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Structure of an Iridium Bis(phosphine)diene Complex, a Catalyst for Homogeneous Hydrogenation

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Abstract. (η^4-1,5-Cyclooctadiene)bis(triphenylphosphine)iridium(I) hexafluorophosphate, $[\mathrm{Ir(C_8H_{12})(PPh_3)_2}][\mathrm{PF_6}]$, $\mathrm{C_{44}H_{42}F_6IrP_3.0.5CH_2Cl_2}$, $M_r = 1012.4$, monoclinic, $P2_1/c$, $a = 11.666\,(1)$, $b = 18.885\,(3)$, $c = 19.492\,(2)$ Å, $\beta = 97.07\,(1)°$, $V = 4261.7$ Å^3, $Z = 4$, $D_x = 1.58$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0.71069$ Å, $\mu = 33.5$ cm^{-1}, $F(000) = 2012$, $T = 295$ K, $R = 0.050$, $wR = 0.070$ for 5438 observed reflections with $|F^2| > 2\sigma(F^2)$. The geometry at iridium is approximately square planar, but the iridium—phosphorus bond lengths are significantly different: Ir—P1 2.367 (2), Ir—P2 2.326 (3) Å, P1—Ir—P2 = 94.3 (1), M1—Ir—P1 = 90.5, M1—Ir—M2 = 83.3, M2—Ir—P2 = 93.2° (M1 and M2 are the mid-points of the C1—C2 and C5—C6 bonds).

Experimental. The complex was prepared by the addition of triphenylphosphine to $[\mathrm{Ir(cod)(py)_2}][\mathrm{PF_6}]$ (Crabtree & Moorehouse, 1986) and well formed prismatic crystals obtained by diffusion of ether into a solution in dichloromethane (cod = 1,5-cyclooctadiene, py = pyridine). Lattice parameters were derived from the setting angles for 25 reflections with $7.5 < \theta < 9.7°$. Data collected using a crystal *ca* 0.25 × 0.25 × 0.25 mm, on an Enraf–Nonius CAD-4 diffractometer, monochromated Mo $K\alpha$ radiation in the θ—2θ mode, with $\Delta\theta = (0.8 + 0.35\tan\theta)°$ and a maximum scan time of 1 min. A total of 8119 measured reflections for $2 < \theta < 25°$ and h 0→13, k 0→22, l −23→23, 7737 unique reflections, $R_{\mathrm{int}} = 0.017$, and 5438 observed reflections with $|F^2| > 2\sigma(F^2)$, where $\sigma(F^2) = \{\sigma^2(I) + (0.041I)^2\}^{1/2}/\mathrm{Lp}$, were used in the refinement. Two reference reflections remeasured every hour showed 14% decay, for which a correction was made. An absorption correction was applied using *DIFABS* (Walker & Stuart, 1983), after isotropic refinement, and gave maximum and minimum corrections of 1.14 and 0.81. Lorentz and polarization corrections were made. The structure was solved by routine heavy-atom methods and non-H atoms refined anisotropically by full-matrix least squares. H atoms were held fixed at calculated positions with $U_{\mathrm{iso}} = 1.3\ U_{\mathrm{eq}}$ for the atoms to which they are bonded. Solvent $\mathrm{CH_2Cl_2}$ at half occupancy and disordered, modelled with two Cl atoms disordered over three sites and H atoms omitted. With a weighting scheme of $w = 1/\sigma^2(F)$, $\sum w(|F_o| - |F_c|)^2$ minimized, the final residuals were $R = 0.050$ and $wR = 0.070$, 5438 observed reflections, 503 variables, $S = 2.0$, $(\Delta/\sigma)_{\mathrm{max}} = 0.01$, $\Delta\rho_{\mathrm{max}} = 1.9$, $\Delta\rho_{\mathrm{min}} = -0.9$ e Å^{-3} near the disordered solvent molecule. Programs from the Enraf–Nonius *SDP-Plus* (Frenz, 1984) package were run on a MicroVAX computer, drawing by *ORTEP*II (Johnson, 1976). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Atomic parameters are given in Table 1,* selected intramolecular bond distances and angles in Table 2. Fig. 1 shows the molecular structure and the numbering scheme. A packing diagram is given in Fig. 2.

