metal-organic papers

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

J. Marthinus Janse van Rensburg,[a] Andreas Roodt[b]* and Alfred Muller[b]

[a]Department of Chemistry, University of Johannesburg, PO Box 524, Auckland Park, Johannesburg 2006, South Africa, and [b]Department of Chemistry, University of the Free State, PO Box 339, Bloemfontein 9300, South Africa

Correspondence e-mail: roodta.sci@mail.uovs.ac.za

Molecules of the title compound, [Rh(C$_9$H$_6$NO)-{(C$_{14}$H$_{21}$O)$_3$P}(CO)]·0.5(CH$_3$)$_2$CO, where (C$_9$H$_6$NO) = 8-hydroxyquinolinato and {(C$_{14}$H$_{21}$O)$_3$P} = tris(2,4-di-tert-butylphenyl)phosphite, pack in a tail-to-tail fashion with an intermolecular quinoline ligand-to-ligand π-stacking distance of 3.312 (1) Å. 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) Å.

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 [Rh(O*X*)(CO)$_2$], where O*X* is 8-hydroxyquinolinate (C$_9$H$_6$NO), leading to carbonyl substitution *trans* to the N atom, since this is the better σ-electron donor (Steyn *et al.*, 1997).
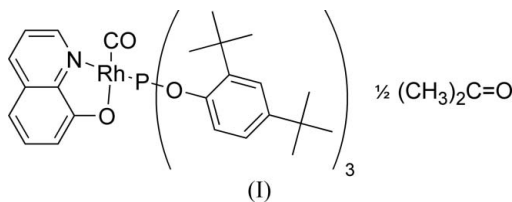
In (I) (Fig. 1), a dihedral angle of 3.4 (1)° exists between the benzene and pyridine rings of the oxine ligand, evidence of a slight distortion. Further distortion is observed between the bidentate oxine backbone and the metal coordination plane, as evident from the dihedral angle of 7.09 (8)°. The 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) Å from the coordination plane (r.m.s. displacement of fitted atoms = 0.005 Å), 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) Å (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
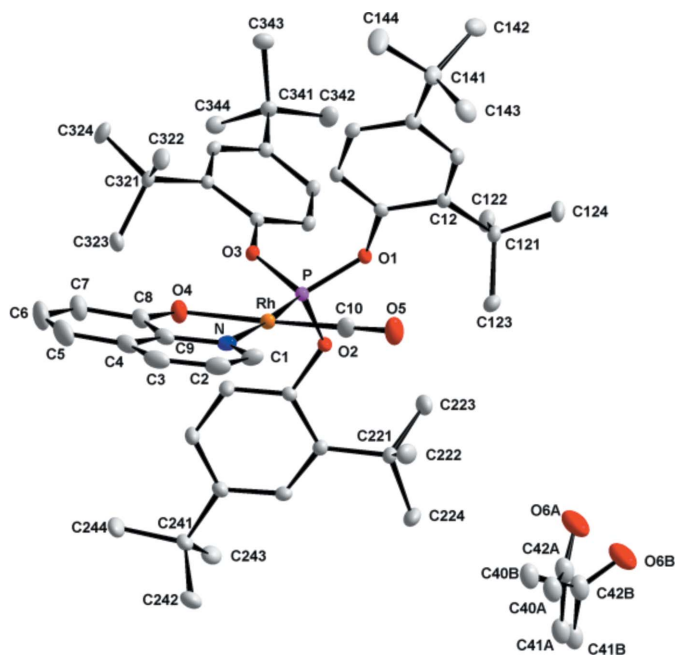
Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 30% probability level. H atoms have been omitted.
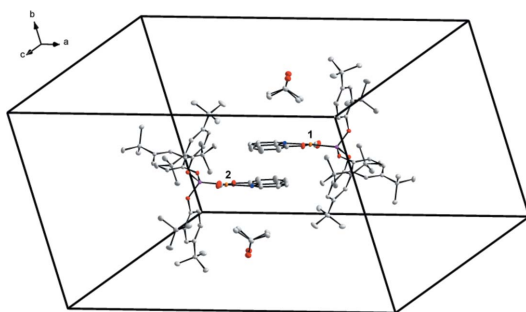

Figure 2
Part of the unit-cell contents viewed along the oxine plane, indicating oxine ligand-to-ligand π-stacking. [Symmetry operators for molecules 1 and 2: (1) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (2) $x, \frac{1}{2} - y, \frac{1}{2} + z$.]

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 $^1J_{(Rh-P)}$ coupling constants for the phosphite complexes compared to the

phosphine complexes. The comparable $^1J_{(Rh-P)}$ 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

Crystal data

[Rh(C$_9$H$_6$NO)(C$_{42}$H$_{63}$O$_3$P)(CO)]·0.5C$_3$H$_6$O	$Z = 8$
$M_r = 951$	$D_x = 1.175$ Mg m^{-3}
Orthorhombic, $Pccn$	Mo $K\alpha$ radiation
$a = 34.945$ (5) Å	$\mu = 0.39$ mm^{-1}
$b = 17.307$ (5) Å	$T = 150$ (2) K
$c = 17.778$ (5) Å	Block, yellow
$V = 10752$ (5) Å^3	$0.3 \times 0.28 \times 0.21$ mm

Data collection

Bruker X8 ApexII CCD diffractometer	86538 measured reflections
ω and φ scans	13332 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)	10688 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.892$, $T_{\max} = 0.922$	$R_{\text{int}} = 0.043$
	$\theta_{\max} = 28.3°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0709P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$+ 8.2813P]$
$wR(F^2) = 0.130$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{\max} = 0.002$
13332 reflections	$\Delta\rho_{\max} = 1.14$ e Å^{-3}
600 parameters	$\Delta\rho_{\min} = -0.48$ e Å^{-3}
H-atom parameters constrained	

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)

metal-organic papers

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

PR_3	Rh—P	Rh—N	Rh—O	N—Rh—O	Θ_E (°)	$^1J_{Rh-P}$ (Hz)
P(Obtbp)[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(Obtbp) = 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.* (2005*b*); (v) Janse van Rensburg *et al.* (2005*a*); (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 aniso-tropic displacement parameters were restrained to approximate isotropic behaviour. The highest peak in the difference density is located 0.16 Å from C14*B*.

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).

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.
Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Release 3.1b. Crystal Impact GbR, Bonn, Germany.
Bruker (2004). *SAINT-Plus* (Version 7.12) and *SADABS* (Version 2004/1). Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2005). *APEX2*. Version 1.0-27. Bruker AXS Inc., Madison, Wisconsin, USA.
Crous, R., Datt, M., Foster, D., Bennie, L., Steenkamp, C., Huyser, J., Kirsten, L., Steyl, G. & Roodt, A. (2005). *J. Chem. Soc. Dalton Trans.* pp. 1108–1116.
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.
Janse van Rensburg, J. M., Roodt, A., Muller, A. & Meijboom, R. (2005*a*). *Acta Cryst.* E**61**, m1741–m1743.
Janse van Rensburg, J. M., Roodt, A., Muller, A. & Meijboom, R. (2005*b*). *Acta Cryst.* E**61**, m2743–m2745.
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.
Otto, S., Roodt, A. & Smith, J. (2000). *Inorg. Chim. Acta*, **303**, 295–299.
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.
Steyn, G. J. J., Roodt, A., Poletaeva, I. & Varshavsky, Y. S. (1997). *J. Organomet. Chem.* **536–537**, 197–205.