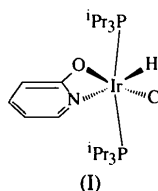Richards, S., Pedersen, B., Silverton, J. V. & Hoard, J. L. (1964). *Inorg. Chem.* **3**, 27–33.

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Chlorohydrido[2(1H)-pyridonato-N,O]bis-[tris(1-methylethyl)phosphine]iridium(III)

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Abstract

The title compound, [IrCl(H)(C₅H₄NO)(C₉H₂₁P)₂], is a mononuclear complex of chelated 2(1H)-pyridone exhibiting distorted octahedral geometry, in which the phosphine ligands tilt away from the N atom towards the assumed hydrido ligand.

Comment

2(1H)-Pyridonato ligands commonly bridge two metals (Cotton, Fanwick, Niswander & Sekutowski, 1978; Rodman & Mann, 1988; Sherlock, Cowie, Singleton & de V. Steyn, 1989). A more unusual coordination mode involves N,O-chelation (Clegg, Berry & Garner, 1980; Rodman & Mann, 1985; Lahuerta, Latorre, Sanaú, Cotton & Schwotzer, 1988; Morrison, Palmer & Tocher, 1988; Leeaphon, Fanwick & Walton, 1991; Steed & Tocher, 1992). A structurally uncharacterized complex was reported to contain both N,O-chelating and mono-coordinate pyridonato ligands (Lahuerta, Latorre, Sanaú, Cotton & Schwotzer, 1988). We envisaged that mononuclear complexes of Ir with 2(1H)-pyridone would be formed with a sterically hindered ligand environment. Thus, 2(1H)-pyridone was combined with two moles of ^{i}Pr₃P and 0.5 moles of the Ir^I derivative [(C₈H₁₄)₂Ir(μ-Cl)]₂ to provide a diamagnetic oxidative addition product whose IR and ^{1}H NMR spectral properties clearly indicated that an isomer of the title compound, (I), had been formed. In particular, the presence of a hydride

ligand on the metal was strongly implicated by an IR absorption at $2236 \, \text{cm}^{-1}$ and a ^{1}H NMR resonance at exceptionally high field, δ -25.47 p.p.m. (Muetterties, 1971). However, because neither the coordination mode of the heterocycle nor the stereochemistry about the Ir center were clear from spectral data, an X-ray structure determination was undertaken.

(I)

Initial refinement indicated coordination of five non-H atoms to Ir in a distorted octahedral arrangement. However, because IR and NMR spectral evidence point to the presence of a hydrido ligand on the metal, an unsuccessful attempt was made to determine the hydride atom position. The largest Fourier difference peak prior to the final refinement was designated as the missing hydride and its positional and isothermal parameters were allowed to refine. Although the refined hydride position corresponded approximately to the sixth octahedral site in direction, the Ir—H bond distance of 1.18 (12) Å was well outside that of other metal–hydride bond distances established by neutron diffraction (see, for example, Garlaschelli, Khan, Bau, Longoni & Koetzle, 1985). Therefore, we did not consider the hydride position to be accurately determined; a situation that has been encountered by others (Lavin, Holt & Crabtree, 1989; Luo, Schulte & Crabtree, 1990). We subsequently removed the proposed hydride atom and performed the final refinement of the parameters given here.