Related literature. This complex has proved to be useful as a hydrogenation catalyst (Abbassioun

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* Lists of structure factors, anisotropic temperature factors, 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 54634 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0495]

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Ir	2303.9 (3)	2174.2 (2)	3358.5 (2)	34.6 (1)
P1	2123.0 (21)	2193.0 (14)	2136.0 (12)	38 (1)
P2	2114.9 (20)	950.6 (13)	3425.7 (12)	36 (1)
P3	2590.0 (34)	7471.6 (25)	6170.7 (21)	86 (2)
F1	1510 (8)	7964 (6)	6004 (5)	175 (7)
F2	2946 (12)	7697 (8)	5475 (6)	192 (11)
F3	1904 (13)	6916 (7)	5760 (10)	222 (12)
F4	3685 (9)	7000 (6)	6319 (7)	184 (8)
F5	2179 (12)	7264 (10)	6823 (6)	291 (13)
F6	3255 (13)	8074 (8)	6544 (9)	266 (12)
C1	2168 (10)	3350 (5)	3298 (5)	55 (6)
C2	3297 (9)	3189 (6)	3487 (6)	55 (6)
C3	3867 (10)	3309 (7)	4211 (6)	73 (7)
C4	3820 (12)	2705 (7)	4670 (7)	80 (8)
C5	2814 (10)	2208 (5)	4491 (5)	53 (6)
C6	1664 (11)	2420 (6)	4341 (5)	62 (6)
C7	1267 (11)	3179 (7)	4402 (6)	81 (7)
C8	1342 (12)	3605 (6)	3766 (6)	78 (7)
C9	2087 (9)	1399 (5)	1598 (5)	42 (5)
C10	1053 (10)	1026 (6)	1483 (6)	60 (6)
C11	950 (12)	431 (7)	1085 (7)	84 (8)
C12	1890 (15)	184 (8)	759 (7)	104 (10)
C13	2926 (13)	547 (7)	873 (7)	94 (8)
C14	3043 (10)	1179 (6)	1301 (6)	64 (6)
C15	776 (9)	2597 (5)	1749 (5)	45 (5)
C16	−93 (9)	2776 (5)	2136 (5)	46 (5)
C17	−1158 (9)	3037 (6)	1813 (6)	58 (6)
C18	−1310 (11)	3127 (7)	1107 (6)	70 (7)
C19	−472 (10)	2953 (6)	722 (6)	59 (6)
C20	565 (9)	2685 (6)	1036 (5)	51 (6)
C21	3287 (8)	2714 (5)	1839 (5)	41 (5)
C22	4416 (10)	2506 (7)	2078 (7)	72 (7)
C23	5338 (10)	2874 (7)	1852 (8)	82 (8)
C24	5199 (10)	3425 (8)	1401 (6)	75 (7)
C25	4083 (11)	3643 (6)	1187 (6)	72 (7)
C26	3117 (9)	3294 (6)	1406 (5)	51 (5)
C27	2303 (9)	501 (5)	4264 (5)	46 (5)
C28	3270 (9)	51 (6)	4475 (6)	56 (6)
C29	3342 (12)	−341 (7)	5075 (6)	75 (7)
C30	2477 (12)	−292 (7)	5480 (6)	85 (8)
C31	1538 (10)	163 (7)	5321 (6)	73 (7)
C32	1464 (9)	551 (6)	4708 (6)	60 (6)
C33	683 (8)	609 (5)	3127 (5)	40 (5)
C34	453 (9)	−105 (5)	3138 (6)	52 (5)
C35	−644 (10)	−345 (6)	2938 (6)	65 (7)
C36	−1517 (10)	106 (7)	2742 (7)	77 (8)
C37	−1321 (8)	821 (6)	2754 (6)	60 (6)
C38	−218 (8)	1076 (5)	2955 (5)	50 (5)
C39	3185 (8)	523 (5)	2960 (5)	41 (5)
C40	2995 (9)	−79 (6)	2569 (5)	54 (6)
C41	3908 (10)	−385 (6)	2266 (6)	67 (7)
C42	4984 (10)	−79 (7)	2375 (6)	77 (7)
C43	5191 (9)	502 (6)	2769 (6)	64 (6)
C44	4288 (8)	807 (6)	3068 (5)	51 (5)
C45	3129 (24)	6248 (15)	4419 (14)	85 (8)*
Cl1	1883 (14)	6124 (9)	4152 (8)	137 (5)*
Cl2	3930 (14)	5493 (9)	4358 (9)	144 (6)*
Cl3	3649 (13)	6646 (9)	3925 (8)	134 (5)*

