

Structure of the Precursor of an Iridium-Containing Hydrogenation Catalyst

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(Received 18 November 1988; accepted 13 December 1988)

Abstract. (η^4 -1,5-Cyclooctadiene)bis(pyridine)-iridium(I) tetraphenylborate, $[\text{Ir}(\text{C}_8\text{H}_{12})(\text{C}_5\text{H}_5\text{N})_2]\text{B}(\text{C}_6\text{H}_5)_4$, $M_r = 777.8$, monoclinic, $P2_1/c$, $a = 13.367$ (8), $b = 14.431$ (7), $c = 18.289$ (10) Å, $\beta = 103.88$ (5)°, $U = 3424.8$ Å³, $Z = 4$, $D_x = 1.51$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 39.1$ cm⁻¹, $F(000) = 1560$, $T = 295$ K, $R = 0.040$, $wR = 0.060$, $(\Delta/\sigma)_{\text{max}} = 0.01$ for 3569 reflections with $|F^2| > \sigma(F^2)$. The geometry at iridium is approximately square planar. Ir–N(1) = 2.103 (8), Ir–N(2) = 2.084 (8) Å, N(1)–Ir–N(2) = 84.5 (3), M1–Ir–N(1) = 93.2, M1–Ir–M2 = 88.7, M2–Ir–N(2) = 93.7°, where M1 and M2 are the midpoints of the C=C double bonds.

Experimental. The complex was prepared by the addition of pyridine to $[\{\text{Ir}(\text{cod})\text{Cl}\}_2]$ followed by the addition of Na[BPh₄] (Crabtree & Morehouse, 1986). Well formed yellow needles obtained by slow diffusion of pentane into a solution in dichloromethane. Data collected using a crystal ca 0.2 × 0.2 × 0.1 mm, Enraf–Nonius CAD-4 diffractometer, monochromated Mo $K\alpha$ radiation, θ –2 θ mode, with $\Delta\theta = (0.8 + 0.35 \tan\theta)^\circ$ and a maximum scan time of 1 min. A total of 6550 unique reflections were measured for $2 < \theta < 25^\circ$ and $+h+k \pm l$. After averaging equivalent reflections ($R_{\text{av}} = 0.039$) there were 6285 unique reflections of which 3569 with $|F^2| > \sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}$ /Lp. There was no crystal decay. An absorption correction was applied using DIFABS (Walker & Stuart, 1983) after isotropic refinement, and gave maximum and minimum corrections of 1.28 and 0.81. The structure was solved by routine heavy-atom methods and refined by full-matrix least squares with non-hydrogen atoms anisotropic. Hydrogen atoms were fixed at calculated positions with $B_{\text{iso}} = 1.3 B_{\text{eq}}$ for the C atoms to which they are bonded. The weighting scheme was $w = 1/\sigma^2(F)$ and the final residuals were $R = 0.040$ and $wR = 0.060$, $S = 1.66$, $(\Delta/\sigma)_{\text{max}} = 0.01$, for 415 variables. A final difference map had maximum values of +0.68 and –0.73 e Å⁻³. Programs from the Enraf–Nonius SDP Plus package were run on a MicroVAX computer. Positional parameters and equivalent isotropic temperature factors for the non-hydrogen atoms are given in Table 1, selected

distances and angles in Table 2.* Fig. 1 shows the molecular structure and numbering scheme.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, complete intramolecular distances and angles, least-squares planes and a packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51679 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors with estimated standard deviations in parentheses

