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trans-Carbonyl(pentafluorophenyl-C)bis-[(pentafluorophenyl)diphenylphosphine-P]-iridium(I)

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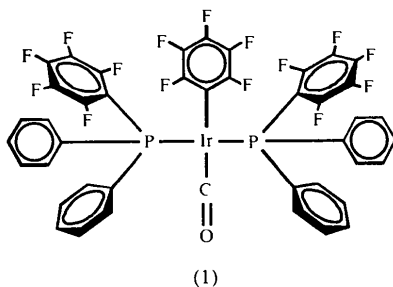
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Abstract

In *trans*-[Ir(C₆F₅){P(C₆F₅)(C₆H₅)₂}(CO)], the Ir—P and Ir—C distances are comparable to those of the triphenylphosphine analogue. F···F interactions appear to dominate the configuration, resulting in virtually eclipsed C₆F₅(Ir) and C₆F₅(P) rings.

Comment

It has been shown that a σ -pentafluorophenyl ligand can markedly influence the tendency of low-valent metal complexes to undergo oxidative addition reactions (Bennett, Bruce & Goodfellow, 1973; Bennett, Bruce & Gardner, 1973; Rausch & Moser 1974). We have been investigating crystallographically the steric and electronic effects of F atoms in arylphosphine and -phosphite ligands (Atherton *et al.*, 1995, 1997), and during this work obtained crystals of the title compound, (1).



The structural features of this complex can be directly compared to those of *trans*-carbonyl(pentafluorophenyl)bis(triphenylphosphine)iridium(I), (2) (Clearfield *et al.*, 1975). The Ir coordination environments are very similar: Ir—P distances of 2.305 (1) and 2.304 (1) Å in (1), *cf.* 2.326 (4) and 2.305 (5) Å in (2), Ir—C_{carbonyl} 1.863 (5) Å in (1), *cf.* 1.891 (17) Å in (2), and Ir—C_{aryl} 2.092 (4) Å in (1), *cf.* 2.090 (16) Å in (2). The Ir—C_{aryl} distances suggest little π overlap between the ligand and the metal centres, indicating that the reduced reactivity of these pentafluorophenyl derivatives towards oxidative addition reactions is predominately a steric effect. This is in marked contrast to the results of our work on fluorophenylimido molybdenum dimers (Fawcett *et al.*, 1994; Bhattacharyya *et al.*, 1997), which showed that the introduction of the —N(C₆F₅) ligand had a significant electronic influence on the metal centres.

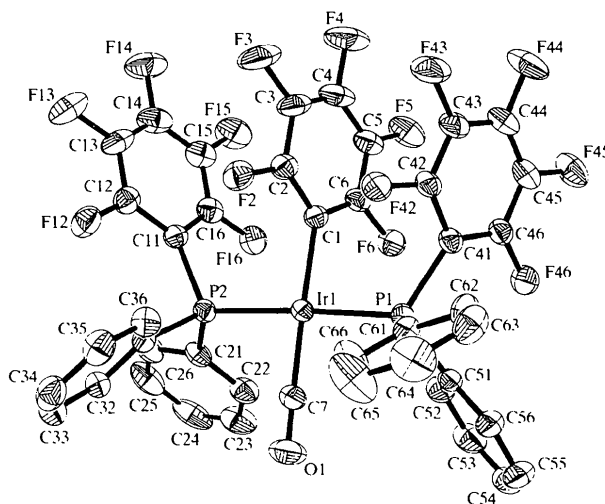


Fig. 1. The molecular structure of the title compound, showing the atom-numbering scheme and 30% displacement ellipsoids. H atoms have been omitted for clarity.

In the structure determination of (2), the atoms in the pentafluorophenyl ring were seen to have large displacement parameters, affording unusual C—C and C—F bond lengths. In (1), the metal-bound pentafluorophenyl ring is well defined and the average C—C [1.378 (17) Å] and C—F [1.348 (6) Å] distances are virtually identical to the corresponding distances in the P-bound pentafluorophenyl rings [1.378 (15) and 1.340 (7) Å, respectively]. In contrast to the staggered arrangement of the phosphine aryl groups in (2) and in most *trans*-bis(phosphine) metal complexes, in (1), the phosphine aryl groups are eclipsed and both of the C₆F₅(P) rings and the C₆F₅(Ir) ring line up, presumably as a result of interactions between the F atoms, resulting in very small C41—P1—Ir1—C1 and C11—P2—Ir1—C1 torsion angles [3.7 (2) and 7.1 (2)°, respectively]. There is slight bending of the P1—Ir1—P2 axis [175.4 (1)°]

away from the σ -aryl ligand, to relieve some steric crowding. As a result of the eclipsed arrangement of the rings, the molecule exhibits an approximate and non-crystallographic twofold axis through C1, Ir1, C7 and O1. Additionally, in an extended view of the crystal across several unit cells, the protio-aryl rings and the fluoro-aryl rings align with each other to give fluorinous and hydrocarbon channels within the crystal. We (Fawcett *et al.*, 1997) and others (Guillevic *et al.*, 1997) have noted a similar tendency for highly fluorinated ligands in metal complexes to align in the solid state; this effect in these classes of metal complexes requires further investigation.

