ELSEVIER Inorganica Chimica Acta 233 (1995) 103–107

Cyclometallation of a pentafluorobenzaldehyde azine phosphine via a C–F bond fission by iridium(I): crystal structure of $[IrCl_2(CO)\{PPh_2CH_2C(Bu^t)=N\text{–}N=CH(C_6F_4)\}]$

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Received 20 September 1994; revised 14 December 1994

Abstract

Condensation of Z-$PPh_2CH_2C(Bu^t)=NNH_2$ (**1**) with pentafluorobenzaldehyde gave the azine phosphine *Z,E*-$PPh_2CH_2C(Bu^t)=N\text{–}N=CH(C_6F_5)$ (**2**). When **2** was heated in benzene with $[IrCl(CO)_2(p\text{-toluidine})]$, it gave the cyclometallated dichlorocarbonyliridium(III) complex $[IrCl_2(CO)\{PPh_2CH_2C(Bu^t)=N\text{–}N=CH(C_6F_4)\}]$ (**4**), the formation of which involved a C–F bond fission. Proton, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and ^{19}F NMR data are given. Crystals of **4** are monoclinic, space group $P2_1/c$ with $a=10.6313(11)$, $b=16.0243(14)$, $c=17.968(2)$ Å, $\beta=100.258(7)°$ and $Z=4$, $R_1=0.0299$ for 6085 observed reflections with $I>2.0\sigma(I)$.

Keywords: Crystal structures; Cyclometallation; Iridium complexes; Azine phosphine complexes; Carbonyl complexes

1. Introduction

The C–F bond is considered to be one of the least reactive bonds due to its high bond dissociation energy (BDE) (e.g. BDE = 154 kcal mol^{-1} for hexafluorobenzene (C_6F_6) [1]). For example, because of its relative inertness C_6F_6 has been used as a solvent in a Ph–H bond fission reaction by the iridium(I) complex $[(\eta^5\text{-}C_5H_5)Ir(CO)_2]$, giving $[(\eta^5\text{-}C_5H_5)IrH(Ph)(CO)]$ [2]. There are many reports on C–X (X = H, I, Br or Cl) bond activation [1–7] but there are relatively few on inter- or intramolecular C–F bond activation reactions. The area has been recently reviewed [8]. The cyclometallation of the pentafluorophenyl group with C–F bond fission has been reported with ligands such as $C_6F_5N=NC_6F_5$ [9,10]; $C_6F_5N=NPh$ [10]; $C_6F_5CH=NC_6H_4NH_2\text{-}2$ [11]; $C_6F_5CH=NCH_2CH_2NMe_2$ [12–14]; $C_6F_5CH=NPh$ [14]; $C_6F_5PPh_2$ [15,16] or $C_6F_5CH=NCH_2(C_6H_4X\text{-}2)$ (X = H, Cl or Br) [17,18]. These have been used to promote cyclometallation (or orthometallation) with metals such as Ru(II) [9]; Mn(I) [10]; W(0) [11,12]; Pt(II) [13–18] or Ni(0) [8]. Literature reports on intermolecular C–F bond activation by iridium(I) are (i) thermolysis of $[MeIr(PEt_3)_3]$ in C_6F_6 to give $[Ir(C_6F_5)(PEt_3)_2(PFEt_2)]$ [19] and (ii) photolysis of $[(\eta^5\text{-}C_5H_5)IrH_2(PMe_3)]$ to give $[(\eta^5C_5H_5)IrH(C_6F_5)(PMe_3)]$ [20]. Neither of these cases provided spectroscopic evidence for the formation of an Ir–F bond. In previous papers [21–25] we have used azine phosphines of the type $PPh_2CH_2C(Bu^t)=N\text{–}N=CHR$ (R = aryl, heterocyclic or alkyl group), derived from the phosphino hydrazone Z-$PPh_2CH_2C(Bu^t)=NNH_2$ (**1**) [26], to promote agostic interaction (C–H → Ru) [21] or aryl fluoride coordination (ArF → Ru) [22] or to promote C–H bond activation with Ir(I) [23] or C–X (X = I, Br or Cl) bond activation with W(0) [24] or C–X (X = H, I or Br) bond activation with Pt(II) [25]. In the present paper we describe the cleavage of the C–F bond of pentafluorobenzaldehyde azine phosphine *Z,E*-$PPh_2CH_2C(Bu^t)=N\text{–}N=CH(C_6F_5)$ (**2**) by iridium(I) to give the cyclometallated iridium(III) complex $[IrCl_2(CO)\{PPh_2CH_2C(Bu^t)=N\text{–}N=CH(C_6F_4)\}]$ (**4**).

2. Experimental

The apparatus used and general techniques were the same as other recent publications from this laboratory [26]. The phosphines **1** [26] and **2** [22], and $[IrCl(CO)_2(p\text{-toluidine})]$ [27] were prepared according to published procedures.

