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Carbonyl(8-hydroxyquinolinato)[tris(2,6-dimethylphenyl)phosphite]rhodium(I)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.046
wR factor = 0.097
Data-to-parameter ratio = 15.6

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

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In the title compound, [Rh(C_9H_6NO)($C_{24}H_{27}O_3P$)(CO)], the molecules pack in a tail-to-tail fashion, with a π–π stacking distance of 3.76 (6) Å, due to the steric effect of the phosphite ligand. The effective cone angle (Θ_E) for the phosphite ligand is 183°.

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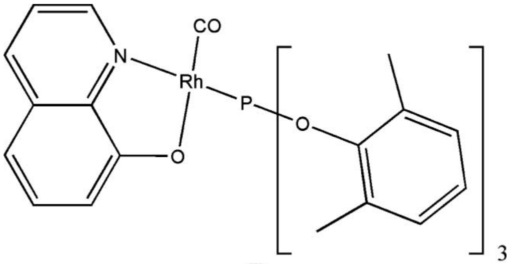
Comment

Previous work has been carried out on rhodium–phosphine complexes containing the bidentate ligand OX (OX = oxinate, 8-hydroxyquinolinate in the present study), illustrating the catalytic importance of the rhodium(I) square-planar moiety (Roth *et al.*, 1971). In this type of complex, starting with the [Rh(OX)$(CO)_2$] complexes, the different donor atoms of the bidentate ligand (OX) result in the displacement of the carbonyl group *trans* to the stronger donor (less electronegative) atom. This opens the possibility of determining the relative *trans* influence of the donor atoms. In 8-hydroxyquinoline, the N atom has a larger *trans* influence, due to its better σ-electron donor capability, compared with that of the O atom. This results in carbonyl displacement *trans* to the N atom, as shown by Leipoldt *et al.* (1981).



(I)

The title compound, (I), reported here forms part of our study of complexes of the type [Rh(OX)(CO)(ER_3)], where *E* = P, As or Sb, and *R* = alkyl, aryl, alkoyl or aroyl. The Rh atom lies on a general position and is slightly displaced out of the coordination plane (Fig. 1, Table 1) by 0.039 (1) Å. In the five-membered chelate ring, the oxinate ligand has a small bite angle of 80.34 (13)° and a C10—Rh—P bond angle of 90.31 (13)°. This illustrates the distorted square-planar metal coordination polyhedron. There is a slight distortion in the oxinate ligand, with a dihedral angle of 1.5 (2)° between the two aromatic rings. There is further distortion observed between the bidentate oxinate backbone and the metal coordination plane, with a dihedral angle of 6.3 (1)°.

The molecules of (I) pack in a tail-to-tail fashion, with a π–π stacking distance of 3.76 (6) Å (Fig. 2). This tail-to-tail stacking is not a result of metal–metal interactions [Rh···Rh =

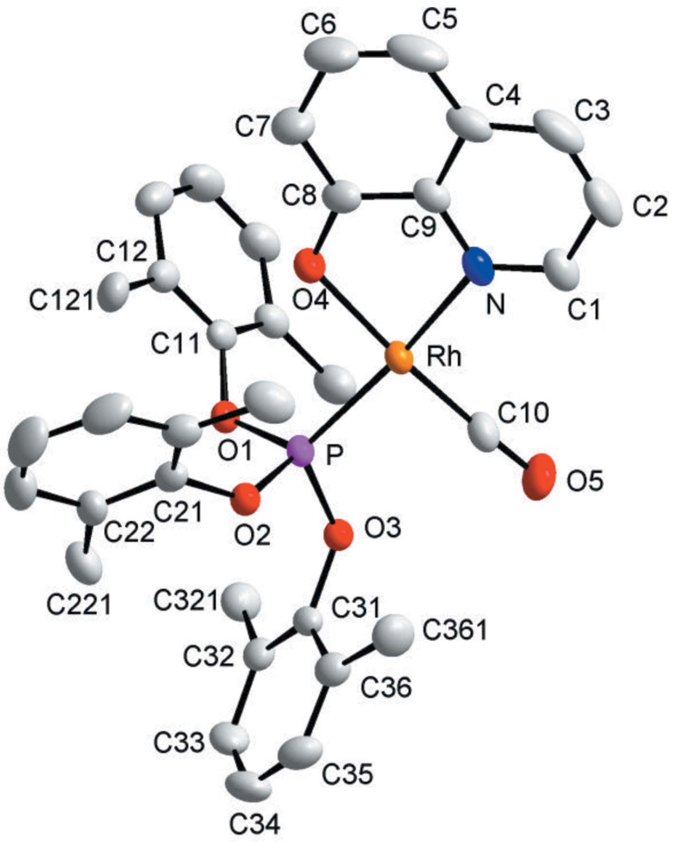


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. For the phenyl C atoms, the first digit indicates the ring number and the second digit indicates the position of the atom in the ring.

