

Related literature. As mentioned in *Experimental*, the room-temperature structure determination was carried out previously by Willett & Chow (1974). The low-temperature structure was the main thrust of this work, and the room-temperature structure determination was performed only for purposes of comparison. The low-temperature structure determination was carried out in order to see if a significant structural difference existed between RT and LT, a question which was raised in an EPR study performed by Bencini, Gatteschi & Zanchini (1985).

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Structure of a Chiral Iridium Bis(phosphine)–Diene Complex, a Catalyst for Homogeneous Hydrogenation

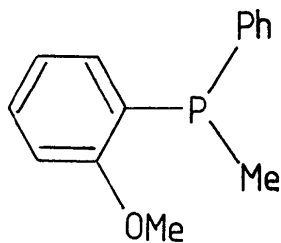
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Abstract. (η^4 -1,5-Cyclooctadiene)bis[(*S*)-(2-methoxyphenyl)(methyl)(phenyl)phosphine]iridium(I) hexafluorophosphate, $[\text{Ir}(\text{C}_8\text{H}_{12})(\text{C}_{14}\text{H}_{15}\text{OP})_2][\text{PF}_6]$, $M_r = 833.8$, orthorhombic, $C222_1$, $a = 26.995$ (6), $b = 22.122$ (5), $c = 13.927$ (5) Å, $V = 8316.9$ Å³, $Z = 8$, $D_x = 1.33$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 33.6$ cm⁻¹, $F(000) = 3312$, $T = 295$ K, $R = 0.055$, $wR = 0.074$ for 2501 reflections with $|F^2| > 3\sigma(F^2)$. The geometry at iridium is approximately square planar, with the expected distortions due to the size of the phosphine ligands: Ir—P1 2.320 (5), Ir—P2 2.323 (5) Å, P1—Ir—P2 92.3 (2), M1—Ir—P2 93.0, M1—Ir—M2 84.4, M2—Ir—P1 90.5° (M1 and M2 are the midpoints of the C1—C2 and C5—C6 bonds, respectively).

Experimental. The complex was prepared by the addition of (*S*)-(2-methoxyphenyl)(methyl)(phenyl)phosphine [(*S*)-pamp] [(1)] to $[\text{Ir}(\text{cod})(\text{py})_2][\text{PF}_6]$



(1)

0108-2701/91/020437-03\$03.00

(Crabtree & Moorehouse, 1986) (cod = 1,5-cyclooctadiene, py = pyridine) and well formed crystals were obtained by diffusion of ether into a solution in dichloromethane. Data collected using a crystal ca 0.25 × 0.25 × 0.2 mm, coated in epoxy glue, on an Enraf–Nonius CAD-4 diffractometer, monochromated Mo $K\alpha$ radiation in the θ – 2θ mode, with $\Delta\theta = (0.8 + 0.35\tan\theta)^\circ$ and a maximum scan time of 1 min. Cell parameters from setting angles of 25 reflections ($7 \leq \theta \leq 10^\circ$). A total of 4017 unique reflections were measured for $2 < \theta < 25^\circ$ and h 0 → 32, k 0 → 26, l 0 → 16, and 2501 reflections with $|F^2| > 3\sigma(F^2)$, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}/Lp$, were used in the refinement. Two reference reflections remeasured every 30 min showed no significant variation. An absorption correction was applied using *DIFABS* (Walker & Stuart, 1983), after isotropic refinement, and gave maximum and minimum corrections of 1.10 and 0.82. The structure was solved by routine heavy-atom methods and non-H atoms refined anisotropically (on F) by full-matrix least squares. H atoms were held fixed at calculated positions with $B_{\text{iso}} = 1.3 B_{\text{eq}}$ for the atoms to which they are bonded. With a weighting scheme of $w = 1/\sigma^2(F)$, the maximum shift/e.s.d. was 0.7, the final residuals were $R = 0.055$ and $wR = 0.074$, 214 variables, $\Delta\rho_{\text{max}} = 1.9$, $\Delta\rho_{\text{min}} = -0.9$ e Å⁻³. The corresponding residuals for a refinement as the opposite absolute structure were $R = 0.0673$, $wR = 0.0897$. Programs from the Enraf–Nonius *SDP-Plus* package

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Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

