O(161)—Nd—O(6)	75.5 (2)	O(361)—Nd—O(6)	142.5 (2)
O(2)—Nd—O(261)	63.0 (2)	O(4)—Nd—O(5)	87.2 (2)
O(2)—Nd—O(3)	77.3 (2)	O(4)—Nd—O(6)	84.4 (2)
O(2)—Nd—O(361)	133.2 (2)	O(5)—Nd—O(6)	80.7 (2)

Data were corrected for Lp effects. H atoms were not included in either model. The refinement was by blocked-matrix least-squares methods. Programs used were *SHELXS*86 (Sheldrick, 1985), *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965). Most of the calculations were performed on a VAX 6420 computer at the Instituto de Física e Química de São Carlos.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71577 (108 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1055]

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An Iridium Complex of Tris(4-methoxyphenyl)phosphine

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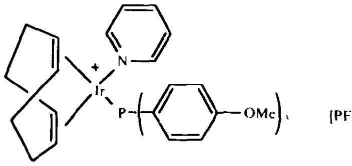
Abstract

The structure determination of (η^4-1,5-cyclooctadiene)(pyridine)[tris(4-methoxyphenyl)phosphine]iridium(I) hexafluorophosphate, [$Ir(C_{21}H_{21}O_3P)(C_8H_{12})(C_5H_5N)$][$PF_6$], revealed approximately square-planar coordination at the Ir atom. The geometry is less distorted than in related complexes with more bulky phosphines.

Comment

We have been interested for some time in the structures and the conformation in solution of cationic Ir complexes of a range of monophosphines (Abbassioun, Hitchcock & Chaloner, 1989; Abbassioun, Chaloner & Hitchcock, 1990*a*,*b*; Abbassioun, Chaloner, Hitchcock & Koziorowski, 1991; Chaloner, Hitchcock & Reisinger, 1992). Many such complexes have been used as catalysts for homogeneous hydrogenation of hindered alkenes (Crabtree, 1979). The title complex (I) was prepared by reaction of [{IrCl(cod)}$_2$] (cod = 1,5-cyclooctadiene) with the phosphine in light petroleum/dichloromethane (1:3) to give [IrCl(cod){$P(C_6H_4\text{-}4\text{-}OMe)_3$}], which was used without further purification (Winkhaus & Singer, 1966). This was reacted with pyridine in methanol, and then with ammonium hexafluorophosphate to give the required salt in 74% yield. The structure of the complex is shown in Fig. 1. The geometry at Ir is approximately square planar, as expected. By comparison with [Ir(cod)(py)(PCy_3)][PF_6] (Abbassioun, Hitchcock & Chaloner, 1989) and [Ir(cod)(py){$P(C_6H_4$-2-



(I)

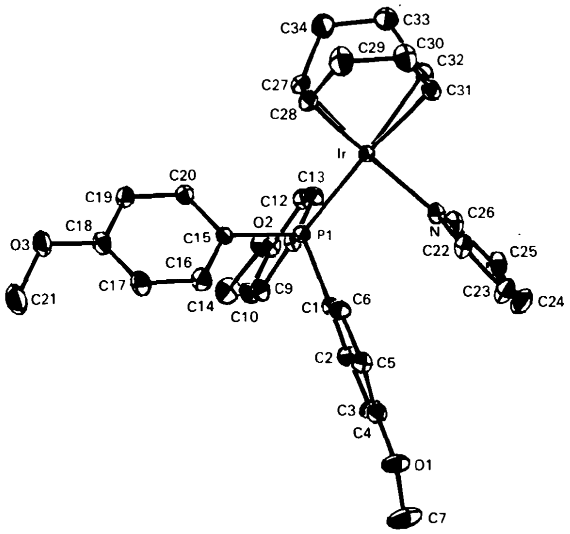


Fig. 1. Molecular structure and atom-numbering scheme of the title compound.

