

Carbonyl(8-hydroxyquinolinato)[tris(2,4-di-*tert*-butylphenyl)phosphite]rhodium(I) acetone hemisolvate

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
Disorder in solvent or counterion
R factor = 0.039
wR factor = 0.130
Data-to-parameter ratio = 22.2

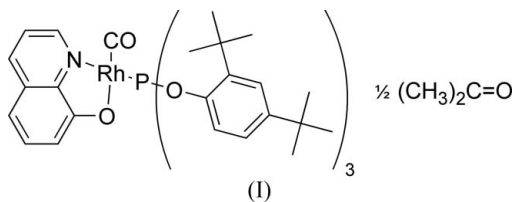
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Molecules of the title compound, $[\text{Rh}(\text{C}_9\text{H}_6\text{NO})\{\text{(C}_{14}\text{H}_{21}\text{O})_3\text{P}\}(\text{CO})] \cdot 0.5(\text{CH}_3)_2\text{CO}$, where $(\text{C}_9\text{H}_6\text{NO}) = 8$ -hydroxyquinolinato and $\{\text{(C}_{14}\text{H}_{21}\text{O})_3\text{P}\} = \text{tris}(2,4\text{-di-}i\text{tert-butylphenyl})\text{phosphite}$, pack in a tail-to-tail fashion with an intermolecular quinoline ligand-to-ligand π -stacking distance of 3.312 (1) \AA . The effective cone angle (Θ_{E}) for the phosphite ligand is 192°. The bidentate oxine ligand has a bite angle of 81.00 (8)° and the Rh—P bond length is 2.1819 (6) \AA .

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Comment

This work is part of an ongoing investigation aimed at determining the factors influencing molecular packing in non-symmetrical bidentate ligand complexes of Rh^{I} . Rh^{I} complexes containing bulky phosphites are useful in catalysed hydroformylation of alkenes (Crous *et al.*, 2005). The title compound, (I), was prepared by addition of the phosphite ligand to $[\text{Rh}(\text{OX})(\text{CO})_2]$, where OX is 8-hydroxyquinolinato ($\text{C}_9\text{H}_6\text{NO}$), leading to carbonyl substitution *trans* to the N atom, since this is the better σ -electron donor (Steyn *et al.*, 1997).



In (I) (Fig. 1), a dihedral angle of 3.4 (1)° exists between the benzene and pyridine rings of the oxine ligand, evidence of a slight distortion. Further distortion is observed between the bidentate oxine backbone and the metal coordination plane, as evident from the dihedral angle of 7.09 (8)°. The oxine ligand exhibits a bite angle of 81.00 (8)° and the C10—Rh—P bond angle is 89.88 (7)°, illustrating the distorted square-planar coordination polyhedron of Rh. The Rh atom is displaced by 0.043 (1) \AA from the coordination plane (r.m.s. displacement of fitted atoms = 0.005 \AA), and the carbonyl ligand is bound in an approximately linear manner [Rh—C10—O5 = 177.0 (2)°]. Molecules of (I) pack in a tail-to-tail fashion, with an intermolecular ligand-to-ligand π -stacking distance of 3.312 (6) \AA (Fig. 2).

The steric demand of the tris(2,4-di-*tert*-butylphenyl)phosphite 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 192° in (I) is significantly larger than that of 172° observed for a similar complex containing