	x	y	z	U_{eq}
Ir	1360.4 (3)	1639.9 (3)	3740.1 (6)	43 (1)
P1	2111 (2)	1745 (2)	4534 (4)	47 (1)
P2	1448 (2)	2568 (2)	2980 (4)	46 (1)
P3	5000	2534 (13)	2500	190 (9)
P4	2104 (9)	0	0	164 (8)
F1	5347 (9)	2533 (12)	3399 (18)	178 (10)
F2	5342 (11)	2947 (13)	1876 (22)	222 (13)
F3	4682 (12)	2040 (14)	3005 (24)	254 (16)
F4	2220 (10)	-634 (12)	521 (18)	182 (10)
F5	1911 (11)	390 (12)	897 (22)	216 (13)
F6	2618 (12)	167 (17)	650 (22)	271 (16)
O1	1653 (6)	1785 (7)	6373 (14)	87 (5)
O2	1497 (7)	2043 (8)	1103 (14)	90 (5)
C1	561 (5)	1647 (8)	3551 (10)	26 (3)
C2	749 (9)	1334 (11)	2744 (19)	72 (7)
C3	763 (10)	639 (11)	2630 (21)	80 (8)
C4	1208 (11)	363 (12)	3091 (22)	91 (9)
C5	1402 (8)	657 (9)	4017 (14)	52 (5)
C6	1120 (7)	916 (9)	4690 (16)	53 (6)
C7	549 (9)	876 (12)	4814 (21)	78 (8)
C8	287 (10)	1405 (12)	4360 (20)	86 (8)
C9	2243 (7)	2480 (10)	5085 (18)	56 (6)
C10	2597 (9)	1590 (11)	3726 (19)	77 (7)
C11	3108 (9)	1750 (10)	4010 (17)	69 (7)
C12	3479 (10)	1611 (13)	3417 (21)	90 (8)
C13	3430 (11)	1329 (13)	2586 (26)	102 (10)
C14	2940 (10)	1174 (12)	2289 (22)	91 (9)
C15	2554 (9)	1326 (10)	2853 (17)	69 (7)
C16	2233 (8)	1242 (9)	5540 (16)	54 (6)
C17	2558 (8)	799 (10)	5512 (16)	60 (6)
C18	2690 (11)	438 (12)	6247 (24)	94 (9)
C19	2406 (10)	531 (12)	7124 (20)	84 (8)
C20	2080 (8)	970 (10)	7181 (17)	60 (6)
C21	1977 (8)	1313 (10)	6406 (18)	65 (6)
C22	1307 (7)	3172 (8)	3826 (16)	53 (5)
C23	1030 (8)	3069 (9)	4583 (15)	54 (6)
C24	872 (9)	3527 (10)	5211 (19)	71 (7)
C25	1028 (11)	4143 (13)	4954 (27)	101 (9)
C26	1383 (13)	4234 (14)	4234 (23)	108 (10)
C27	1503 (9)	3754 (11)	3645 (20)	76 (7)
C28	1040 (8)	2717 (10)	1945 (16)	55 (6)
C29	1110 (9)	2398 (10)	1076 (18)	69 (7)
C30	789 (10)	2537 (12)	283 (19)	78 (8)
C31	446 (11)	2910 (13)	354 (22)	95 (9)
C32	337 (10)	3212 (12)	1203 (23)	93 (8)
C33	672 (10)	3157 (11)	2015 (20)	78 (8)
C34	2052 (9)	2758 (10)	2531 (19)	63 (6)
C35	1495 (13)	1631 (17)	182 (31)	137 (13)
C36	1383 (16)	1858 (19)	7263 (35)	163 (16)

Table 2. Selected intramolecular distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Ir—M1	2.10 (2)	Ir—M2	2.09 (2)
Ir—P1	2.320 (5)	Ir—P2	2.323 (5)
Ir—C1	2.175 (14)	Ir—C2	2.26 (3)
Ir—C5	2.21 (2)	Ir—C6	2.18 (2)
M1—Ir—M2	84.4 (8)	M1—Ir—P1	173.9 (6)
M1—Ir—P2	93.0 (6)	M2—Ir—P1	90.5 (6)
M2—Ir—P2	176.7 (6)	P1—Ir—P2	92.3 (2)
Ir—P1—C9	117.3 (7)	Ir—P1—C10	109.0 (9)
Ir—P1—C16	117.6 (7)	C9—P1—C10	107 (1)
C9—P1—C16	101 (1)	C10—P1—C16	104 (1)
Ir—P2—C22	109.4 (7)	Ir—P2—C28	116.9 (7)
Ir—P2—C34	117.2 (8)	C22—P2—C28	104 (1)
C22—P2—C34	104 (1)	C28—P2—C34	103 (1)

M1 and M2 are the midpoints of the C1—C2 and C5—C6 bonds, respectively.

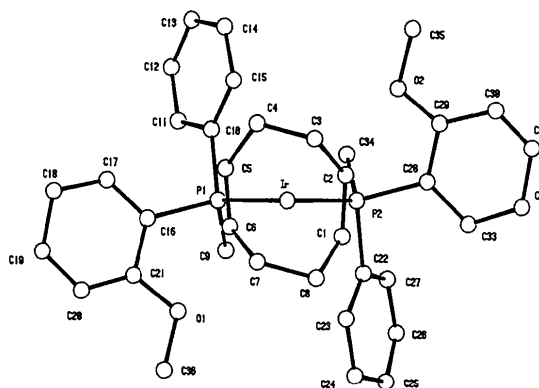


Fig. 1. Molecular structure and numbering scheme for [Ir{P(2-MeOC₆H₄)PhMe}₂(cod)]⁺.

(Frenz, 1985) were run on a MicroVAX computer. 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.