$OMe)_3\}][PF_6]$ (Abbassioun, Chaloner & Hitchcock, 1990*a*), the P—Ir bond is shortened [2.327 (1) Å in comparison with 2.366 (4) Å in the PCy_3 derivative and 2.345 (7) Å in the $P(C_6H_4\text{-}2\text{-}OMe)_3$ complex], and the Ir—N bond is lengthened [2.106 (4) Å compared with 2.064 (11) Å in the PCy_3 and 2.04 (2) Å in the $P(C_6H_4\text{-}2\text{-}OMe)_3$ complex]. The P—Ir—N angle is also reduced, as might be expected given the lower steric demand of this phosphine.

Experimental

Crystal data

$[Ir(C_{21}H_{21}O_3P)(C_8H_{12})(C_5H_5N)][PF_6]$
$M_r = 876.8$
Triclinic
$P\bar{1}$
$a = 9.821\ (2)$ Å
$b = 12.576\ (3)$ Å
$c = 15.068\ (5)$ Å
$\alpha = 104.63\ (2)°$
$\beta = 97.21\ (2)°$
$\gamma = 105.98\ (2)°$
$V = 1692.6$ Å^3
$Z = 2$

$D_x = 1.72$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 7\text{-}10°$
$\mu = 4.09$ mm^{-1}
$T = 293$ K
Plate
0.2 × 0.2 × 0.05 mm
Red-orange
Crystal source: recrystallization from CH_2Cl_2/Et_2O

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta\text{-}2\theta$ scans
Absorption correction: *DIFABS* (Walker & Stuart, 1983)
$T_{min} = 0.84$, $T_{max} = 1.24$
5930 measured reflections
5930 independent reflections

5154 observed reflections $[|F^2| > 2\sigma(F^2)]$
$\theta_{max} = 25°$
$h = 0 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 17$
2 standard reflections
frequency: 60 min
intensity variation: 1.4%

Refinement

Refinement on F
$R = 0.033$
$wR = 0.040$
$S = 1.2$
5154 reflections
424 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.94$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Enraf-Nonius *MolEN* (Fair, 1990) programs