SSDI 0020-1693(95)04457-K

2.1. [$IrCl_2(CO)\{PPh_2CH_2C(Bu^t)=N–N=CH(C_6F_4)\}$] (4)

A solution containing [$IrCl(CO)_2$(*p*-toluidine)] (50 mg, 0.128 mmol) and the azine phosphine 2 (61 mg, 0.128 mmol) in benzene (~1.5 cm^3) was heated to 75 °C for 20 min. The resulting solution was concentrated to a low volume (~0.5 cm^3) under reduced pressure. Addition of hexane to the residue gave the dichlorocarbonyliridium(III) complex 4 as yellow microcrystals (46 mg, 48%). *Anal.* Found: C, 41.45; H, 2.7; Cl, 9.6; N, 3.75. Calc. for $C_{26}H_{22}Cl_2F_4IrN_2OP$: C, 41.7; H, 2.95; Cl, 9.45; N, 3.75%. *m/z* (FAB): 713 (*M*−Cl) and 685 (*M*−Cl−CO). IR (KBr disc): ν(C≡O) 2080 cm^{-1}. $^{31}P\{^1H\}$ NMR (36.2 MHz, CD_2Cl_2, relative to TMS) δ_P: −4.9 ppm. ^1H NMR (100 MHz, CD_2Cl_2, relative to TMS) δ_H (ppm): 1.41 (9H, s, Bu^t), 2.69 (1H, dd, ^2J(HH) 18.8 Hz, ^2J(PH) 12.0 Hz, CH_2), 3.62 (1H, dd, ^2J(HH) 18.8 Hz, ^2J(PH) 11.7 Hz, CH_2), 8.50 (1H, t, ^4J(PH) = *J*(FH) 2.1 Hz, CH=N). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, relative to TMS) δ_C (ppm): 26.4 (1C, d, ^1J(PC) 43.2 Hz, CH_2), 29.3 (3C, s, CMe_3), 41.6 (1C, d, ^3J(PC) 6.5 Hz, CMe_3), 122.5 (1C, d, ^1J(PC) 67.3 Hz, C_{ipso}), 126.3 (1C, d, ^1J(PC) 63.3 Hz, C_{ipso}), 128.8 (2C, d, ^3J(PC) 11.5 Hz, C_{meta}), 130.0 (2C, d, ^3J(PC) 12.1 Hz, C_{meta}), 131.5 (2C, d, ^2J(PC) 9.2 Hz, C_{ortho}), 132.5 (1C, d, ^4J(PC) 2.9 Hz, C_{para}), 133.6 (2C, d, ^2J(PC) 11.1 Hz, C_{ortho}), 133.8 (1C, d, ^4J(PC) 3.0 Hz, C_{para}), 161.3 (1C, dd, ^2J(PC) 8.7 Hz, ^5J(FC) 5.5 Hz, C≡O), 164.8 (1C, m, HC=N), 179.1 (1C, d, ^2J(PC) 2.6 Hz, Bu^tC=N) (resonances due to Ir(C_6F_4) carbons were not identified). ^{19}F NMR (84.26 MHz, C_6D_6, relative to $CFCl_3$) δ_F (ppm): −121.2 (1F, dd, *J*(FF) 14.7, 24.4 Hz), −138.1 (1F, m), −147.7 (1F, m), −164.1 (1F, t, *J*(FF) 19.6 Hz).

2.2. Single crystal X-ray diffraction analysis of 4

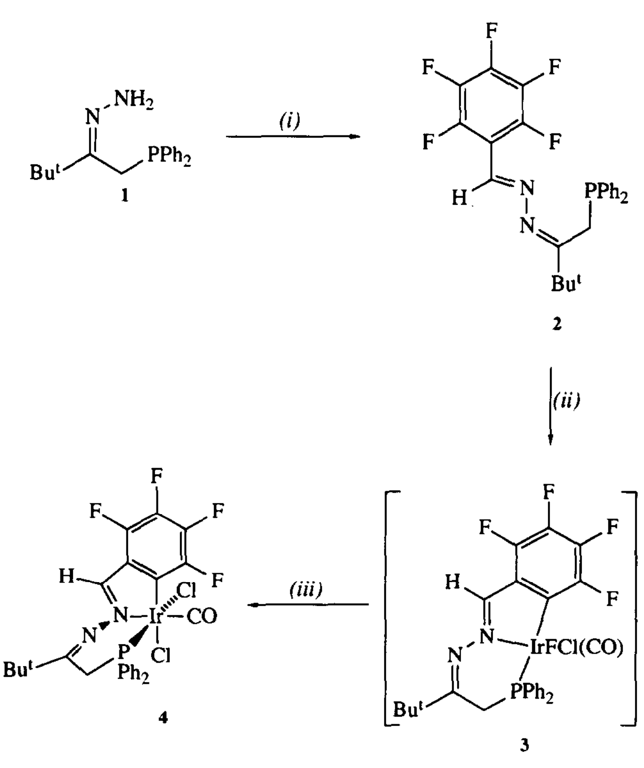
All crystallographic measurements were carried out on a Stoe STADI4 diffractometer operating in the ω–θ scan mode using graphite monochromated Mo Kα X-radiation (λ = 71.069 pm) and an on-line profile fitting method [28]. The data set was corrected for absorption using azimuthal ψ-scans (maximum and minimum transmission factors 0.5400 and 0.6576, respectively).