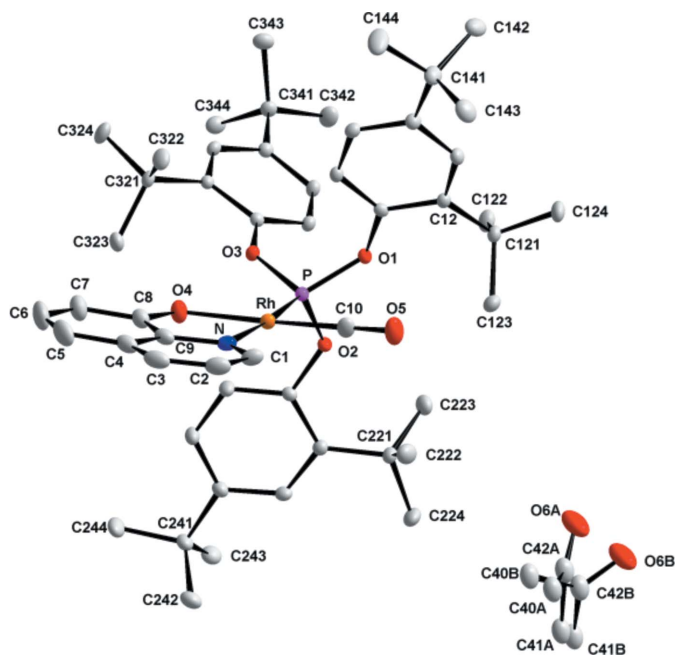


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 30% probability level. H atoms have been omitted.

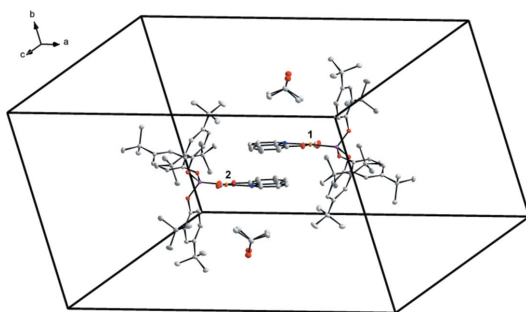


Figure 2
Part of the unit-cell contents viewed along the oxine plane, indicating oxine ligand-to-ligand π -stacking. [Symmetry operators for molecules 1 and 2: (1) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (2) $x, \frac{1}{2} - y, \frac{1}{2} + z$.]

the bidentate 3,5,7-tribromotropolonate ligand (Crous *et al.*, 2005). In solution, the ligand substituent orientation might differ, resulting in a variation in cone angle size (Ferguson *et al.*, 1978).

Bond lengths, bite angles and the effective cone angle for (I) are compared with those of similar structures in Table 2. The steric contribution from triphenylphosphite (quantified by Θ_E) shows an approximate 10% increase compared with the triphenylphosphine ligand. The increasing Θ_E from entry (2) to (4) compared with (1) emphasizes the dependence of this parameter on the substituents on the phenyl rings. The bond distances and angles in the quinoline rings show little variation among the structures. The shorter Rh–P bonds for the phosphite complexes reflect that the phosphite ligand is a weaker σ -donor but better π -acceptor than the phosphine ligand, thereby leading to a stronger Rh–P bond. This is also seen in the significant increase (*ca* 120 Hz) in $^1J_{(\text{Rh}-\text{P})}$ coupling constants for the phosphite complexes compared to the

phosphine complexes. The comparable $^1J_{(\text{Rh}-\text{P})}$ values for each of the phosphite complexes indicate that the methyl groups on the phenyl rings have negligible electronic influence on the P donor atom.

Experimental

$[\text{RhCl}(\text{CO})_2]_2$ was prepared according to a literature method (McCleverty & Wilkinson, 1990). Other chemicals and solvents were obtained from Sigma–Aldrich and used as received. $[\text{Rh}(\text{OX})(\text{CO})_2]$ was synthesized by mixing solutions of 8-hydroxyquinoline (82 mg, 0.565 mmol) in DMF (1 ml) and $[\text{RhCl}(\text{CO})_2]_2$ (100 mg, 0.257 mmol) in DMF (1 ml). Upon addition of ice–water (50 ml), the complex precipitated and was filtered off. Ligand substitution on the complex $[\text{Rh}(\text{OX})(\text{CO})_2]$ was performed by dissolving 40 mg (0.074 mmol) in acetone (40 ml), followed by slow addition of $\text{P}(\text{OC}_{14}\text{H}_{21})_3$ (52 mg, 0.081 mmol) in acetone (2 ml). Single crystals (yield 64 mg, 75%) of (I) were obtained by slow evaporation of the mixture. Spectroscopic data: $^{31}\text{P}\{\text{H}\}$ NMR (CDCl_3 , 121.494 MHz, p.p.m.): 118.3 [$^1J_{(\text{Rh}-\text{P})} = 279$ Hz]; IR (acetone) $\nu(\text{CO})$: 1986 cm^{-1} ; (KBr) $\nu(\text{CO})$: 1985 cm^{-1} .

