Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71137 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: VS1005]

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Structure of an Iridium Complex of 1,1′-Bisdiphenylphosphinoferrocene†

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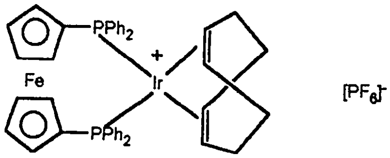
Abstract

The structure of [1,1′-bis(diphenylphosphino)ferrocene](η^4-1,5-cyclooctadiene)iridium(I) hexafluorophosphate, $[Ir(C_8H_{12})\{(C_5H_4\text{-}PPh_2)_2Fe\}][PF_6]$, shows approximately square-planar geometry at iridium. The cyclopentadienyl rings of the dppf ligand are close to parallel and staggered.

Comment

We have been interested for some time in the structures and solution conformations of cationic iridium complexes of hindered monophosphines, (Abbassioun, Hitchcock & Chaloner, 1989, 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). There have been fewer structural studies on complexes of chelating biphosphines. The structures of [IrCl(cod)(diop)] [cod = 1,5-cyclooctadiene; diop = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (Brunie, Mazan, Langlois & Kagan, 1976)], [IrCl(cod)(diphol)] [diphol = (2*R*,3*R*)-2,3-*O*-isopropylidene-1,4-bis(5*H*-dibenzophosphol-5-yl)-2,3-butanediol (Hayashi, Tanaka, Ogata, Kodama, Takahashi, Uchida & Uchida, 1983)] and [IrMe(cod)(dppe)] [dppe = 1,2-bis(diphenylphosphino)ethane (Churchill & Bezman, 1973)] have been determined, but all of these are neutral and five-coordinate. Complex (1) was prepared by reaction of $[Ir(cod)(py)_2][PF_6]$ (py = pyridine) with 1,1′-bis(diphenylphosphino)ferrocene (dppf) (Crabtree & Moorehouse, 1986). A previous synthesis of $[Ir(cod)(dppf)][ClO_4]$ used $[\{IrCl(cod)\}_2]$, dppf and $Ag[ClO_4]$ (Mague & Lloyd, 1988).



(1)

The structure of the complex is shown in Fig. 1. The geometry at iridium is approximately square planar, as expected. The Fe···Ir distance is 4.340 (2) Å, too long for any significant intermetallic interaction. It is useful to compare the geometry of the dppf ligand with that in a number of other complexes, most of which have found uses as hydrogenation catalysts. The angle between the cyclopentadienyl rings is 3.25°, as compared with 6.2° in $[PdCl_2(dppf)]$ or $[NiBr_2(dppf)]$ (Butler, Cullen, Kim, Rettig & Trotter, 1985). The P(1)···P(2) distance is 3.583 (4) Å which lies within the previously reported range [3.45–3.78 Å (Hayashi, Konishi, Kobori, Kumada, Higuchi & Hirotsu, 1984)]. The distances between the Fe atom and the cyclopentadienyl rings (1.630–1.640 Å) are also within normal ranges

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† $[2(\eta^4)$-1,5-Cyclooctadiene]-bis[μ-2κP:1(η^5)-cyclopentadienylidenediphenylphosphine]iridiumiron hexafluorophosphate.

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(Cullen, Kim, Einstein & Jones, 1985) as is the P—*M*—P angle [99.2 (1)°]. The cyclopentadienyl rings are close to staggered; the deviation of 5.4° from the fully staggered structure is again within the range previously reported.

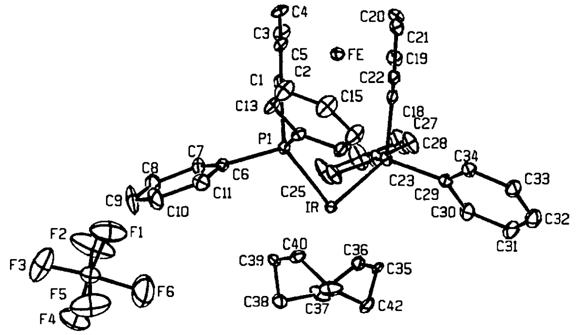

Fig. 1. Molecular structure and numbering scheme.

Experimental

Crystal data

$[FeIr(C_8H_{12})(C_{17}H_{14}P)_2]$-$[PF_6]$
$M_r = 999.7$
Monoclinic
$P2_1/n$
$a = 9.222\ (8)$ Å
$b = 22.620\ (10)$ Å
$c = 18.138\ (6)$ Å
$\beta = 91.74\ (5)$°
$V = 3781.9$ Å^3
$Z = 4$
$D_x = 1.76$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8$-9°
$\mu = 4.0$ mm^{-1}
$T = 298$ K
Block
0.05 × 0.2 × 0.2 mm
Deep red
Crystal source: recrystallization from CH_2Cl_2/Et_2O

Data collection

Enraf-Nonius CAD-4 diffractometer
θ-2θ scans
Absorption correction: refined from ΔF using *DIFABS* (Walker & Stuart, 1983)
$T_{min} = 0.72$, $T_{max} = 1.56$
7220 measured reflections
6792 independent reflections