* U_{iso}.

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

*M*1 and *M*2 are mid-points of the C1—C2 and C5—C6 bonds.

Ir—P1	2.367 (2)	Ir—P2	2.326 (3)
Ir—*M*1	2.128	Ir—*M*2	2.089
Ir—C1	2.229 (10)	Ir—C2	2.238 (11)
Ir—C5	2.216 (9)	Ir—C6	2.190 (11)
P1—C15	1.825 (10)	P1—C21	1.827 (10)
P2—C27	1.831 (10)	P2—C33	1.819 (9)
P2—C39	1.820 (10)	C1—C2	1.36 (2)
C1—C8	1.49 (2)	C2—C3	1.50 (2)
C3—C4	1.45 (2)	C4—C5	1.51 (2)
C5—C6	1.40 (2)	C6—C7	1.51 (2)
C7—C8	1.49 (2)		
*M*1—Ir—*M*2	83.3	*M*1—Ir—P1	90.5
*M*1—Ir—P2	171.0	*M*2—Ir—P1	169.2
*M*2—Ir—P2	93.2	P1—Ir—P2	94.3 (1)
C2—C1—C8	125.9 (9)	C1—C2—C3	122 (1)
C2—C3—C4	114 (1)	C3—C4—C5	116 (1)
C4—C5—C6	125 (1)	C5—C6—C7	123 (1)
C6—C7—C8	113 (1)	C1—C8—C7	116 (1)

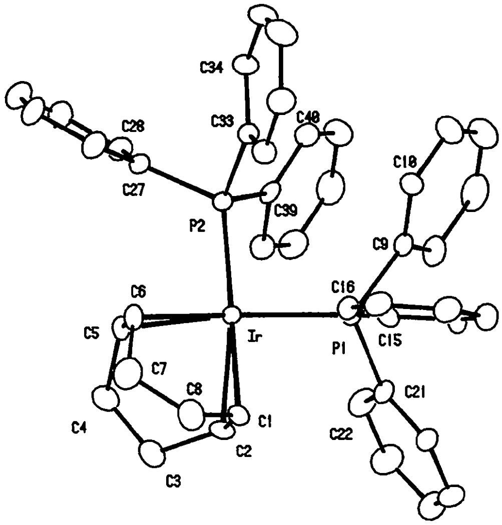

Fig. 1. Molecular structure and numbering scheme for $[Ir(PPh_3)_2(cod)]^+$ (20% thermal ellipsoids).

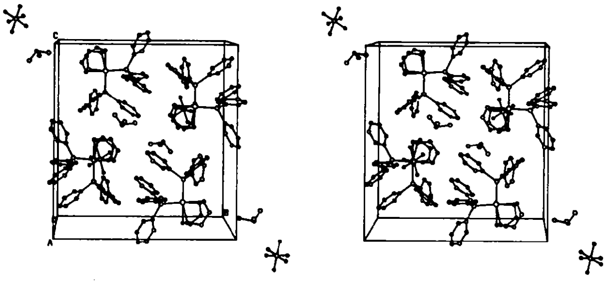

Fig. 2. Packing diagram for $[Ir(PPh_3)_2(cod)][PF_6]$.