The most prominent distortions of the complex (shown in Fig. 1) from idealized octahedral geometry include the acute N—Ir—O bond angle of 62.4 (3)°, which is an inescapable consequence of chelation of the heterocycle. Furthermore, tilting of the bulky phosphine ligands away from the N atom of the heterocycle and toward the assumed hydride is revealed by large P—Ir—N angles [95.4 (2) and 97.8 (2)°] and a small P—Ir—P angle [165.4 (1)°]. In contrast, the P—Ir—Cl and P—Ir—O angles are near the ideal octahedral value. The N—Ir—O angles are within the normal range shown by the aforementioned N,O-chelate complexes and tilting of phosphine ligands towards a hydride has been observed previously (Luo, Schulte & Crabtree, 1990). Among N,O-chelate complexes, (I) exhibits unexceptional Ir—Cl and Ir—O bond lengths. The Ir—N distance [2.214 (7) Å], however, somewhat exceeds the largest value [2.166 (6) Å; Steed & Tocher, 1992] found for this class of complex. The high *trans* influence of the hydrido ligand may be responsible for this lengthening of the Ir—N bond (Lavin, Holt & Crabtree, 1989).
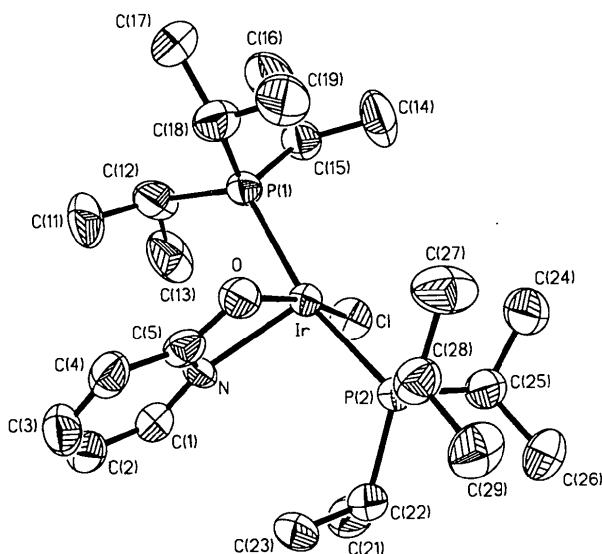
Fig. 1. The structure of the title compound shown with 50% probability displacement ellipsoids. H atoms are omitted for clarity.
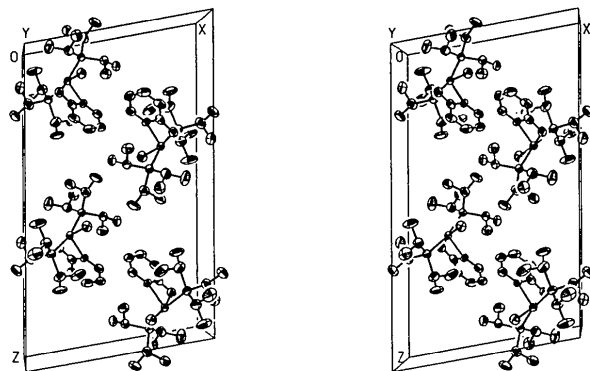

Fig. 2. Stereoview of the packing in the unit cell of the title compound.

Experimental

An NMR tube was charged with $[(C_8H_{14})_2Ir(\mu\text{-}Cl)]_2$ (35.4 mg, 0.0395 mmol), $2(1H)$-pyridone (7.6 mg, 0.0799 mmol) and deoxygenated C_6D_6 (0.5 ml). To the resulting yellow–orange suspension was added $^iPr_3P$ (31 μl, 0.159 mmol) by syringe, leading to a clear dark yellow solution. After 24 h, chromatography (SiO_2, ethyl acetate/hexanes 1:15) afforded (I) as pale yellow crystals in 68–76% yield. Crystallization was carried out from hexanes/benzene/methanol. ^1H NMR (C_6D_6): δ 8.20 (d, $J = 5$ Hz, 1H), 6.84 (dt, $J = 2$, 8 Hz, 1H), 6.20 (t, $J = 6$ Hz, 1H), 5.85 (d, $J = 8$ Hz, 1H), 2.46–2.66 (m, 6H), 1.31 (q, $J = 7$ Hz, 18H), 1.11 (q, $J = 7$ Hz, 18H), −25.47 p.p.m. (t, $J = 12.8$ Hz, 1H, Ir—H); $^{13}C\{^1H\}$ NMR: δ 181.2, 147.5, 136.9, 129.0, 128.9, 22.4 (t, $J = 13$ Hz), 19.1 p.p.m.; IR (KBr): 2236 cm^{-1} (s, Ir—H). Analysis: calculated for $C_{23}H_{47}ClIrNOP_2$, C 42.94, H 7.38, N 2.18%; found C 42.98, H 7.31, N 2.36%.

Crystal data

$[IrCl(H)(C_5H_4NO)(C_9H_{21}P)_2]$
$M_r = 643.2$
Monoclinic
$P2_1/c$
$a = 13.660\,(3)$ Å
$b = 8.940\,(2)$ Å
$c = 23.207\,(7)$ Å
$\beta = 100.14\,(2)°$
$V = 2789.8\,(12)$ Å^3
$Z = 4$
$D_x = 1.531$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5$–$15°$
$\mu = 5.010$ mm^{-1}
$T = 298$ K
Parallelepiped
$0.24 \times 0.24 \times 0.11$ mm
Pale amber

Data collection

Siemens $R3m/V$ diffractometer
ω scans
Absorption correction:
  ψ scan of six reflections
  (*SHELXTL/PC*; Sheldrick, 1990)
  $T_{min} = 0.435$, $T_{max} = 0.937$
3782 measured reflections
3670 independent reflections

2727 observed reflections
  $[F > 4\sigma(F)]$
$R_{int} = 0.0192$
$\theta_{max} = 22.5°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 24$
3 standard reflections
  monitored every 47
  reflections
  intensity decay: <1%

