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Chlorido(6-diphenylphosphino-2-pyridonato-κ^2P,N)-(6-diphenylphosphino-2-hydroxypyridine-κ^2P,N)-hydridoiridium(III) chloroform 1.896-solvate

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.030
wR factor = 0.066
Data-to-parameter ratio = 22.7

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

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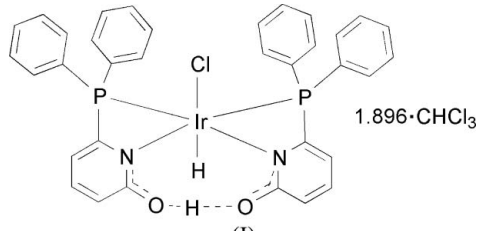
The title complex, $[Ir(C_{17}H_{13}NOP)ClH(C_{17}H_{14}NOP)]\cdot 1.896CHCl_3$, contains hydride, chloride, 6-diphenylphosphino-2-hydroxypyridine (pyphosH) and 6-diphenylphosphino-2-pyridonate (pyphos) ligands coordinated to an Ir^{III} metal centre to give a distorted octahedral coordination geometry. The two P and two N atoms of the pyphosH and pyphos ligands lie with a *cis* coordination in the equatorial plane. An intramolecular O—H···O hydrogen bond is observed between the pyphosH and pyphos ligands.

Comment

The 6-diphenylphosphino-1*H*-pyridin-2-one/6-diphenylphosphino-2-hydroxypyridine tautomer system is known to dimerize in aprotic solvents to form predominantly symmetrical pyridone dimers through hydrogen bonding (Breit & Seiche, 2003). Ruthenium (Chevallier & Breit, 2006) and rhodium (Breit & Seiche, 2003, 2005; Weis *et al.*, 2006) complexes having 2-pyridone/2-hydroxypyridine or analogous ligands serve as effective catalysts. Here, we report the synthesis and crystal structure of the title complex (I).



(I)

The Ir^{III} metal centre of (I) adopts a distorted octahedral coordination geometry. The two P and two N atoms of the pyphosH and pyphos ligands lie with *cis* coordination in the equatorial plane (Fig. 1). The Ir^{III} centre has two four-membered irida-chelate rings (Table 1) and an eight-membered irida-chelate ring containing an O—H···O hydrogen bond between the pyphosH and pyphos ligands (Table 2).

The axial chloride and hydride ligands are each disordered over two orientations with occupancies of 0.88 and 0.12. The Ir—P bond distances [2.2479 (8) and 2.2501 (7) Å] are shorter than those of the hydridoirida-β-diketone complex, $[IrH\{Ph_2P(o\text{-}C_6H_4O)_2H\}Cl]$ [2.347 (2) and 2.335 (2) Å; Garralda *et al.*, 2003].

Experimental

$[IrCl(coe)_2]_2$ (100.5 mg, 0.112 mmol; coe = cyclooctene) and 6-diphenylphosphino-2-pyridone (125.0 mg, 0.447 mmol) were loaded

into a Schlenk tube and degassed with a vacuum (0.5 h) and argon. Toluene (10 ml) was added to the solid and the mixture was stirred for 18 h at ambient temperature. The reaction mixture changed from a yellow to a pale-yellow suspension. Removal of volatile materials *in vacuo* and washing with diethyl ether (4 × 5 ml) afforded a pale-yellow powder [176.3 mg, 99.7%; m.p. 564 K (decomposition in capillary under vacuum)]. Single crystals of (I) suitable for X-ray analysis were grown from a solution in a chloroform–hexane mixture (1:1 *v*/*v*). ^{1}H NMR ($CDCl_3$, 300 MHz, 303 K, δ, p.p.m.): 18.29 (*s*, 1H, OH), 6.38–7.98 (*m*, 66H, Ph+NC_5H_3), −17.59 (*t*, 1H, IrH); ^{31}P{^{1}H} NMR ($CDCl_3$, 121.48 MHz, 303 K, δ, p.p.m.): −62.05 (*s*); IR (KBr tablet, cm^{-1}): 3419 (*br*, *m*, ν_{O-H}), 2294 (*br*, *m*, ν_{Ir-H}), 1653 (*vs*, $\nu_{C=O}$).

Crystal data

$[Ir(C_{17}H_{13}NOP)ClH\text{-}(C_{17}H_{14}NOP)]\cdot 1.896CHCl_3$
M_r = 1013.22
Monoclinic, $P2_1/n$
a = 11.2208 (14) Å
b = 14.8301 (15) Å
c = 23.188 (3) Å
β = 94.284 (6)°
V = 3847.8 (8) Å^3
Z = 4
D_x = 1.749 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 4.06 mm^{-1}
T = 120 (1) K
Prism, yellow
0.60 × 0.30 × 0.20 mm

