Ru(2)—Ru(4)—C(12)	168.0 (5)	169.6 (4)
Ru(3)—Ru(4)—C(12)	118.9 (4)	117.5 (4)
C(10)—Ru(4)—C(12)	77.3 (5)	76.3 (6)
C(11)—Ru(4)—C(12)	95.3 (6)	97.1 (6)
Ru(1)—Ru(4)—C(13)	109.9 (4)	106.1 (4)
Ru(2)—Ru(4)—C(13)	90.2 (4)	91.7 (4)
Ru(3)—Ru(4)—C(13)	149.8 (4)	150.4 (4)
C(10)—Ru(4)—C(13)	167.9 (5)	166.7 (5)
C(11)—Ru(4)—C(13)	91.1 (6)	91.3 (5)
C(12)—Ru(4)—C(13)	90.6 (6)	90.4 (6)
Ru(2)—C(7)—Ru(3)	78.9 (5)	76.2 (4)
Ru(2)—C(7)—O(7)	129.8 (9)	128.2 (9)
Ru(3)—C(7)—O(7)	151.4 (10)	155.6 (10)
Ru(3)—C(10)—Ru(4)	75.5 (4)	77.9 (5)
Ru(3)—C(10)—O(10)	161.4 (12)	156.4 (12)
Ru(4)—C(10)—O(10)	122.7 (10)	125.6 (11)

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55959 (34 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1022]

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Structure of an Iridium(I) Complex of Tris(2,6-dimethoxyphenyl)phosphine, $[Ir(C_8H_{12})(C_5H_5N)(P\{2,6-(CH_3O)_2C_6H_3\}_3)][PF_6]$

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Abstract

The structure of (η^4-1,5-cyclooctadiene)(pyridine)[tris(2,6-dimethoxyphenyl)phosphine]iridium(I) hexafluorophosphate shows approximately square-pyrimidal geometry at the Ir atom with one of the methoxy groups of the phosphine ligand being weakly bound in the apical position [Ir···O = 2.724 (6) Å].

Comment

We have been interested for some time in the structures and solution conformations of cationic iridium–phosphine complexes, particularly of rather hindered phosphines (Abbassioun, Hitchcock & Chaloner, 1989, 1990; 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). 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 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. There has been little structural work on derivatives of this phosphine; only the structures of the free phosphine (Livant, Sun & Webb, 1991) and the phosphine selenide (Allen, Bell, March & Nowell, 1990) have been determined.

The complex (I) was prepared by reaction of $[Ir(cod)(py)_2][PF_6]$ with tris(2,6-dimethoxyphenyl)phosphine (Crabtree & Moorehouse, 1986) and its structure is shown in Fig. 1. The Ir atom adopts distorted square-pyramidal geometry, partly resulting from the bulk of the phosphine ligand. There is one short contact between an ether O atom and the metal centre, Ir···O2 = 2.724 (6) Å, and the ether may be described as occupying an approximately apical site in the square-based pyramid. The Ir atom is some 0.17 Å above the square-basal plane. The metal–oxygen distance is quite long by comparison with other related interactions. For example, in $[Rh(\eta^3\text{-TMPP})_2][BF_4]_2$ the Rh···O distances are 2.398 (5) and 2.201 (6) Å, in $[Rh(CO)(\eta^2\text{-TMPP})(TMPP)][BF_4]$ they are 2.319 (7) and 2.611 (7) Å (Haefner, Dunbar & Bender, 1991) and in $[RhCl_3(Me_2AsC_6H_4\text{-}2\text{-}OMe)_2]$ they are 2.24 Å (Graziani, Bombieri, Volponi, Panattoni & Clark, 1969). True bonds to alkoxide ligands are considerably shorter, typically of the order of 2.0 Å for $[Ir\{(Me_3C)_2PC_6H_4\text{-}2\text{-}O\}_2]$ and related complexes (Mason, Thomas, Empsall, Fletcher, Heys, Hyde, Jones & Shaw, 1974). The relatively long bond between the ether and the metal suggests that this will be labile in solution. The

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molecule does indeed show interesting fluxional behaviour in its NMR spectra, and this will be reported in detail elsewhere (Avent, Bedford & Chaloner, 1992).

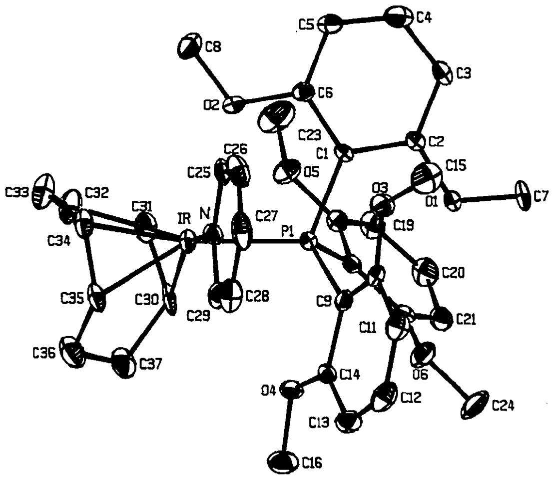

Fig. 1. Molecular structure and numbering scheme.