Crystal data

$[\text{Rh}(\text{C}_9\text{H}_6\text{NO})(\text{C}_{42}\text{H}_{63}\text{O}_3\text{P})\text{CO}] \cdot 0.5\text{C}_3\text{H}_6\text{O}$
 $M_r = 951$
Orthorhombic, $Pccn$
 $a = 34.945$ (5) Å
 $b = 17.307$ (5) Å
 $c = 17.778$ (5) Å
 $V = 10752$ (5) Å³

$Z = 8$
 $D_x = 1.175$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 0.39$ mm⁻¹
 $T = 150$ (2) K
Block, yellow
0.3 × 0.28 × 0.21 mm

Data collection

Bruker X8 ApexII CCD diffractometer
 ω and φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2004)
 $T_{\text{min}} = 0.892$, $T_{\text{max}} = 0.922$

86538 measured reflections
13332 independent reflections
10688 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$
 $\theta_{\text{max}} = 28.3^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.130$
 $S = 1.07$
13332 reflections
600 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0709P)^2 + 8.2813P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 1.14$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.48$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Rh–C10	1.818 (3)	P–O1	1.6042 (16)
Rh–O4	2.0234 (18)	O1–C11	1.401 (2)
Rh–N	2.0842 (19)	O2–C21	1.402 (3)
Rh–P	2.1819 (6)	O3–C31	1.402 (2)
P–O3	1.5965 (16)	O5–C10	1.145 (3)
P–O2	1.6030 (16)		
C10–Rh–N	95.37 (9)	O3–P–Rh	110.51 (6)
O4–Rh–N	81.00 (8)	O2–P–Rh	120.66 (6)
C10–Rh–P	89.88 (7)	O1–P–Rh	119.36 (6)
O4–Rh–P	93.64 (5)	O5–C10–Rh	177.0 (2)
O4–Rh–P–O3	23.54 (9)	C10–Rh–P–O2	82.07 (11)

Table 2
Comparative geometric data (Å, °) for [Rh(OX)(CO)(PR₃)₃] complexes..

PR ₃	Rh–P	Rh–N	Rh–O	N–Rh–O	Θ _E (°)	¹ J _{Rh–P} (Hz)
P(Otbp) ⁱ	2.182 (7)	2.084 (2)	2.023 (2)	81.0 (1)	192	279
P(OPh) ₃ ⁱⁱ	2.186 (1)	2.097 (2)	2.022 (2)	80.8 ⁱⁱⁱ	163	281
P(O2MP) ₃ ^{iv}	2.189 (1)	2.088 (3)	2.032 (3)	81.2 (1)	168	278
P(O2,6DMP) ₃ ^v	2.198 (1)	2.091 (3)	2.029 (3)	80.3 (1)	183	280
PPh ₃ ^{vi}	2.261 (2)	2.098 (9)	2.042 (5)	80.0 (3)	153	161

References and notes: (i) this work, P(Otbp) = tris(2,4-di-tert-butylphenyl)phosphite; (ii) Simanko *et al.* (2000); (iii) data extracted from the Cambridge Structural Database (Version 5.26), no s.u. values (Allen, 2002); (iv) Janse van Rensburg *et al.* (2005b); (v) Janse van Rensburg *et al.* (2005a); (vi) Leipoldt *et al.* (1981).

H atoms were positioned geometrically and refined using a riding model with C–H = 0.93 Å, $U_{iso}(H) = 1.2U_{eq}(C)$ for Csp^2 and C–H = 0.96 Å, $U_{iso}(H) = 1.5U_{eq}(C)$ for Csp^3 . The acetone solvent molecule is disordered and incorporated with a total occupancy of 50%, distributed over two orientations with site occupancy factors 0.301 (3) and 0.199 (3). Geometrical restraints were applied, and the anisotropic displacement parameters were restrained to approximate isotropic behaviour. The highest peak in the difference density is located 0.16 Å from C14B.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus*; 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).

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