7.0 (1) Å], but is due to the steric effect of the phosphite ligand.

The steric behaviour of the ligand at the metal centre was determined by calculating the cone angle, as described previously by Tolman (1977) and Otto *et al.* (2000). For the current structure, the actual Rh—P bond distance [2.1982 (13) Å] was used, yielding the effective cone angle Θ_E. The substituents of the phosphite may have different orientations, resulting in variations in solid-state cone angles, as observed by Ferguson *et al.* (1978), and may therefore not necessarily be a true indication of the steric properties of the phosphite in solution compared with the solid state. The benzene rings of the tris(2,6-dimethylphenyl)phosphite ligand are arranged in such a way as to give an effective cone angle $\Theta_E = 183^\circ$, which is comparable with that reported by Meijboom *et al.* (2004) for the corresponding Vaska-type rhodium complex.

Bond distances, bite angles and the effective cone angle for (I) are compared with those of similar structures in Table 2. The steric contribution of the methyl groups on the phenyl ring of the tris(2,6-dimethylphenyl)phosphite ligand is clearly illustrated by the 30° increase in the size of the cone angle compared with that for the triphenylphosphine and the triphenylphosphite ligand complexes. A reasonable correlation between the bond distances and angles for the quinoline rings is observed. The shorter Rh—P bonds for the phosphite complexes are a result of the phosphite being a weaker σ donor but a better π acceptor than the phosphine ligand, leading to a stronger bond.

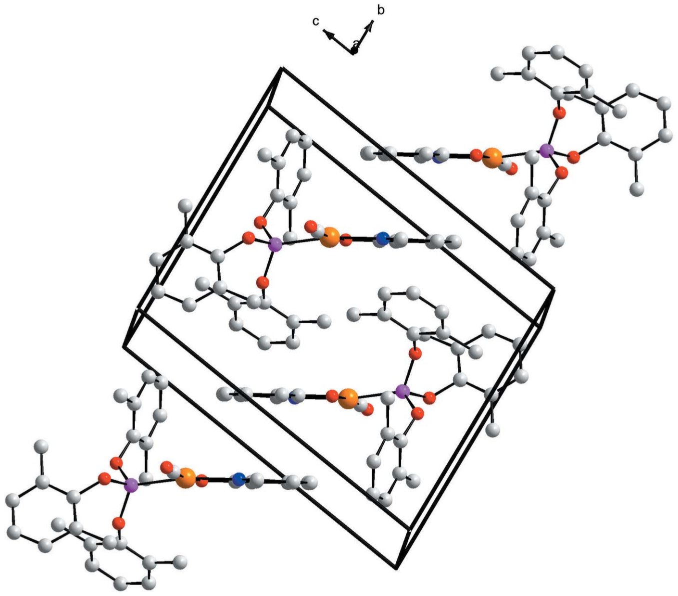


Figure 2
The unit-cell contents of (I) viewed along the *a* axis, indicating the π–π stacking between the quinoline rings.

The comparable $^1J_{(\mathrm{Rh-P})}$ values of the triphenylphosphite and tris(2,6-dimethylphenyl)phosphite complexes are indications that the methyl groups on the benzene ring have little or no electronic influence. The significant difference in coupling constants between phosphine and phosphite complexes (161 *versus ca* 280 Hz, respectively) is assumed to be due to the π-accepting nature of phosphites, leading to a corresponding significant shortening of the Rh—P bond (*ca* 2.26 *versus* 2.19 Å, respectively). The additional increase from entry 3 to entry 4 is due to the change from $\mathrm{Rh^I}$ to $\mathrm{Rh^{III}}$ following CH_3I oxidative addition.

Experimental

$[RhCl(CO)_2]_2$ was prepared according to the literature method of McCleverty & Wilkinson (1990). $P(OC_8H_9)_3$ was prepared by reaction of the corresponding tris(2,6-dimethylphenyl)phenol 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. Ligand substitution on the complex $[Rh(OX)(CO)_2]$ was performed by dissolving a quantity (20 mg, 0.065 mmol) in acetone (40 ml) followed by slow addition of $P(OC_8H_9)_3$ (29 mg, 0.072 mmol) in acetone (2 ml) (yield 33.5 mg, 76%). Spectroscopic analysis: $^{31}P\{H\}$ NMR ($CDCl_3$, 121.465 MHz, δ, p.p.m.): 124.1 [$^1J_{(\mathrm{Rh-P})}$ = 280 Hz]; IR (acetone): ν(CO) 1976 cm^{-1}; (KBr): ν(CO) 1980 cm^{-1}.

