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Carbonyl(8-hydroxyquinolinato)[tris(2-methylphenyl) phosphite]rhodium(I)

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.005 Å
R factor = 0.042
wR factor = 0.094
Data-to-parameter ratio = 19.3

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

The molecules of the title compound, [Rh(C_9H_6NO)($C_{21}H_{21}O_3P$)(CO)], pack in a 'tail-to-tail' fashion, with a π-stacking distance of 3.500 (1) Å. The effective cone angle (Θ_E) for the phosphite ligand is 168°. The bidentate oxine ligand has a bite angle of 81.27 (11)° and the Rh—P bond distance is 2.189 (1) Å.

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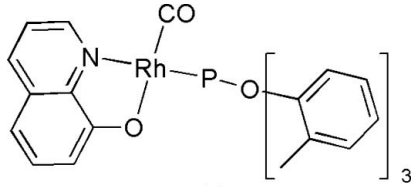
Comment

The well known bidentate ligand OX (8-hydroxyquinolinate), possesses both nitrogen and oxygen donor atoms. In (8-hydroxyquinolinato)rhodium(I) complexes, the better σ-electron donor capability of nitrogen compared with that of oxygen promotes selective carbonyl displacement *trans* to the N atom.



(I)

The title compound, (I), reported here forms part of our study on complexes of the type [Rh(OX)(ER_3)(CO)] (E = P, As and Sb; R = alkyl, aryl, alkoyl and aroyl). The Rh atom lies

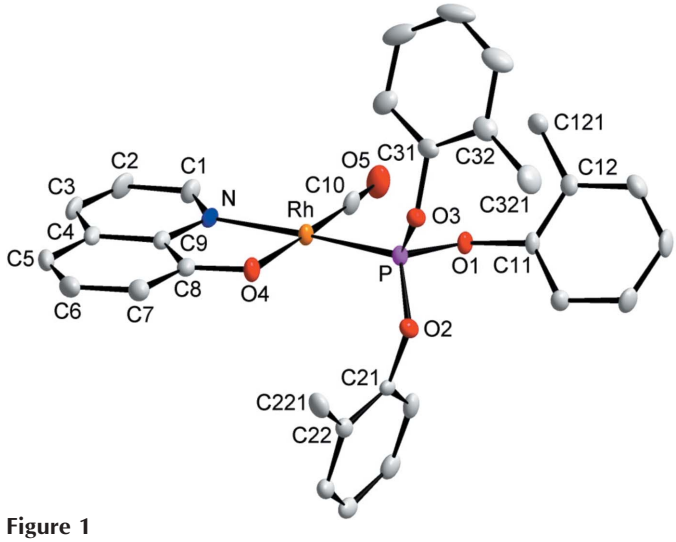


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. For the unlabelled C atoms, the first digit indicates ring number and the second digit the position of the atom in the ring.

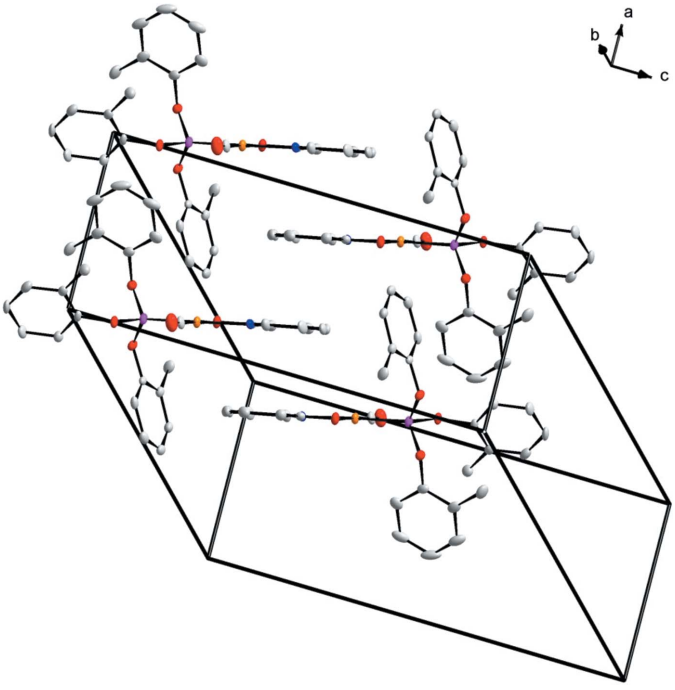


Figure 2
Unit-cell view, indicating π-stacking between quinoline rings. H atoms have been omitted.