Refinement

Refinement on F^2
$R(F) = 0.0356$
$wR(F^2) = 0.0472$
$S = 0.83$
2727 reflections
263 parameters
H atoms refined as riding
$w = 1/[\sigma^2(F) + 0.0020F^2]$
$(\Delta/\sigma)_{max} = 0.013$
$\Delta\rho_{max} = 0.98$ e Å^{-3}
  (<1.5 Å from Ir)
$\Delta\rho_{min} = -0.63$ e Å^{-3}

Extinction correction:
  $F^* = F[1 + (0.002\chi$
    $\times F^2/\sin2\theta)]^{-1/4}$
Extinction coefficient:
  $\chi = 6\,(2) \times 10^{-5}$
Atomic scattering factors
  from *International Tables
  for X-ray Crystallography*
  (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ir	0.2539 (1)	0.1412 (1)	0.1161 (1)	0.037 (1)
Cl	0.3420 (2)	−0.0745 (3)	0.0944 (1)	0.056 (1)
P(1)	0.1465 (2)	−0.0049 (3)	0.1609 (1)	0.046 (1)
P(2)	0.3275 (2)	0.2859 (3)	0.0512 (1)	0.040 (1)
O	0.2000 (5)	0.3347 (8)	0.1514 (3)	0.048 (3)
N	0.3401 (5)	0.2300 (9)	0.1987 (3)	0.036 (3)
C(1)	0.4202 (8)	0.2223 (14)	0.2408 (4)	0.053 (4)
C(2)	0.4329 (9)	0.3219 (14)	0.2864 (5)	0.064 (5)
C(3)	0.3649 (10)	0.4322 (17)	0.2877 (5)	0.071 (5)
C(4)	0.2811 (9)	0.4457 (13)	0.2444 (5)	0.059 (4)
C(5)	0.2716 (8)	0.3400 (11)	0.1974 (5)	0.048 (4)
C(11)	0.1943 (11)	0.0507 (18)	0.2840 (5)	0.099 (7)
C(12)	0.1908 (9)	−0.0711 (15)	0.2379 (5)	0.068 (5)
C(13)	0.2923 (11)	−0.1451 (16)	0.2407 (6)	0.091 (6)
C(14)	0.0716 (12)	−0.1620 (16)	0.0563 (5)	0.100 (7)
C(15)	0.1155 (9)	−0.1831 (12)	0.1210 (5)	0.059 (4)
C(16)	0.0551 (11)	−0.3014 (16)	0.1471 (6)	0.097 (7)
C(17)	−0.0455 (9)	0.0167 (18)	0.1951 (6)	0.094 (7)
C(18)	0.0329 (9)	0.0984 (14)	0.1663 (6)	0.067 (5)
C(19)	−0.0171 (9)	0.1741 (19)	0.1106 (6)	0.095 (7)

C(21)	0.5264 (8)	0.2378 (17)	0.0991 (5)	0.073 (5)
C(22)	0.4530 (7)	0.3636 (13)	0.0777 (4)	0.052 (4)
C(23)	0.4540 (9)	0.4864 (13)	0.1249 (5)	0.066 (5)
C(24)	0.2562 (9)	0.1037 (18)	−0.0483 (6)	0.096 (7)
C(25)	0.3477 (8)	0.1743 (13)	−0.0134 (5)	0.056 (4)
C(26)	0.4090 (10)	0.2444 (20)	−0.0536 (5)	0.096 (7)
C(27)	0.1435 (8)	0.4186 (16)	0.0038 (6)	0.087 (6)
C(28)	0.2509 (8)	0.4546 (13)	0.0281 (5)	0.060 (4)
C(29)	0.2930 (9)	0.5684 (14)	−0.0104 (6)	0.073 (5)