$$B_{\text{eq}} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{\text{eq}}(\text{Å}^2)$
Ir	2079.6 (3)	2417.8 (2)	1747.2 (2)	3.18 (1)
N(1)	3234 (7)	2276 (6)	2749 (5)	4.2 (2)
N(2)	1740 (6)	3652 (5)	2228 (4)	3.6 (2)
C(1)	2903 (9)	1521 (8)	1174 (7)	4.7 (3)
C(2)	2123 (10)	1008 (8)	1413 (7)	5.3 (3)
C(3)	1162 (11)	701 (9)	905 (8)	7.0 (4)
C(4)	213 (11)	1367 (10)	847 (9)	7.6 (4)
C(5)	638 (10)	2350 (8)	986 (7)	5.1 (3)
C(6)	1278 (8)	2811 (8)	641 (6)	4.5 (3)
C(7)	1732 (12)	2362 (9)	47 (7)	6.4 (4)
C(8)	2757 (11)	1865 (10)	354 (8)	6.9 (4)
C(9)	4004 (7)	2920 (8)	2899 (6)	3.9 (2)
C(10)	4699 (10)	2989 (9)	3607 (6)	5.8 (3)
C(11)	4631 (11)	2340 (9)	4120 (7)	6.0 (3)
C(12)	3832 (9)	1661 (8)	3970 (6)	5.1 (3)
C(13)	3190 (8)	1636 (7)	3277 (6)	4.3 (3)
C(14)	1342 (8)	3643 (7)	2839 (6)	4.4 (3)
C(15)	1280 (11)	4431 (9)	3254 (7)	6.2 (3)
C(16)	1632 (10)	5240 (8)	3026 (7)	5.3 (3)
C(17)	2058 (10)	5263 (7)	2395 (7)	4.9 (3)
C(18)	2077 (8)	4475 (7)	2020 (6)	4.2 (2)
B	2936 (9)	8301 (7)	3312 (6)	3.1 (2)
C(19)	3228 (7)	7394 (6)	3839 (5)	2.9 (2)
C(20)	2668 (9)	7037 (7)	4347 (6)	4.3 (3)
C(21)	2914 (9)	6220 (8)	4740 (6)	5.0 (3)
C(22)	3725 (9)	5699 (8)	4643 (6)	5.0 (3)
C(23)	4251 (9)	6002 (8)	4148 (7)	5.5 (3)
C(24)	4059 (8)	6833 (7)	3776 (6)	4.7 (3)
C(25)	2323 (7)	7909 (6)	2480 (5)	2.9 (2)
C(26)	2878 (7)	7669 (7)	1943 (5)	3.8 (2)
C(27)	2416 (11)	7290 (8)	1240 (6)	5.8 (3)
C(28)	1352 (9)	7166 (9)	1053 (6)	4.7 (3)
C(29)	788 (8)	7342 (8)	1587 (7)	5.0 (3)
C(30)	1277 (7)	7723 (7)	2250 (5)	3.5 (2)
C(31)	2173 (7)	9025 (6)	3634 (5)	2.7 (2)
C(32)	2284 (9)	9185 (7)	4402 (5)	4.2 (3)
C(33)	1660 (8)	9795 (8)	4694 (6)	4.3 (3)
C(34)	883 (10)	10284 (8)	4204 (7)	5.9 (3)
C(35)	782 (8)	10174 (8)	3442 (6)	4.4 (3)
C(36)	1403 (8)	9546 (7)	3168 (6)	4.2 (2)
C(37)	3931 (6)	8924 (6)	3297 (5)	2.9 (2)
C(38)	4032 (7)	9472 (7)	2696 (6)	3.5 (2)
C(39)	4871 (10)	10088 (7)	2732 (7)	6.0 (3)
C(40)	5620 (9)	10160 (8)	3388 (8)	5.9 (3)
C(41)	5518 (9)	9661 (9)	3971 (8)	6.5 (4)
C(42)	4711 (9)	9043 (9)	3958 (7)	5.6 (3)

Table 2. Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

Ir—N(1)	2.103 (8)	Ir—N(2)	2.084 (8)
Ir—C(1)	2.131 (12)	Ir—C(2)	2.129 (11)
Ir—C(5)	2.091 (11)	Ir—C(6)	2.127 (11)
Ir—M1	2.005	Ir—M2	1.997
M1—Ir—M2	88.7	M1—Ir—N(1)	93.2
M1—Ir—N(2)	175.8	M2—Ir—N(1)	178.1
M2—Ir—N(2)	93.7	N(1)—Ir—N(2)	84.5 (3)

M1 and M2 are the midpoints of the C(1)—C(2) and C(5)—C(6) bonds.