& Chaloner, 1989), and is related to $[Ir(PCy_3)(py)(cod)][PF_6]$, which has been widely used as a catalyst for the reduction of hindered alkenes (Crabtree, 1979). The structures of $[Ir(PCy_3)(py)(cod)][PF_6]$, $[Ir\{P(2\text{-}MeOC_6H_4)_3P\}py(cod)][PF_6]$, $\{Ir\{P(4\text{-}MeOC_6H_4)_3\}_2(cod)][PF_6]$ and $[Ir\{(S)\text{-}PMePh(2\text{-}MeOC_6H_4)\}_2(cod)][PF_6]$ have been determined, and show distortions due to the differing bulk of the phosphine ligands (Abbassioun, Chaloner & Hitchcock, 1989, 1990*a*,*b*; Abbassioun, Chaloner, Hitchcock & Koziorowski, 1991). In most of these cases the metal–phosphine bond lengths are much more similar than is observed here. The conformation of the cod ligand is similar to that found in these complexes.

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Structure of Sodium *p*-Nitrophenolate Dihydrate

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Abstract. $[Na(C_6H_4NO_3)].2H_2O$, $M_r = 197.12$, orthorhombic, $Ima2$, $a = 6.892\,(1)$, $b = 19.692\,(2)$, $c = 6.439\,(1)$ Å, $V = 873.8\,(1)$ Å^3, $Z = 4$, $D_x = 1.498$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 15.1$ cm^{-1}, $F(000) = 408$, $T = 295$ K, $R = 0.066$ for 357 observed reflections. The *p*-nitrophenolate molecule, as well as the Na cation, is located on the crystallographic mirror plane. The Na cation is in contact with four O atoms, the distances being between 2.32 and 2.66 Å. The solvated water molecule is hydrogen bonded to the two O atoms of the NO_2 group.

Experimental. Crystals were grown as yellow square bipyramids from methanol solution. A well shaped crystal with dimensions of 0.50 × 0.50 × 0.80 mm was mounted on a Rigaku automated four-circle diffractometer. Unit-cell parameters were determined by a least-squares fit of 2θ values for 25 reflections in the range 45.7–69.8°. Intensities were measured by the θ–2θ-scan technique using Ni-filtered Cu $K\alpha$ radiation. The scan rate was 4° min^{-1} in 2θ and the scan width was $\Delta(2\theta) = (1.6 + 0.30\tan\theta)°$. Background intensities were measured for 5 s at the end of each scan. Four standard reflections (0,0,12, 228, 044, 400) were remeasured every 60 reflections, no significant loss of intensities was observed. 663 reflections were collected with 2θ up to 116° ($\sin\theta/\lambda = 0.550$ Å^{-1}) and an index range of $h = 0$ to 7, $k = 0$ to 21, $l = -7$ to 7. By averaging Friedel-pair reflections, 367 independent reflections were obtained ($R_{\text{int}} = 0.010$). Corrections for Lorentz and polarization effects were applied, while neither absorption nor extinction corrections were carried out.

The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986) and refined by the block-diagonal least-squares procedure with program *HBLS*-V (Ashida, 1979). On the difference Fourier maps all the H atoms were found at the expected positions and were included in further refinements. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma(F_o)^2 + 0.010|F_o|^2]^{-1}$. At the final stage of the refinement, nine strong reflections (080, 170, 200, 220, 400, 011, 211, 202 and 222) affected by extinction were excluded. The number of observations per refined parameters was 357/91 = 3.92 and $S = 1.11$. The final R and wR were 0.066 and 0.088 for 357 observed reflections [$|F_o| \geq 3\sigma(|F_o|)$], respectively. $(\Delta/\sigma)_{\max}$ for the non-H atoms in the final refinement cycle was 0.24. The peaks in the final $\Delta\rho$ map were between 0.21 and

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