Related literature. This complex has proved useful as a hydrogenation catalyst (Abbassioun & Chaloner, 1989), and is related to [Ir(PCy₃)(py)(cod)][PF₆] (Cy = cyclohexyl), which has been widely used as a catalyst for the reduction of hindered alkenes (Crabtree,

1979). The structures of [Ir(PCy₃)(py)(cod)][PF₆], [Ir{P(2-MeOC₆H₄)₃(py)}][PF₆] and [Ir{P(4-MeOC₆H₄)₃}₂(cod)][PF₆] have been determined, and show distortions due to the bulk of the phosphine ligands (Abbassioun, Hitchcock & Chaloner, 1989, 1990a,b). The conformation of the cod ligand is similar in these complexes. The pamp ligand has been used to prepare catalysts for enantioselective hydrogenation (Vineyard, Knowles, Sabacky, Bachman & Wein-kauff, 1977).

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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 53467 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Structure of a Key Intermediate† in the Total Synthesis of Dendrobine

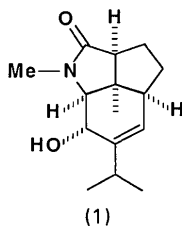
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Abstract. (1*R**,4*R**,5*S**,8*R**,11*S**)-3,11-Dimethyl-5-hydroxy-6-isopropyl-3-azatricyclo[6.2.1.0^{4,11}]undec-6-en-2-one, C₁₅H₂₃NO₂, *M_r* = 249.35, monoclinic, *P*2₁/*c*, *a* = 7.782 (2), *b* = 23.119 (4), *c* = 7.932 (2) Å, β = 101.53 (2)°, *V* = 1398.1 (5) Å³, *Z* = 4, *D_x* = 1.184 g cm⁻³, Mo *K*α, λ = 0.7107 Å, μ = 0.7259 cm⁻¹, *F*(000) = 544, *T* = 298 K, *R* = 0.0464 for 1887 reflections {*F_o* ≥ 4[σ(*F_o)]}]. The molecules are H-bonded into infinite columns parallel to *c* involving the hydroxyl group and the carbonyl O atom [O15...O13(*x*,*y*,*z* - 1) 2.756 (2); H15...O13 1.84 (3) Å; O—H...O 173 (3)°]. The bonds from the bridgehead atom of the tricyclic ring to other ring atoms appear to be elongated [av. 1.549 (2) Å] compared to the other *Csp*³—*Csp*³ bonds in the molecule.*

Experimental. (1) was synthesized in two steps from a tricyclic precursor that was prepared by an intramolecular Diels–Alder reaction of an unsaturated dienamide. Details of the synthetic procedure are described elsewhere (Li, 1988).



The data crystal was a colorless block that was cut from a larger crystal and had approximate dimensions 0.31 × 0.34 × 0.38 mm. Crystals were obtained by slow evaporation from ether. The data were

† IUPAC name: (1*R**,4*R**,7*R**,10*S**,11*S**)-10-hydroxy-9-isopropyl-2,11-dimethyl-2-azatricyclo[5.3.1.0^{4,11}]undec-8-en-3-one.

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collected at room temperature using graphite-monochromatized Mo *K*α radiation on a Nicolet P3 diffractometer. Lattice parameters were obtained from the least-squares refinement of 24 reflections with 22.2 < 2θ < 30.0°. Data were collected using the ω-scan technique (5330 reflections, 2457 unique, *R_{int}* = 0.0169), with a 2θ range 4.0–50° in 2θ, over a 1.2° ω scan at 10° min⁻¹ (*h* = 0→9, *k* = -27→27, *l* = -9→9). Four reflections (061; 112̄; 022; 102̄) were remeasured every 96 reflections to monitor instrument and crystal stability (maximum correction on *I* was < 1%). The data were also corrected for Lp effects but not for absorption. Data reduction and decay correction were performed using *SHELXTL-Plus* (Sheldrick, 1988). Reflections having *F_o* < 4σ(*F_o*) were considered unobserved (570 reflections). The structure was solved by direct methods and refined by full-matrix least squares (Sheldrick, 1976). The non-H atoms were refined with anisotropic thermal parameters. Initially, the H atoms were calculated in ideal positions but were allowed to refine without constraint in the final refinement cycles. All H atoms were refined with isotropic thermal parameters. In all, 255 parameters were refined. The function Σ*w*(|*F_o*| - |*F_c*|)² was minimized, where *w* = 1/[σ(*F_o*)²] and σ(*F_o*) = (0.5*kI*^{-1/2}{[σ(*I*)]² + (0.02*I*)²})^{1/2}. The intensity, *I*, is given by (*I_{peak}* - *I_{background}*) × (scan rate); 0.02 is a factor to downweight intense reflections and to account for instrument instability and *k* is the correction due to Lp effects and decay. σ(*I*) was estimated from counting statistics; σ(*I*) = [(*I_{peak}* + *I_{background}*)^{1/2} × (scan rate)]. The final *R* = 0.0464 for 1887 reflections, *wR* = 0.0512 (*R_{all}* = 0.0645, *wR_{all}* = 0.0551) and goodness of fit = 1.663. Max. |Δ|σ| < 0.1 in the final refinement cycle and min. and max. peaks in the final Δ*F* map were -0.15 and 0.16 e Å⁻³, respectively. Scattering factors for the non-H atoms were taken from Cromer & Mann (1968), with anomalous-dispersion corrections from