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Crystal data

$[Rh(C_9H_6NO)(C_{24}H_{27}O_3P)(CO)]$
$M_r = 669.49$
Triclinic, $P\overline{1}$
$a = 10.580$ (2) Å
$b = 10.944$ (2) Å
$c = 13.886$ (3) Å
$\alpha = 83.49$ (3)°
$\beta = 75.25$ (3)°
$\gamma = 88.58$ (3)°
$V = 1545.0$ (5) Å^3

$Z = 2$
$D_x = 1.439$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 925 reflections
$\theta = 5.5$–45.9°
$\mu = 0.65$ mm^{-1}
$T = 293$ (2) K
Plate, yellow
0.36 × 0.12 × 0.07 mm

Data collection

Bruker SMART CCD 1K area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{min} = 0.801$, $T_{max} = 0.956$
9255 measured reflections

6014 independent reflections
4122 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 26°$
$h = -12 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -17 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.097$
$S = 1.02$
6014 reflections
385 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 0.3605P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Rh—C10	1.805 (5)	P—O2	1.596 (3)
Rh—O4	2.029 (3)	P—O3	1.597 (3)
Rh—N	2.091 (3)	P—O1	1.610 (3)
Rh—P	2.1982 (13)	O5—C10	1.146 (5)
C10—Rh—N	97.11 (16)	O2—P—Rh	118.07 (11)
O4—Rh—N	80.34 (13)	O3—P—Rh	114.36 (10)
C10—Rh—P	90.31 (13)	O1—P—Rh	117.80 (11)
O4—Rh—P	92.87 (8)	O5—C10—Rh	177.6 (4)
O1—P—Rh—C10	−130.17 (18)	O3—P—Rh—C10	−6.13 (17)
O2—P—Rh—C10	107.74 (18)		

Table 2
Comparative geometrical data (Å, °, Hz) for $[Rh(OX)(CO)(PR_3)]$ complexes.

R	Rh—P	Rh—N	Rh—O	N—Rh—O	Θ_E	$^1J_{Rh-P}$
O(2,6-DMP)[a]	2.198 (1)	2.091 (3)	2.029 (3)	80.3 (1)	183	280
OPh[b]	2.186 (1)	2.097 (2)	2.022 (2)	80.8†	154	281
Ph[c]‡	2.261 (2)	2.098 (9)	2.042 (5)	80.0 (3)	153	161
Ph[d]	2.317 (2)	2.084 (7)	2.037 (4)	81.2 (2)	153	163

† Data extracted from the Cambridge Structural Database (Version 5.26; Allen, 2002); no s.u. values available. ‡ Rh^{III} iodomethane oxidative addition product containing apical *trans* methyl and iodo ligands. References: (*a*) this work (2,6-DMP = 2,6-dimethylphenyl); (*b*) Simanko *et al.* (2000); (*c*) Leipoldt *et al.* (1981); (*d*) van Aswegen *et al.* (1991).

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

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 1999); 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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References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Altomare, A. Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Aswegen, K. G. van, Leipoldt, J. G., Potgieter, I. M., Lamprecht, G. J., Roodt, A. & Van Zyl, G. J. (1991). *Transition Met. Chem.* **16**, 369–371.
Brandenburg, K. & Berndt, M. (2001). *DIAMOND*. Release 2.1e. Crystal Impact GbR, Bonn, Germany.
Bruker (1999). *SAINT-Plus*. Version 6.02 (including *XPREP*). Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1998). *SMART-NT* (Version 5.050) and *SADABS* (Version 2004/1). Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Ferguson, G., Roberts, P. J., Alyea, E. C. & Khan, M. (1978). *Inorg. Chem.* **17**, 2965–2967.
Leeuwen, P. W. N. M. van & Roobeek, C. F. (1983). *J. Organomet. Chem.* **258**, 343–350.
Leipoldt, J. G., Basson, S. S. & Dennis, C. R. (1981). *Inorg. Chim. Acta*, **50**, 121–124.
McCleverty, J. A. & Wilkinson, G. (1990). *Inorg. Synth.* **28**, 84–86.
Meijboom, R., Muller, A. & Roodt, A. (2004). *Acta Cryst.* E**60**, m455–m457.
Otto, S., Roodt, A. & Smith, J. (2000). *Inorg. Chim. Acta*, **303**, 295–299.
Roth, J. F., Craddock, J. H., Hershman, A. & Paulik, F. E. (1971). *Chem. Technol.* pp. 600–605.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Simanko, W., Mereiter, K., Schmid, R., Kirchner, K., Trzeciak, A. M. & Ziolkowski, J. J. (2000). *J. Organomet. Chem.* **602**, 59–64.
Tolman, C. A. (1977). *Chem. Rev.* **77**, 313–348.

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