Related literature. This complex is the immediate precursor of $[\text{Ir}(\text{cod})(\text{py})(\text{PCy}_3)]$, which has been of considerable value as a hydrogenation catalyst (Crabtree, 1979). The conformations of cod in $[\{\text{Ir}(\text{cod})\text{Cl}\}_2]$ and $[\text{Ir}_2(\text{cod})_2\text{Cl}_2(\mu_2\text{-OH})_2(\mu\text{-O})]$ (Cotton, Lahuerta, Sanau & Schwotzer, 1986) are similar to those observed here. The iridium nitrogen bonds are comparable in length with that found in $[\text{Ir}(\text{cod})(\text{py})(\text{PCy}_3)][\text{PF}_6]$, with the bonds to the diene being slightly shorter, probably reflecting the lower degree of steric crowding (Abbassioun, Hitchcock & Chaloner, 1989). There are many examples of structures of $[\text{L}_2\text{Rh}(\text{diene})]^+$ complexes (Knowles, 1983; Anderson & Pignolet, 1981); the geometries about the metal are all similar.

We thank Johnson Matthey for the loan of iridium complexes.

Acta Cryst. (1989). **C45**, 954–956

Structure of Diaqua(benzoato)chlorodioxouranium(VI)

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(Received 1 December 1988; accepted 16 December 1988)

Abstract. $[\text{U}(\text{C}_6\text{H}_5\text{O}_2)\text{ClO}_2(\text{H}_2\text{O})_2]$, $M_r = 462.63$, orthorhombic, *Pnna*, $a = 8.0247(15)$, $b = 9.7759(9)$, $c = 13.7205(12)$ Å, $V = 1076.3(5)$ Å³, $Z = 4$, $D_x = 2.855(1)$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 145.56$ cm⁻¹, $F(000) = 832$, $T = 297$ K, $R = 0.024$ for 533 observations with $I > 3\sigma(I)$. The structure is of molecular type: the individual molecules are bisected by the diad axis parallel to the [001] direction, on which lie U, Cl and three C atoms. The water molecules are engaged in intermolecular hydrogen bonding with Cl atoms [O(3)—Cl = 3.15(1) Å] and carboxylic O atoms [O(3)—O(2) = 2.70(1) Å].

Experimental. Yellow single crystal of dimensions 0.75 × 0.100 × 0.150 mm, grown during the reaction

0108-2701/89/060954-03\$03.00

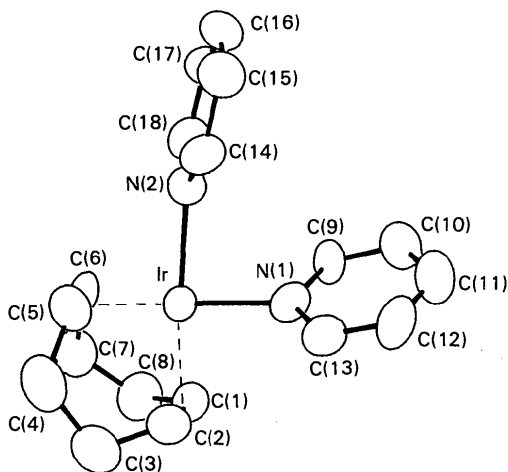


Fig. 1. Molecular structure and numbering scheme for $[\text{Ir}(\text{py})_2(\text{cod})]^+$.

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between UO_2Cl_2 and $\text{C}_6\text{H}_5\text{COOAg}$ in aqueous solution, Enraf–Nonius CAD-4 diffractometer with graphite monochromator, lattice parameters by least-squares procedure from setting angles of 25 reflections, θ between 8 and 12°, collection of data up to $2\theta = 50^\circ$, measured for $0 \leq h \leq 9$, $0 \leq k \leq 11$, $0 \leq l \leq 16$ using an $\omega/2\theta$ scan technique, corrections for background and Lorentz–polarization effects, negligible loss of intensity from three standard reflexions remeasured every hour, empirical absorption correction based on ψ scans of top reflexions applied, max. and min. transmissions 0.896 and 0.997. 1155 reflexions measured, 947 unique. Structure solved by Patterson method, using the *Enraf–Nonius SDP* programs (Frenz, 1983); H atoms of the phenyl ring introduced with ideal