on a general position, adopting a slightly distorted square-planar coordination geometry with a 0.014 (1) Å displacement from the coordination plane (r.m.s. displacement of fitted atoms = 0.006 Å) (Fig. 1 and Table 1).

A slight distortion of the oxinato ligand occurs, as evidenced by a dihedral angle of 0.7 (2)° between the two aromatic rings. Similarly, slight distortion is observed between the bidentate oxinate backbone and the metal coordination plane, with a dihedral angle of 1.07 (15)°. The distortion from square-planar geometry of the metal coordination is illustrated by the deviation from 90° in the C10—Rh—P bond angle and the N—Rh—O4 bite angle, *viz.* 91.02 (10) and 81.16 (9)°, respectively.

There is an intramolecular hydrogen-bonding interaction, C16—H16···O2, with an angle of 121° (Table 2) that might affect the methylphenyl ring arrangement. The molecules pack in a 'tail-to-tail' fashion with a π-stacking distance of 3.500 (1) Å (Fig. 2). This 'tail-to-tail' stacking is due to the steric effect caused by the phosphite ligand.

The effective cone angle (Θ_E), using the Rh—P bond distance of 2.189 (1) Å, was calculated for the phosphite ligand, as described previously (Tolman, 1977; Otto *et al.*, 2000). The phosphite substituents may have different orientations, resulting in variations in solid-state cone angles, as previously observed by Ferguson *et al.* (1978), and the effective cone angle may therefore not necessarily be a true indication of the steric properties of the ligand in solution. The methylphenyl rings of the tris(2-methylphenyl)phosphite ligand are thus arranged to yield an effective cone angle (Θ_E) of 168°, which is comparable to the value of 167° reported by Meijboom *et al.* (2004) for the corresponding Vaska-type rhodium complex *trans*-[RhCl(CO)L_2]. An *o*-methyl substituent on the phosphite phenyl rings increases the total cone angle of these triphenylphosphite ligands progressively by *ca* 15° for every methyl group introduced, *i.e.* Θ_{eff} *ca* 154, 168 and 183° for the triphenyl-, tris(2-methylphenyl)- and tris(2,6-dimethylphenyl)phosphite, respectively (Table 3). The comparable $^1J_{(Rh-P)}$ values of these three ligand systems indicate that the methyl groups on the phenyl rings have little or no electronic influence on the Rh—P bond.

Bond distances, bite angles and the effective cone angle for (I) are compared with those of similar structures in Table 3. A reasonable correlation between the bond distances and angles for the quinoline rings is observed. The shorter Rh—P bonds (*ca* 2.26 *versus* 2.19 Å) for the phosphite complexes is a result of the phosphite being a weaker σ-donor but better π-acceptor than the phosphine ligand, leading to a stronger bond. This is also seen in the significant difference in coupling constants between phosphine and phosphite complexes (161 *versus ca* 278 Hz, respectively), presumably due to the π-accepting nature of phosphites. The additional increase from entry 4 to 5 is due to the change from Rh^I to Rh^{III} following CH_3I oxidative addition.

