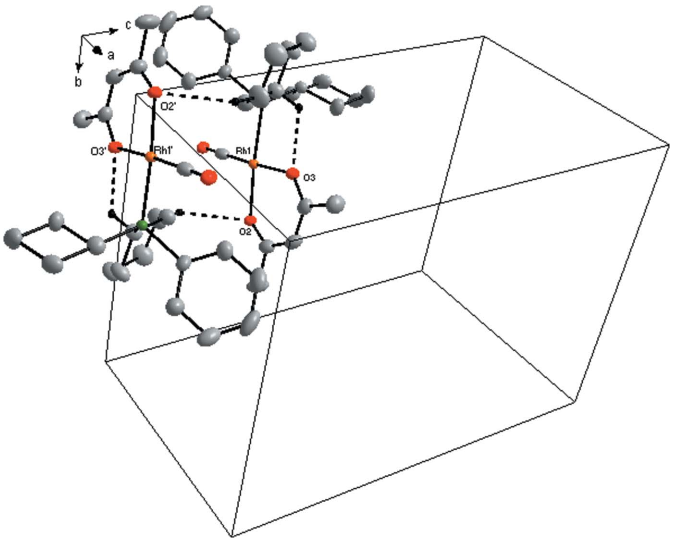


Figure 2
A portion of the crystal packing showing the hydrogen-bonded (dashed lines) centrosymmetric dimer in (I). The primed atoms are related to the unprimed ones by the symmetry operation (1 − *x*, −*y*, −*z*).

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).

Bond distances and $^1J(^{31}P-^{103}Rh)$ first-order coupling constants for (I) are compared in Table 3 with others of similar structure. The IR carbonyl stretching frequency decreases systematically from [Rh(acac)(CO)(PPh_3)] to [Rh(acac)(CO)(PCy_3)] (Trzeciak *et al.*, 2004), indicating a stronger Rh—CO bond, consistent with the steric increase of the P ligand. Unfortunately, this is not substantiated by the Rh—CO bond distances reported in Table 3, which may be due to the fact that the [Rh(acac)(CO)(PPh_3)] data (Leipoldt *et al.*, 1978) were not collected at 100 K as were the other structures.

Experimental

[RhCl(CO)$_2$]$_2$ was prepared according to the literature method of McCleverty & Wilkinson (1990). All other chemicals were obtained from Sigma Aldrich and used as received. [Rh(acac)(CO)$_2$] was synthesized by the slow addition of acetylacetonate solution (66.7 mg, 0.666 mmol) in dimethylformamide (DMF, 2 ml) to a solution of [RhCl(CO)$_2$]$_2$ (108.9 mg, 0.280 mmol) in DMF (2 ml). Upon addition of ice–water (30 ml), the complex precipitated; it was filtered off and dried. Ligand substitution on the complex [Rh(acac)(CO)$_2$] was performed by dissolving (20.0 mg, 0.077 mmol) in acetone (5 ml) followed by slow addition of PCy_2Ph (24.4 mg, 0.089 mmol) in acetone (2 ml). Single crystals of (I) were obtained by slow evaporation of the solvent. $^{31}P\{H\}$ NMR ($CDCl_3$, 121.495 MHz, p.p.m.): 59.0 [*d*, ^1J(Rh—P) = 168.3 Hz]; IR υ(CO): 1948.8 cm^{-1}; (CH_2Cl_2) υ(CO): 1967 cm^{-1}.

Crystal data

[Rh($C_5H_7O_2$)(CO)($C_{18}H_{27}P$)]
M_r = 504.39
Monoclinic, $P2_1/n$
a = 10.076 (5) Å
b = 12.990 (5) Å
c = 17.937 (5) Å
β = 90.576 (5)°
V = 2347.6 (16) Å^3
Z = 4
D_x = 1.427 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.82 mm^{-1}
T = 100 (2) K
Block, yellow
0.18 × 0.09 × 0.05 mm

Data collection

Bruker X8 ApexII 4K diffractometer
ω and φ scans
Absorption correction: multi-scan *SADABS* (Bruker, 2004)
T_{min} = 0.867, T_{max} = 0.960
25476 measured reflections
4885 independent reflections
4185 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 26.8°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.070
S = 1.05
4885 reflections
264 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2 + 1.34P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O2—Rh1	2.0783 (17)	P1—Rh1	2.2424 (9)
O3—Rh1	2.0411 (18)	C1—O1	1.152 (3)
P1—C11	1.825 (2)	C1—Rh1	1.797 (3)
P1—C21	1.833 (2)	Rh1—O3	2.0411 (18)
P1—C31	1.842 (2)		
O1—C1—Rh1	179.9 (2)	C1—Rh1—P1	89.34 (7)
O3—Rh1—O2	88.20 (7)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C31—H31···O3	1.00	2.40	2.974 (3)	116
C33—H33*A*···O2^i	0.99	2.60	3.455 (3)	145

Symmetry code: (i) $-x+1, -y, -z$.

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Table 3

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

P—Lig	Rh—P	C1—O1	υ(CO)	^{1}J(Rh—P)	notes
PPh_3	2.244 (2)	1.153 (11)	1983	177.4	(*a*,*c*)
PCy_2Ph	2.2425 (9)	1.151 (3)	1949	168.3	(*b*)
PCy_3	2.2613 (10)	1.160 (4)	1945	170.0	(*c*)

Notes: (*a*) Leipoldt *et al.* (1978); (*b*) this work; (*c*) Trzeciak *et al.* (2004).

The methyl, methine and aromatic H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with [C—H = 0.95–1.00 Å, and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) and 1.2$U_{\rm eq}$(C)]. The methyl H atoms were refined as a rigid rotor.

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: *SIR97* (Altomare *et al.*, 1999); 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).

Financial assistance from the South African National Research Foundation (NRF), the Research Fund of the University of the Free State and SASOL is gratefully acknowledged. Part of this material is based on work supported by the South African National Research Foundation (GUN 2038915). Opinions, findings, conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the NRF. Dr A. Muller is acknowledged for collection of the X-ray data and help with the refinement of the structure.

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