Table 2. *Selected geometric parameters (Å, °)*

Ir—Cl	2.374 (3)	Ir—P(1)	2.339 (3)
Ir—P(2)	2.341 (3)	Ir—O	2.102 (7)
Ir—N	2.214 (7)	P(1)—C(12)	1.879 (12)
P(1)—C(15)	1.854 (11)	P(1)—C(18)	1.829 (13)
P(2)—C(22)	1.852 (10)	P(2)—C(25)	1.863 (12)
P(2)—C(28)	1.860 (12)	O—C(5)	1.316 (12)
N—C(1)	1.334 (12)	N—C(5)	1.354 (13)
C(1)—C(2)	1.370 (17)	C(2)—C(3)	1.359 (19)
C(3)—C(4)	1.390 (16)	C(4)—C(5)	1.430 (16)
C(11)—C(12)	1.522 (19)	C(12)—C(13)	1.528 (20)
C(14)—C(15)	1.527 (15)	C(15)—C(16)	1.530 (19)
C(17)—C(18)	1.543 (20)	C(18)—C(19)	1.511 (18)
C(21)—C(22)	1.529 (17)	C(22)—C(23)	1.550 (16)
C(24)—C(25)	1.503 (16)	C(25)—C(26)	1.495 (19)
C(27)—C(28)	1.511 (15)	C(28)—C(29)	1.531 (18)
Cl—Ir—P(1)	91.2 (1)	Cl—Ir—P(2)	91.2 (1)
P(1)—Ir—P(2)	165.4 (1)	Cl—Ir—O	167.6 (2)
P(1)—Ir—O	89.8 (2)	P(2)—Ir—O	90.9 (2)
Cl—Ir—N	105.2 (2)	P(1)—Ir—N	95.4 (2)
P(2)—Ir—N	97.8 (2)	O—Ir—N	62.4 (3)
Ir—P(1)—C(12)	118.5 (4)	Ir—P(1)—C(15)	111.4 (4)
C(12)—P(1)—C(15)	102.2 (5)	Ir—P(1)—C(18)	110.8 (4)
C(12)—P(1)—C(18)	103.2 (6)	C(15)—P(1)—C(18)	110.2 (5)
Ir—P(2)—C(22)	118.1 (4)	Ir—P(2)—C(25)	111.3 (4)
C(22)—P(2)—C(25)	102.0 (5)	Ir—P(2)—C(28)	110.5 (4)
C(22)—P(2)—C(28)	103.5 (5)	C(25)—P(2)—C(28)	110.9 (5)
Ir—O—C(5)	94.9 (6)	Ir—N—C(1)	149.2 (7)
Ir—N—C(5)	88.9 (5)	C(1)—N—C(5)	121.9 (9)
N—C(1)—C(2)	120.6 (10)	C(1)—C(2)—C(3)	119.7 (10)
C(2)—C(3)—C(4)	121.7 (12)	C(3)—C(4)—C(5)	116.5 (11)
O—C(5)—N	113.8 (9)	O—C(5)—C(4)	126.6 (10)
N—C(5)—C(4)	119.5 (9)	P(1)—C(12)—C(11)	114.2 (9)
P(1)—C(12)—C(13)	108.3 (9)	C(11)—C(12)—C(13)	111.3 (10)
P(1)—C(15)—C(14)	113.6 (8)	P(1)—C(15)—C(16)	119.2 (9)
C(14)—C(15)—C(16)	109.2 (10)	P(1)—C(18)—C(17)	117.0 (9)
P(1)—C(18)—C(19)	115.4 (10)	C(17)—C(18)—C(19)	109.8 (10)
P(2)—C(22)—C(21)	110.3 (8)	P(2)—C(22)—C(23)	113.1 (8)
C(21)—C(22)—C(23)	111.6 (8)	P(2)—C(25)—C(24)	115.5 (9)
P(2)—C(25)—C(26)	117.1 (9)	C(24)—C(25)—C(26)	110.1 (10)
P(2)—C(28)—C(27)	113.3 (9)	P(2)—C(28)—C(29)	117.3 (8)
C(27)—C(28)—C(29)	111.3 (10)		

The initial structure solution was obtained using Patterson synthesis (*SHELXTL/PC*; Sheldrick, 1990) to give the position of the Ir atom. Subsequent difference Fourier maps revealed the remaining non-H atoms. The plots were produced using the *SP* program in the *SHELXTL/PC* package.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1010). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(methanol-O)(2,3,7,8,12,13,17,18-octaethylporphyrinato-N,N',N'',N''')-iron(III) Perchlorate Bis(methanol) Solvate, [Fe^III(oep)(HOCH_3)_2](ClO_4).2CH_3OH

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Abstract

Simple treatment of [Fe^III(oep)Cl] (where oep is octaethylporphyrin) with dilute perchloric acid leads to facile preparation of the title compound, [Fe(C_{36}H_{44}N_4)(CH_4O)_2](ClO_4).2CH_4O. The structure consists of discrete [Fe(oep)(HOCH_3)_2]^+ cations, perchlorate anions and methanol molecules of solvation, which are connected by hydrogen bonds in an infinite network. The Fe atom is located in the plane of the N atoms and is coordinated by two methanol O atoms in the axial positions, with an average Fe—N distance of 2.026 (3) Å and Fe—O bond lengths of 2.159 (3) Å.

Comment

The study of spin state and stereochemistry in iron porphyrins has been of continuing interest because of natural processes involving hemoproteins (Hoard, 1971; Scheidt & Reed, 1981; Scheidt & Lee, 1987). During synthetic studies on iron octaethylporphyrin (oep) derivatives, it was found that simple treatment of