Experimental

Crystal data

$[Ir(C_{24}H_{27}O_6P)(C_8H_{12})(C_5H_5N)][PF_6]$
$M_r = 966.9$
Monoclinic
$P2_1/n$
$a = 16.609\ (3)$ Å
$b = 13.662\ (5)$ Å
$c = 17.280\ (4)$ Å
$\beta = 101.32\ (2)°$
$V = 3845.0$ Å^3
$Z = 4$
$D_x = 1.67$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 7$–$10°$
$\mu = 3.61$ mm^{-1}
$T = 295$ K
Blocks
0.2 × 0.2 × 0.15 mm
Yellow-orange
Crystal source: recrystallization from CH_2Cl_2/Et_2O

Data collection

Enraf-Nonius CAD-4 diffractometer
θ-2θ scans
Absorption correction: refined from ΔF
$T_{\min} = 0.79$, $T_{\max} = 1.42$
7293 measured reflections
7055 independent reflections
3896 observed reflections $[F^2 > 2\sigma(F^2)]$

$R_{\rm int} = 0.03$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 16$
$l = -20 \rightarrow 20$
2 standard reflections
frequency: 60 min
intensity variation: 2.4%

Refinement

Refinement on F
Final $R = 0.045$
$wR = 0.047$
$S = 1.2$
3896 reflections
505 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.03$
$\Delta\rho_{\max} = 0.77$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}
Atomic scattering factors from Enraf-Nonius (1990) *MolEN* programs

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

The $[PF_6]^-$ anion has two ordered *trans* F atoms, with the other four F atoms disordered and approximated by seven sites each given half occupancy. $U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{\rm eq}$
Ir	0.36255 (2)	0.10312 (3)	0.14989 (2)	0.0359 (1)
P1	0.47213 (13)	0.22167 (17)	0.17237 (13)	0.031 (1)
P2	0.97617 (19)	0.25909 (24)	0.15043 (21)	0.069 (2)
F1	0.9381 (4)	0.2151 (5)	0.2196 (4)	0.102 (4)
F2	1.0150 (4)	0.3062 (7)	0.0829 (5)	0.126 (5)
F3	1.0531 (9)	0.2781 (19)	0.2077 (9)	0.180 (14)
F4	0.9141 (9)	0.3407 (9)	0.1420 (9)	0.121 (9)
F5	0.9933 (15)	0.1553 (12)	0.1220 (12)	0.187 (15)
F6	0.9216 (11)	0.1937 (11)	0.0909 (11)	0.158 (12)
F7	1.0551 (7)	0.2038 (10)	0.1768 (9)	0.146 (8)
F8	0.8934 (8)	0.2951 (14)	0.1122 (9)	0.172 (10)
F9	1.0008 (10)	0.3564 (10)	0.2086 (10)	0.105 (10)
O1	0.5668 (4)	0.3980 (5)	0.2284 (4)	0.053 (3)
O2	0.2977 (4)	0.2869 (5)	0.1397 (4)	0.046 (3)
O3	0.4882 (4)	0.3027 (5)	0.3418 (4)	0.053 (4)
O4	0.5712 (4)	0.0544 (5)	0.1907 (4)	0.044 (3)
O5	0.4184 (4)	0.2962 (5)	0.0180 (4)	0.055 (4)
O6	0.6656 (4)	0.2223 (5)	0.1916 (4)	0.060 (4)
N	0.3626 (4)	0.1138 (5)	0.2729 (4)	0.038 (4)
C1	0.4330 (5)	0.3435 (6)	0.1838 (5)	0.035 (4)
C2	0.4871 (5)	0.4237 (6)	0.2084 (6)	0.041 (5)
C3	0.4572 (6)	0.5180 (7)	0.2117 (6)	0.051 (5)
C4	0.3745 (7)	0.5326 (8)	0.1917 (7)	0.061 (6)
C5	0.3194 (6)	0.4600 (7)	0.1676 (6)	0.048 (5)
C6	0.3490 (5)	0.3660 (7)	0.1649 (5)	0.037 (5)
C7	0.6250 (7)	0.4701 (8)	0.2520 (9)	0.091 (8)
C8	0.2130 (6)	0.3045 (9)	0.1189 (7)	0.070 (7)
C9	0.5381 (5)	0.1828 (7)	0.2662 (5)	0.035 (4)
C10	0.5388 (5)	0.2265 (7)	0.3394 (5)	0.039 (5)
C11	0.5883 (6)	0.1870 (8)	0.4071 (6)	0.056 (6)
C12	0.6329 (6)	0.1041 (10)	0.4012 (6)	0.066 (6)
C13	0.6297 (6)	0.0560 (8)	0.3298 (6)	0.055 (6)
C14	0.5809 (5)	0.0938 (7)	0.2634 (5)	0.039 (4)
C15	0.4978 (8)	0.3625 (10)	0.4096 (7)	0.082 (8)
C16	0.6224 (7)	−0.0252 (9)	0.1799 (7)	0.072 (7)
C17	0.5408 (5)	0.2550 (6)	0.1032 (5)	0.035 (4)
C18	0.5037 (5)	0.2955 (7)	0.0315 (5)	0.043 (5)
C19	0.5474 (6)	0.3364 (8)	−0.0208 (6)	0.058 (6)
C20	0.6314 (6)	0.3395 (8)	−0.0015 (6)	0.062 (6)
C21	0.6723 (6)	0.2981 (7)	0.0678 (6)	0.055 (5)
C22	0.6270 (6)	0.2562 (7)	0.1200 (6)	0.042 (5)
C23	0.3747 (8)	0.3504 (11)	−0.0455 (8)	0.103 (9)
C24	0.7512 (6)	0.2209 (10)	0.2118 (8)	0.085 (8)
C25	0.3168 (6)	0.1809 (7)	0.3024 (6)	0.048 (5)
C26	0.3188 (7)	0.1831 (8)	0.3846 (6)	0.062 (6)
C27	0.3633 (7)	0.1183 (8)	0.4334 (6)	0.068 (6)
C28	0.4080 (7)	0.0488 (9)	0.4032 (6)	0.061 (6)
C29	0.4071 (6)	0.0500 (8)	0.3236 (6)	0.046 (5)
C30	0.4047 (6)	0.0453 (7)	0.0514 (6)	0.054 (5)
C31	0.3308 (6)	0.0963 (8)	0.0241 (5)	0.057 (5)
C32	0.2481 (7)	0.0469 (10)	−0.0073 (7)	0.075 (7)
C33	0.2017 (7)	0.0233 (10)	0.0560 (7)	0.078 (7)
C34	0.2535 (6)	0.0182 (8)	0.1368 (6)	0.051 (5)
C35	0.3206 (6)	−0.0446 (8)	0.1548 (6)	0.053 (5)
C36	0.3493 (8)	−0.1125 (9)	0.0969 (8)	0.079 (7)
C37	0.4122 (7)	−0.0647 (9)	0.0547 (7)	0.077 (7)