Experimental

The title complex was formed by allowing a solution of *mer*-[IrF₃(CO){PPh₂(C₆F₅)₂]₂ in CD₂Cl₂ to stand at room temperature for several weeks. Decanting of the solvent afforded a few yellow crystals.

Crystal data

[Ir(C ₆ F ₅)(C ₁₈ H ₁₀ F ₅ P) ₂ (CO)]	Mo K α radiation
$M_r = 1091.73$	$\lambda = 0.71073 \text{ \AA}$
Triclinic	Cell parameters from 40 reflections
$P\bar{1}$	$\theta = 5.09\text{--}12.26^\circ$
$a = 11.695 (2) \text{ \AA}$	$\mu = 3.525 \text{ mm}^{-1}$
$b = 11.910 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 15.535 (2) \text{ \AA}$	Irregular block
$\alpha = 72.61 (1)^\circ$	$0.76 \times 0.41 \times 0.26 \text{ mm}$
$\beta = 79.83 (1)^\circ$	Yellow
$\gamma = 77.16 (2)^\circ$	
$V = 1999.1 (7) \text{ \AA}^3$	
$Z = 2$	
$D_x = 1.814 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Siemens P4 diffractometer	6507 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.030$
Absorption correction:	$\theta_{\text{max}} = 26^\circ$
ψ scan (XEMP in SHELXTL/PC; Sheldrick, 1996)	$h = -1 \rightarrow 12$
$T_{\text{min}} = 0.27, T_{\text{max}} = 0.46$	$k = -13 \rightarrow 14$
8709 measured reflections	$l = -19 \rightarrow 19$
7531 independent reflections	3 standard reflections every 100 reflections
	intensity decay: $< 1\%$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = -0.001$
$R[F^2 > 2\sigma(F^2)] = 0.033$	$\Delta\rho_{\text{max}} = 1.246 \text{ e \AA}^{-3}$
$wR(F^2) = 0.084$	$(0.95 \text{ \AA from Ir})$
$S = 0.976$	$\Delta\rho_{\text{min}} = -0.698 \text{ e \AA}^{-3}$
7531 reflections	Extinction correction: none
559 parameters	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
H atoms constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0530P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Selected geometric parameters ($\text{\AA}, ^\circ$)

Ir1—C7	1.863 (5)	C1—C2	1.369 (6)
Ir1—C1	2.092 (4)	C1—C6	1.399 (7)
Ir1—P2	2.3050 (12)	C2—F2	1.356 (6)
Ir1—P1	2.3044 (12)	C2—C3	1.398 (8)
P1—C61	1.821 (4)	C3—F3	1.350 (6)
P1—C51	1.821 (4)	C3—C4	1.357 (9)
P1—C41	1.845 (5)	C4—F4	1.347 (6)
P2—C21	1.821 (5)	C4—C5	1.370 (9)
P2—C31	1.833 (5)	C5—F5	1.339 (7)
P2—C11	1.843 (5)	C5—C6	1.376 (7)
C7—O1	1.133 (6)	C6—F6	1.350 (5)
C7—Ir1—C1	175.7 (2)	C41—P1—Ir1	114.69 (15)
C7—Ir1—P2	87.6 (2)	C21—P2—Ir1	117.0 (2)
C1—Ir1—P2	92.43 (12)	C31—P2—Ir1	108.7 (2)
C7—Ir1—P1	88.9 (2)	C11—P2—Ir1	116.1 (2)
C1—Ir1—P1	91.22 (12)	O1—C7—Ir1	176.1 (5)
P2—Ir1—P1	175.41 (4)	C2—C1—Ir1	124.0 (4)
C61—P1—Ir1	117.2 (2)	C6—C1—Ir1	122.5 (3)
C51—P1—Ir1	110.6 (2)		

Data collection: XSCANS (Fait, 1991). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1996). Program(s) used to refine structure: SHELXTL/PC. Molecular graphics: SHELXTL/PC. Software used to prepare material for publication: SHELXTL/PC.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1027). Services for accessing these data are described at the back of the journal.

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