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.254, T_{max} = 0.481
(expected range = 0.234–0.444)
94476 measured reflections
11703 independent reflections
10697 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 30.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.066
S = 1.07
11703 reflections
515 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0184P)^2 + 12.9527P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 1.63 e Å^{-3}
$\Delta\rho_{min}$ = −1.06 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ir—N2	2.161 (2)	Ir—P2	2.2503 (7)
Ir—N1	2.167 (2)	Ir—Cl1*A*	2.4602 (7)
Ir—P1	2.2479 (7)		
N2—Ir—N1	111.23 (9)	P1—Ir—P2	111.55 (2)
N2—Ir—P1	179.50 (7)	N2—Ir—Cl1*A*	88.17 (6)
N1—Ir—P1	68.63 (6)	N1—Ir—Cl1*A*	88.10 (7)
N2—Ir—P2	68.51 (6)	P1—Ir—Cl1*A*	92.31 (2)
N1—Ir—P2	172.01 (7)	P2—Ir—Cl1*A*	99.84 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1···O1	1.09 (4)	1.35 (4)	2.398 (3)	158 (4)
C28—H28···Cl1*A*	0.95	2.75	3.502 (3)	137

Two sites of chloroform solvent molecules were found in the electron-density map. One chloroform solvent molecule was refined successfully. The other was poorly defined, and five positions (occupancy factors 0.14, 0.24, 0.15, 0.156 and 0.21) could be assigned for it in the difference Fourier map. These occupancy factors for the disordered chloroform solvates were refined anisotropically in the intial refinement cycles and then were fixed in the final refinement cycles. The atoms of the disordered chloroform solvent molecule were refined isotropically. The Cl—C and Cl···Cl bonds for the disordered chloroform solvent molecule were restrained to 1.76 (2) and 2.89 (2) Å, respectively. The hydrido ligand H0*A* and the H atom of the hydroxy group were located in a difference Fourier map and refined isotropically, with U_{iso}(H0*A*) = 1.2U_{eq}(Ir) and U_{iso}(H1) = 1.2U_{eq}(O2). Probable positions of the disordered hydrido ligand H0*B* were calculated at potential energy minima using the program *HYDEX* (Orpen, 1980). The remaining H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H distances in the range 0.95–1.00 Å, and with U_{iso}(H) = 1.2U_{eq}(C), or 1.5U_{eq}(C) for methyl groups. The intramolecular hydrogen bond (O2···H1···O1) is almost symmetrical, with O2···H1 = 1.09 (4) Å and H1···O1 = 1.35 (4) Å. The highest residual electron density peak is located 0.97 Å from atom Cl12 and the deepest hole is located 0.77 Å from atom Cl2.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *TEXSAN* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: modified *SHELXL97*.

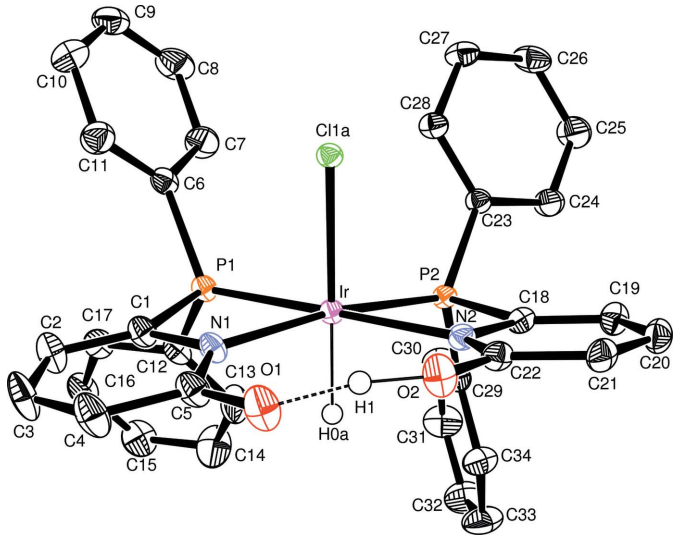


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The chloroform solvent molecules and carbon-bound H atoms have been omitted, as have the disordered hydride and chloride ligands. The remaining H atoms are represented by circles of arbitrary size, and the dashed line denotes a hydrogen bond.

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References

Breit, B. & Seiche, W. (2003). *J. Am. Chem. Soc.* **125**(22), 6608–6609.
Breit, B. & Seiche, W. (2005). *Angew. Chem. Int. Ed.* **44**, 1640–1643.

Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
Chevallier, F. & Breit, B. (2006). *Angew. Chem. Int. Ed.* **45**, 1599–1602.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Garralda, M. A., Hernandez, R., Ibarlucea, L., Pinilla, E. & Torres, M. R. (2003). *Organometallics*, **22**, 3600–3603.
Higashi, H. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Orpen, A. G. (1980). *J. Chem. Soc. Dalton Trans.* pp. 2509–2516.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2004). *TEXSAN*. Version 2.0. Rigaku/MSC, The Woodlands, Texas, USA.
Sheldrick, G. M. (1997). *SHELXL97*. Release 97-2. University of Göttingen, Germany.
Weis, M., Waloch, C., Seiche, W. & Breit, B. (2006). *J. Am. Chem. Soc.* **128**, 4188–4189.