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

*M*1 and *M*2 are the centres of the C30—C31 and C34—C35 bonds.

Ir—*M*1	2.005	Ir—*M*2	2.016
Ir—P1	2.410 (2)	Ir—O2	2.724 (6)
Ir—N	2.130 (7)	Ir—C30	2.117 (11)
Ir—C31	2.135 (9)	Ir—C34	2.125 (10)
Ir—C35	2.142 (10)	P1—C1	1.812 (9)
P1—C9	1.848 (8)	P1—C17	1.864 (10)
*M*1—Ir—*M*2	86.4	*M*1—Ir—P1	97.5
*M*1—Ir—O2	103.4	*M*1—Ir—N	170.9
*M*2—Ir—P1	168.4	*M*2—Ir—O2	119.3
*M*2—Ir—N	88.1	P1—Ir—O2	70.6 (1)
P1—Ir—N	86.2 (2)	O2—Ir—N	85.6 (2)
Ir—P1—C1	111.1 (3)	Ir—P1—C9	104.3 (3)
Ir—P1—C17	126.8 (3)	C1—P1—C9	109.4 (4)
C1—P1—C17	97.1 (4)	C9—P1—C17	107.5 (4)

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55996 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1031]

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Structure of $[Yb(OH)(C_{12}H_8N_2)_2(H_2O)_2]_2Cl_4.2C_{12}H_8N_2.CH_3OH$

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Abstract

The title compound, di-μ-hydroxo-bis[diaquabis(1,10-phenanthroline)ytterbium(III)] tetrachloride bis(1,10-phenanthroline) methanol solvate, lies around a crystallographic inversion center with symmetric [2.196 (2) and 2.208 (2) Å] hydroxy bridges. Two terminal water molecules and two bidentate phenanthroline ligands (phen) complete the eight-coordinate square-antiprismatic Yb coordination sphere. Two phen molecules and one methanol molecule are clathrated in the structure.

Comment

The dimeric cationic units, $[Yb(\mu\text{-OH})(phen)_2(H_2O)_2]_2^{2+}$, are connected *via* hydrogen bonding to the chlorine anions and to the two centrosymmetrically related clathrated phen molecules. The $Yb\cdots Yb^i$ separation in the dimer is 3.616 (1) Å. Coordinated and clathrated phen molecules are almost parallel with several contact distances less than 3.6 Å. The molecular packing is dominated by these graphite-type interactions which could be indicative of dipole–dipole interactions among coordinated (in the dimers) and uncoordinated phen molecules. The complex is isostructural with its yttrium analog (Grillone, Benetollo & Bombieri, 1991) and the differences observed in the corresponding bonding parameters are on average 0.028 Å, slightly shorter than expected given the 0.034 Å differences in the effective ionic radii of eight-coordinate Y^{III} and Yb^{III} (Shannon, 1976). The two structures differ slightly in the position of the clathrated methanol molecule.