Experimental

$[RhCl(CO)_2]_2$ was prepared according to a literature method (McCleverty & Wilkinson, 1990). $P(OC_7H_7)_3$ was prepared by reaction of the corresponding 2-methylphenol with PCl_3 in the presence of NEt_3, similar to the synthesis of tris(2-butylpenyl)phosphite (van Leeuwen & Roobeek, 1983). All other chemicals and solvents were obtained from Sigma–Aldrich and used as received. [Rh(OX)(CO)$_2$] was synthesized by mixing solutions of 8-hydroxyquinoline (50 mg, 0.344 mmol) in dimethylformamide (DMF, 1 ml) and $[RhCl(CO)_2]_2$ (64 mg, 0.164 mmol) in DMF (1 ml). Upon addition of ice–water (20 ml), the complex precipitated and was filtered off. Ligand substitution on the complex [Rh(OX)(CO)$_2$] was performed by dissolving (20 mg, 0.065 mmol) in acetone (40 ml) followed by slow addition of $P(OC_7H_7)_3$ (25 mg, 0.072 mmol) in acetone (2 ml) (yield 29 mg, 64%). $^{31}P\{H\}$ NMR ($CDCl_3$, 121.4 MHz, p.p.m.): 123.5 [$^1J_{(Rh-P)}$ = 278.3 Hz]; IR (acetone) ν(CO): 1988 cm^{-1}; (KBr) ν(CO): 1984 cm^{-1}.

Crystal data

$[Rh(C_9H_6NO)(C_{21}H_{21}O_3P)(CO)]$	D_x = 1.502 Mg m^{-3}
M_r = 627.42	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3375 reflections
a = 7.652 (5) Å	θ = 2.3–28.2°
b = 20.370 (5) Å	μ = 0.71 mm^{-1}
c = 18.173 (5) Å	T = 100 K
β = 101.546 (5)°	Block, yellow
V = 2775 (2) Å^3	0.22 × 0.13 × 0.13 mm
Z = 4	

Data collection

Bruker X8 APEX 4K Kappa CCD diffractometer	6869 independent reflections
ω and φ scans	4794 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)	R_{int} = 0.046
T_{min} = 0.858, T_{max} = 0.915	θ_{max} = 28.3°
15688 measured reflections	$h = -9 \rightarrow 10$
	$k = -27 \rightarrow 27$
	$l = -19 \rightarrow 24$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0334P)^2 + 2.2331P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.094$	$\Delta\rho_{max} = 0.55$ e Å^{-3}
$S = 1.02$	$\Delta\rho_{min} = -0.95$ e Å^{-3}
6869 reflections	
356 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Rh—C10	1.810 (4)	P—O1	1.596 (2)
Rh—O4	2.030 (2)	P—O2	1.603 (2)
Rh—N	2.086 (2)	P—O3	1.611 (2)
Rh—P	2.189 (1)	O5—C10	1.155 (4)
O4—Rh—N	81.16 (9)	O5—C10—Rh	177.5 (3)
C10—Rh—P	91.02 (10)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C16—H16···O2	0.93	2.54	3.118 (4)	121

Table 3
Comparative geometric data (Å, °) for [Rh(OX)(PR_3)(CO)] complexes.

R	Rh—P	Rh—N	Rh—O	N—Rh—O	Θ_E (Å)	$^1J_{Rh-P}$ (Hz)
O(2,6DMP)[i]	2.198 (1)	2.091 (3)	2.029 (3)	80.3 (1)	183	280
O(2MP)[ii]	2.189 (1)	2.088 (3)	2.032 (3)	81.2 (1)	168	278
OPh[iii]	2.186 (1)	2.097 (2)	2.022 (2)	80.8[iv]	154	281
Ph[v]	2.261 (2)	2.098 (9)	2.042 (5)	80.0 (3)	153	161
Ph[vi]	2.317 (2)	2.084 (7)	2.037 (4)	81.2 (2)	153	163

References and notes: (i) Janse van Rensburg *et al.* (2005); (ii) This work (2MP = 2-methylphenyl); (iii) Simanko *et al.* (2000); (iv) data extracted from Cambridge Structural Database (Version 5.26), no s.u. values (Allen, 2002); (v) Leipoldt *et al.* (1981); (vi) van Aswegen *et al.* (1991), Rh^{III} iodomethane oxidative addition product containing apical *trans* methyl and iodo ligands.

The H atoms were positioned geometrically and refined using a riding model with fixed C—H distances of 0.93 Å (CH) [U_{iso}(H) = 1.2U_{eq}(C)] and 0.96 Å (CH_3) [U_{iso}(H) = 1.5U_{eq}(C)].

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 & Berndt, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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