4633 observed reflections $[|F^2| > 2\sigma(F^2)]$
$R_{int} = 0.04$
$\theta_{max} = 2$-25°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 26$
$l = -21 \rightarrow 21$
2 standard reflections
frequency: 60 min
intensity variation: −1.9%

Refinement

Refinement on F
Final $R = 0.055$
$wR = 0.072$
$S = 2.0$
4633 reflections
478 parameters
H-atom parameters not refined

$w = \sigma^{-2}(F)$
$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 3.33$ e Å^{-3} near Ir
$\Delta\rho_{min} = -0.28$ e Å^{-3} near Ir
Atomic scattering factors as embedded in the Enraf-Nonius *MolEN* programs

Refinement was on F where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{0.5}/Lp$. Computations used *MolEN* (Fair, 1990).

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

$U_{eq} = 1/3$(trace of the orthogonalized U_{ij} tensor). Cp1 and Cp2 are the centroids of the C1-C5 and C18-C22 cyclopentadienyl rings, repectively. *M*1 and *M*2 are the midpoints of the C35=C36 and C39=C40 double bonds.

	x	y	z	U_{eq}
Ir	0.17693 (5)	0.13617 (2)	0.27592 (2)	0.0270 (1)
Fe	0.49801 (18)	0.00119 (8)	0.23307 (10)	0.0390 (5)
P1	0.3232 (3)	0.0804 (1)	0.3579 (2)	0.030 (1)
P2	0.2424 (3)	0.0919 (1)	0.1640 (2)	0.032 (1)
P3	0.0913 (4)	0.1612 (2)	0.7985 (2)	0.059 (2)
F1	0.1016 (14)	0.0923 (5)	0.7998 (9)	0.146 (9)
F2	0.2177 (15)	0.1633 (6)	0.7473 (9)	0.197 (9)
F3	0.1853 (18)	0.1709 (10)	0.8616 (9)	0.225 (15)
F4	0.0769 (13)	0.2307 (5)	0.7925 (7)	0.122 (8)
F5	−0.0410 (12)	0.1593 (7)	0.8464 (9)	0.166 (10)
F6	−0.0215 (20)	0.1555 (8)	0.7308 (9)	0.223 (14)
C1	0.4868 (11)	0.0486 (6)	0.3259 (6)	0.036 (6)
C2	0.5830 (12)	0.0755 (6)	0.2780 (7)	0.045 (7)
C3	0.6946 (11)	0.0338 (8)	0.2606 (8)	0.062 (8)
C4	0.6742 (13)	−0.0154 (7)	0.3031 (9)	0.062 (8)
C5	0.5456 (13)	−0.0097 (6)	0.3428 (7)	0.047 (7)
C6	0.3899 (12)	0.1242 (5)	0.4368 (6)	0.033 (6)
C7	0.4962 (14)	0.1663 (6)	0.4233 (7)	0.045 (7)
C8	0.5412 (17)	0.2053 (7)	0.4794 (9)	0.071 (10)
C9	0.4748 (22)	0.2010 (9)	0.5486 (9)	0.100 (12)
C10	0.3730 (20)	0.1607 (8)	0.5610 (7)	0.070 (9)
C11	0.3250 (15)	0.1221 (6)	0.5062 (7)	0.051 (7)
C12	0.2277 (12)	0.0200 (5)	0.3990 (6)	0.036 (6)
C13	0.2862 (13)	−0.0132 (6)	0.4552 (7)	0.047 (7)
C14	0.2230 (16)	−0.0641 (7)	0.4837 (8)	0.065 (9)
C15	0.0911 (16)	−0.0809 (8)	0.4519 (9)	0.074 (10)
C16	0.0309 (14)	−0.0487 (7)	0.3937 (9)	0.063 (9)
C17	0.0974 (12)	0.0013 (6)	0.3680 (7)	0.043 (7)
C18	0.3357 (12)	0.0217 (6)	0.1620 (6)	0.036 (6)
C19	0.4601 (13)	0.0062 (6)	0.1230 (7)	0.047 (7)
C20	0.5007 (15)	−0.0516 (6)	0.1414 (8)	0.054 (8)
C21	0.4008 (16)	−0.0742 (7)	0.1901 (9)	0.067 (9)
C22	0.2962 (12)	−0.0293 (5)	0.2049 (7)	0.037 (6)
C23	0.3601 (14)	0.1402 (6)	0.1135 (6)	0.043 (6)
C24	0.4313 (15)	0.1870 (6)	0.1475 (7)	0.053 (7)
C25	0.5291 (19)	0.2211 (7)	0.1107 (8)	0.083 (10)
C26	0.5503 (18)	0.2129 (7)	0.0368 (9)	0.080 (9)
C27	0.4817 (18)	0.1674 (7)	0.0013 (8)	0.072 (9)
C28	0.3837 (16)	0.1296 (6)	0.0385 (7)	0.058 (8)
C29	0.0854 (12)	0.0787 (5)	0.1032 (6)	0.035 (6)
C30	0.0366 (16)	0.1190 (7)	0.0491 (7)	0.053 (8)
C31	−0.0946 (16)	0.1069 (8)	0.0108 (7)	0.067 (9)
C32	−0.1735 (14)	0.0578 (8)	0.0230 (8)	0.063 (9)
C33	−0.1276 (14)	0.0190 (7)	0.0732 (8)	0.057 (8)
C34	0.0004 (12)	0.0287 (6)	0.1147 (7)	0.041 (6)
C35	−0.0211 (12)	0.1732 (5)	0.2245 (7)	0.040 (6)
C36	0.0902 (13)	0.2072 (6)	0.2048 (6)	0.040 (6)
C37	0.1222 (16)	0.2657 (6)	0.2374 (8)	0.059 (8)
C38	0.1193 (15)	0.2682 (6)	0.3221 (7)	0.047 (7)
C39	0.1576 (13)	0.2090 (5)	0.3573 (7)	0.041 (6)
C40	0.0547 (12)	0.1647 (6)	0.3725 (6)	0.039 (6)
C41	−0.1005 (15)	0.1649 (7)	0.3569 (9)	0.070 (9)
C42	−0.1368 (13)	0.1883 (7)	0.2789 (8)	0.057 (8)
Cp1	0.5968	0.0265	0.3201	
Cp2	0.3987	−0.0255	0.1643	
*M*1	0.0345	0.1902	0.2146	
*M*2	0.1061	0.1869	0.3649	

