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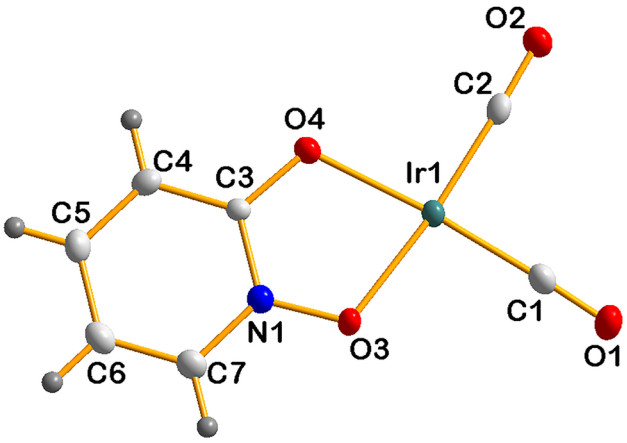
Crystal structure of dicarbonyl(2-oxopyridin-1(2*H*)-olato-$\kappa^2 O,O$)iridium(I), $C_7H_4IrNO_4$



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Abstract

$C_7H_4IrNO_4$, triclinic, $P\bar{1}$ (no. 2), a = 3.5665(2) Å, b = 10.8307(5) Å, c = 10.8865(5) Å, α = 72.9610(10)°, β = 83.631(2)°, γ = 89.189(2)°, V = 399.51(3) Å^3, Z = 2, $R_{gt}(F)$ = 0.0484, $wR_{ref}(F^2)$ = 0.0201, T = 100 K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of materials

The complex was synthesized by modifying the method used before by reduction of hydrated $IrCl_3$ in DMF, which was refluxed for approximately 20 min to give a yellow solution of di-μ-chloro-tetra-carbonyldiiridium(I), $[IrCl(CO)_2]_2$.[5–7]

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Table 1: Data collection and handling.

Crystal:	Red needle
Size:	0.10 × 0.04 × 0.02 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	16.7 mm^{-1}
Diffractometer, scan mode:	Bruker (Venture), $\theta/2\theta$ scans
θ_{max}, completeness:	28.4°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13437, 2009, 0.042
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1,978
$N(param)_{refined}$:	118
Programs:	SHELX[1], Bruker[2], Olex2[3], Diamond[4]

The addition of an equivalent of 2-oxopyridine (opoH) to the aforementioned yellow solution followed by addition of ice water to precipitate the dicarbonyliridium(I) complex, $[Ir(opo)(CO)_2]$. The precipitate was filtered off and dried. Red needle crystals were obtained from DCM and benzene.

2 Experimental details

The aromatic H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with fixed C–H distances for aromatic C–H of 0.93 Å (C–H) [U_{iso}(H) = 1.2U_{eq}]. The graphics were obtained using the DIAMOND[4] program with 50 % probability ellipsoids.

3 Comment

Important stages in many catalytic processes, like the carbonylation of methanol, are represented by oxidative addition reactions to metal complexes.[5] Research has shown that in the catalytic cycles of some processes, the oxidative addition phase is the rate-determining step. Consequently, any alteration to this step may dictate the trajectory of the whole catalytic cycle. Owing to the importance of this reaction, a great deal of study has been done on oxidative addition processes to comprehend its kinetic behavior and reactions to both internal and external influences.[6,7] There has been much discussion regarding the synthesis of M(I) and M(III) complexes (M = Rh and Ir). Many studies involve the synthesis of the precursor complex $[M(L,L'\text{-BID})(CO)_2]$, in

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}^*/U_{eq}
Ir1	0.52333 (4)	0.31437 (2)	0.27591 (2)	0.01459 (6)
O1	0.7167 (12)	0.1772 (4)	0.0776 (3)	0.0310 (8)
O2	0.7426 (10)	0.5685 (3)	0.0830 (3)	0.0249 (7)
O4	0.3791 (9)	0.3916 (3)	0.4231 (3)	0.0190 (6)
O3	0.3683 (9)	0.1513 (3)	0.4225 (3)	0.0188 (6)
C3	0.2335 (11)	0.3036 (4)	0.5300 (4)	0.0128 (7)
N1	0.2294 (11)	0.1782 (4)	0.5296 (4)	0.0181 (7)
C7	0.0797 (13)	0.0822 (4)	0.6377 (4)	0.0202 (8)
H7	0.075533	−0.005285	0.636924	0.024*
C6	−0.0632 (12)	0.1147 (5)	0.7464 (4)	0.0207 (8)
H6	−0.165828	0.049568	0.821465	0.025*
C5	−0.0574 (12)	0.2436 (5)	0.7467 (4)	0.0201 (8)
H5	−0.155687	0.265986	0.821916	0.024*
C4	0.0891 (13)	0.3374 (4)	0.6389 (4)	0.0186 (8)
H4	0.092059	0.425238	0.638630	0.022*
C1	0.6452 (13)	0.2322 (4)	0.1517 (4)	0.0212 (9)
C2	0.6604 (13)	0.4695 (4)	0.1557 (4)	0.0192 (8)

which one of the carbonyl ligands may be replaced by tertiary phosphine ligands to form [M(L,L′-BID)(CO)(PX_3)], where M represents Rh or Ir, L,L′-BID represents monocharged bidentate ligands with different donor atoms (L,L′) such as *O,O′*, *O,N*, *O,S*, and *N,S*, and PX_3 represents various neutral monodentate tertiary phosphine ligands.[5–22]

The 2-oxopyridine (opoH) ligand of the title complex was selected because of its small bite angle, forming a five-membered metallocycle ring when coordinated.

In the title structure, a slightly distorted square planar geometry is observed indicated by the small bite angle of 79.661(2)° for O3–Ir1–O4. The angles between the other atoms of the coordination sphere are affected as a consequence of the small bite angle and have values differing from the ideal 90°; 89.492(2)° for C1–Ir1–C2, 94.903(2)° for C2–Ir1–O4 and 95.942(2)° for C1–Ir1–O3. The Ir1–O3, Ir1–O4, Ir1–C1 and Ir1–C2 bond distances are 2.0372(1), 2.0302(1), 1.8371(1) and 1.8350(1) Å, respectively.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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