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	0.17673 (2)	0.26826 (2)	0.17606 (1)	0.033 (1)
P1	0.13302 (14)	0.38828 (11)	0.30689 (9)	0.034 (1)
P2	0.27612 (18)	0.79050 (14)	0.12784 (11)	0.054 (1)
F1	0.3924 (6)	0.8353 (5)	0.2217 (4)	0.137 (3)
F2	0.1599 (6)	0.7426 (6)	0.0366 (4)	0.143 (3)
F3	0.2030 (6)	0.8818 (5)	0.1646 (5)	0.159 (3)
F4	0.1854 (9)	0.7054 (7)	0.1684 (5)	0.224 (4)
F5	0.3555 (7)	0.7054 (6)	0.0918 (5)	0.198 (4)
F6	0.3718 (8)	0.8773 (6)	0.0910 (5)	0.206 (4)
O1	−0.0188 (5)	0.1156 (4)	0.5726 (3)	0.067 (3)
O2	−0.3095 (4)	0.5898 (4)	0.1797 (3)	0.061 (2)
O3	0.5335 (5)	0.8500 (4)	0.5565 (3)	0.073 (2)
N	−0.0114 (5)	0.1380 (4)	0.1763 (3)	0.039 (1)
C1	0.0747 (5)	0.3066 (4)	0.3865 (3)	0.034 (2)
C2	−0.0615 (6)	0.2830 (5)	0.4084 (4)	0.043 (2)
C3	−0.0965 (6)	0.2179 (5)	0.4693 (4)	0.050 (2)
C4	0.0038 (6)	0.1751 (5)	0.5092 (4)	0.048 (2)
C5	0.1377 (6)	0.1934 (5)	0.4839 (4)	0.045 (2)
C6	0.1710 (6)	0.2571 (5)	0.4237 (4)	0.044 (2)
C7	−0.1474 (9)	0.1074 (7)	0.6071 (5)	0.098 (3)
C8	−0.0103 (5)	0.4446 (4)	0.2716 (3)	0.037 (2)
C9	−0.0656 (6)	0.5107 (5)	0.3367 (4)	0.045 (2)
C10	−0.1655 (6)	0.5609 (5)	0.3094 (4)	0.047 (2)
C11	−0.2108 (6)	0.5458 (4)	0.2150 (4)	0.044 (2)
C12	−0.1564 (6)	0.4799 (5)	0.1492 (4)	0.047 (2)
C13	−0.0569 (6)	0.4312 (5)	0.1768 (4)	0.042 (2)
C14	−0.3615 (7)	0.6656 (6)	0.2433 (5)	0.067 (3)
C15	0.2685 (5)	0.5224 (4)	0.3851 (3)	0.038 (2)
C16	0.3212 (6)	0.5386 (5)	0.4793 (4)	0.050 (2)
C17	0.4094 (7)	0.6476 (6)	0.5380 (4)	0.056 (2)
C18	0.4496 (5)	0.7405 (5)	0.5045 (4)	0.050 (2)
C19	0.4016 (6)	0.7242 (5)	0.4092 (4)	0.051 (2)
C20	0.3113 (6)	0.6180 (5)	0.3513 (4)	0.046 (2)
C21	0.5442 (9)	0.8798 (8)	0.6549 (6)	0.097 (4)
C22	−0.0012 (6)	0.0603 (5)	0.2216 (4)	0.052 (2)
C23	−0.1205 (8)	−0.0189 (6)	0.2319 (5)	0.068 (3)
C24	−0.2557 (7)	−0.0240 (6)	0.1938 (5)	0.072 (3)
C25	−0.2680 (6)	0.0513 (6)	0.1451 (6)	0.069 (3)
C26	−0.1456 (6)	0.1318 (5)	0.1379 (4)	0.053 (2)
C27	0.3224 (7)	0.4084 (5)	0.1445 (4)	0.051 (2)
C28	0.4011 (6)	0.3609 (5)	0.1955 (4)	0.053 (2)
C29	0.4853 (7)	0.2821 (7)	0.1531 (6)	0.083 (3)
C30	0.4001 (7)	0.1652 (6)	0.0941 (5)	0.071 (3)
C31	0.2382 (6)	0.1367 (5)	0.0777 (4)	0.049 (2)
C32	0.1593 (6)	0.1837 (5)	0.0255 (4)	0.052 (2)
C33	0.2254 (10)	0.2740 (7)	−0.0203 (5)	0.079 (3)
C34	0.3038 (12)	0.3901 (7)	0.0407 (5)	0.101 (4)

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

*M*1 and *M*2 are the midpoints of the C27—C28 and C31—C32 bonds, respectively.

Ir—*M*1	2.023 (6)	Ir—*M*2	2.095 (6)
Ir—P1	2.327 (1)	Ir—N	2.106 (4)
Ir—C27	2.141 (6)	Ir—C28	2.134 (5)
Ir—C31	2.199 (6)	Ir—C32	2.212 (6)
P1—C1	1.814 (6)	P1—C8	1.821 (6)
P1—C15	1.836 (4)		
*M*1—Ir—*M*2	86.5 (2)	*M*1—Ir—P1	95.8 (2)
*M*1—Ir—N	175.0 (2)	*M*2—Ir—P1	174.9 (2)
*M*2—Ir—N	89.8 (2)	P1—Ir—N	88.0 (1)
Ir—P1—C1	109.9 (2)	Ir—P1—C8	110.2 (2)
Ir—P1—C15	124.0 (2)	C1—P1—C8	108.0 (3)
C1—P1—C15	103.2 (2)	C8—P1—C15	100.3 (2)

We thank the University of Sussex for a bursary (to RBB) and Johnson Matthey PLC for a generous loan of iridium salts.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71583 (34 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1067]

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An Iridium Complex of Tris(2,4,6-trimethoxyphenyl)phosphine