Table 2. *Geometric parameters* (Å, °)

Ir—*M*1	2.090	Ir—*M*2	2.101
Ir—P1	2.346 (3)	Ir—P2	2.358 (3)
Ir—C35	2.191 (11)	Ir—C36	2.197 (12)
Ir—C39	2.223 (12)	Ir—C40	2.208 (12)
Fe—Cp1	1.630	Fe—Cp2	1.640
Fe—C1	2.002 (12)	Fe—C2	2.016 (13)
Fe—C3	2.006 (12)	Fe—C4	2.067 (14)
Fe—C5	2.039 (13)	Fe—C18	2.000 (11)
Fe—C19	2.019 (13)	Fe—C20	2.049 (14)
Fe—C21	2.068 (15)	Fe—C22	2.035 (11)
P1—C1	1.784 (11)	P1—C6	1.830 (11)
P1—C12	1.800 (12)	P2—C18	1.806 (13)
P2—C23	1.809 (13)	P2—C29	1.818 (11)
Ir···Fe	4.340 (2)		
*M*1—Ir—*M*2	83.4	*M*1—Ir—P1	172.8
*M*1—Ir—P2	87.9	*M*2—Ir—P1	89.6
*M*2—Ir—P2	170.8	P1—Ir—P2	99.2 (1)
Cp1—Fe—Cp2	178.9	Ir—P1—C1	119.1 (4)
Ir—P1—C6	112.2 (4)	Ir—P1—C12	113.1 (4)
C1—P1—C6	101.9 (5)	C1—P1—C12	104.9 (6)
C6—P1—C12	104.2 (5)	Ir—P2—C18	121.7 (4)
Ir—P2—C23	110.6 (4)	Ir—P2—C29	111.8 (4)
C18—P2—C23	103.1 (6)	C18—P2—C29	102.4 (5)
C23—P2—C29	105.7 (6)		

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 thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71128 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1043]

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Ferrocenyl Ligands. Part 4. Structure of [1,1′-Bis(diphenylphosphino)-3,3′-bis(trimethylsilyl)ferrocene]dichlorocobalt†

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Abstract

1,1′-Bis(diphenylphosphino)-3,3′-bis(trimethylsilyl)ferrocene acts as a bidentate ligand when reacted with $CoCl_2$, producing a tetrahedral P_2Cl_2 coordination sphere that is significantly distorted. The influence of the trimethylsilyl groups in this distortion is considerable, restraining the ferrocenyl moiety from adopting the eclipsed configuration preferred for binding tetrahedral ions.

Comment

Recently we have embarked on a study of ferrocenyl ligands with a view to synthesizing novel tunable ligands (Houlton, Roberts, Silver & Drew 1990; Houlton, Ibrahim, Dilworth & Silver, 1990; Houlton, Ahmet, Miller, Silver & Slade, 1993). A part of this study is the investigation of sterically crowded ligands with the aim of introducing stereoselectivity to complex formation, and we have previously reported 1,1′-bis(diphenylphosphino)-3,3′-bis(trimethylsilyl)ferrocene (1) (Brown, Houlton, Roberts, Frampton & Silver, 1993). Here we report the crystal and molecular structure of the cobalt chloride complex of this ligand, (1)$CoCl_2$, and discuss the effect of the 3,3′-substituents compared to complexes of the bis(diphenylphosphino)ferrocene (fdpp).

The structure of the parent ligand reveals a *cisoid* arrangment of the diphenylphosphino groups (Brown, Houlton, Roberts, Frampton & Silver,

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† Dichloro-$2\kappa^2Cl$-bis{μ-diphenyl[3-(trimethylsilyl)-$2\kappa P$:1(η^5)-cyclopentadienylidene]phosphine}-cobaltiron.

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