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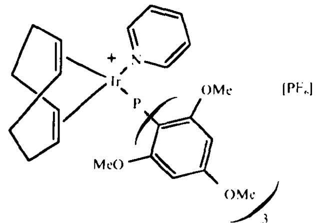
Abstract

The structure determination of (η^4-1,5-cyclooctadiene)(pyridine)[tris(2,4,6-trimethoxyphenyl)phosphine]iridium(I) hexafluorophosphate, [Ir($C_{27}H_{33}O_9P$)(C_8H_{12})(C_5H_5N)][PF_6] revealed approximate square-pyramidal geometry at the Ir atom with one of the methoxy groups of the phosphine ligand being weakly bound in the apical position [Ir···O = 2.857 (4) Å].

Comment

We have been interested for some time in the structures and conformation in solution of cationic iridium phosphine complexes, particularly those involving hindered phosphines (Abbassioun, Hitchcock & Chaloner, 1989; Abbassioun, Chaloner & Hitchcock, 1990; Abbassioun, Chaloner, Hitchcock & Koziorowski, 1991; Chaloner, Hitchcock & Reisinger, 1992; Bedford, Chaloner & Hitchcock, 1993). Many such complexes have been used as catalysts for the homogeneous hydrogenation of hindered alkenes (Crabtree, 1979). There has been considerable interest in the use of the basic hindered phosphine tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) (Wada & Higashizaki, 1984) as a ligand in organometallic chemistry and a number of structures of complexes involving this ligand have been determined (Dunbar, Haefner & Pence, 1989; Chen & Dunbar, 1990, 1991; Dunbar, Haefner & Burzynski, 1990; Dunbar, Haefner & Quillevéré, 1990; Haefner, Dunbar & Bender, 1991). The related ligand tris(2,6-dimethoxyphenyl)phosphine may be expected to be equally sterically demanding, but a little less basic.

The complex (I) was prepared by reaction of [Ir(cod)(py)$_2$][PF_6], where cod is 1,5-cyclooctadiene and py is pyridine, with tris(2,4,6-trimethoxyphenyl)phosphine (Crabtree & Moorehouse, 1986) and its structure is shown in Fig. 1. The Ir atom adopts a distorted square-pyramidal geometry due to the bulk of the phosphine ligand. There is one short contact between an ether O atom and the metal centre, Ir···O = 2.857 (4) Å, and the ether may be described as occupying an approximately apical site in the square-based pyramid. It is relevant to compare this distance with the related parameter in the structure of [Ir(cod)(py){P(C_6H_4-2,6-{OMe}$_2$)$_3$}]-[PF_6], Ir···O = 2.724 (6) Å. We may postulate that



(I)

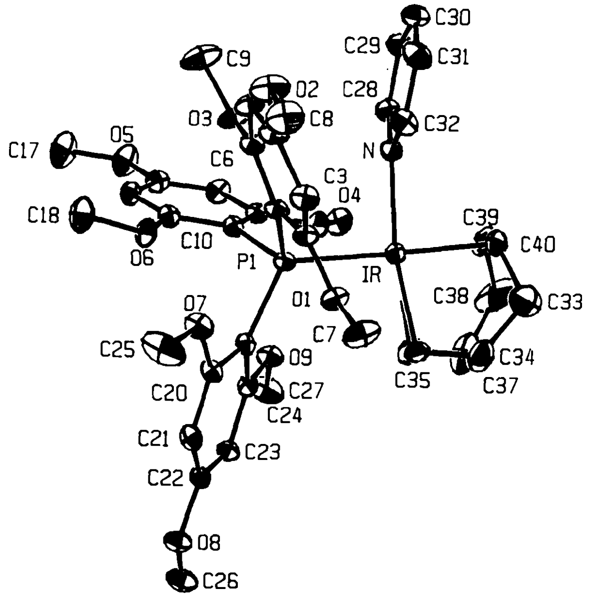


Fig. 1. Molecular structure and atom-numbering scheme of the title compound.