The structure was determined by heavy atom methods using SHELXS-86 [29] and was refined by full-matrix least-squares (based on F^2) using SHELXL-93 [30]. All data were used in the refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters including those of the dichloromethane solvate molecule. Restraints were applied to the phosphine phenyl groups so each group remained flat with overall C_{2v} symmetry. All hydrogen atoms were constrained to calculated positions (C–H = 0.93, 0.96, 0.97 and 0.99 Å for phenyl, methyl, methylene and methine hydrogen atoms, respectively) with fixed isotropic thermal parameters of $n(U_{eq})$ of the parent carbon atom where *n* was 1.5 for methyl hydrogens and 1.2 for all others. The weighting scheme $w = [\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$ (where $P = (F_o^2 + 2F_c^2)/3$) was used. Apart from a small ripple close to one of the chlorine atoms of the solvate molecule, the final Fourier difference synthesis was flat and showed no features of chemical significance (maximum and minimum residual densities 1.203 and −0.844 e Å^{-3}). Final non-hydrogen atomic coordinates are given in Table 1. An ORTEP [31] diagram of 4 is given in Fig. 1.

Crystal data. $C_{26}H_{22}Cl_2F_4IrN_2OP \cdot CH_2Cl_2$, 0.68 × 0.30 × 0.19 mm, *M* = 833.45 (includes solvate molecule), monoclinic, space group $P2_1/c$, *a* = 10.6313(11), *b* = 16.0243(14), *c* = 17.968(2) Å, β = 100.258(7)°, *U* = 3012.1(5) Å^3, *Z* = 4, D_x = 1.838 Mg m^{-3}, μ = 4.89 mm^{-1}, *F*(000) = 1616.

Data collection. $4.0 < 2\theta < 50.0°$; each scan divided into 30 steps, scan widths and step sizes calculated from a learnt profile; scan speeds 1.0–8.0° min^{-1} (subject to a fast pre-scan). Number of data collected = 14558; number of unique data, *n* = 6917; number with $F_o > 4.0\sigma(F_o)$ = 6085; $R_{int}\{=\Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma[F_o^2]\} = 0.0294$; $R_{sig}\{=\Sigma[\sigma F_o^2]/\Sigma[F_o^2]\} = 0.0321$; *T* = 173 K.

Structure refinement. Number of parameters, *p* = 364; $R_1\{=\Sigma||F_o| - |F_c||/\Sigma|F_o|\} = 0.0299$; $wR_2\{=(\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}\} = 0.0513$; goodness of fit $s\{=$



Scheme 1. (i) C_6F_5CHO; (ii) [$IrCl(CO)_2$(*p*-toluidine)]; (iii) chloride from [$IrCl(CO)_2$(*p*-toluidine)].

Table 1
Fractional non-hydrogen atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($Å^2 \times 10^3$) for **4** with e.s.d.s in parentheses

Atom	x	y	z	U_{eq} [a]
Ir(1)	540.88(11)	2285.22(7)	1987.41(6)	18.97(4)
P(1)	613.5(7)	938.2(5)	2402.0(4)	19.20(15)
C(111)	1406(3)	178(2)	1896(2)	22.4(6)
C(112)	1191(3)	223(2)	1108(2)	29.7(7)
C(113)	1747(3)	−361(2)	696(2)	33.1(8)
C(114)	2529(3)	−975(2)	1063(2)	31.4(7)
C(115)	2757(3)	−1021(2)	1845(2)	31.1(7)
C(116)	2183(3)	−446(2)	2266(2)	25.6(6)
C(121)	1282(3)	861(2)	3399(2)	23.4(6)
C(122)	2602(3)	973(2)	3631(2)	30.5(7)
C(123)	3122(4)	1018(2)	4394(2)	41.8(9)
C(124)	2331(4)	965(3)	4928(2)	45.4(10)
C(125)	1035(4)	853(2)	4706(2)	41.0(9)
C(126)	507(3)	794(2)	3945(2)	29.8(7)
Cl(1)	157.5(8)	3728.8(5)	1628.8(4)	28.1(2)
Cl(2)	−1059.7(7)	1884.2(5)	908.0(4)	27.8(2)
C(2)	−1042(3)	590(2)	2282(2)	22.3(6)
C(3)	−2108(3)	1191(2)	2380(2)	22.7(6)
C(31)	−3468(3)	839(2)	2207(2)	29.8(7)
C(32)	−3574(3)	63(2)	2689(2)	42.0(9)
C(33)	−3781(4)	610(3)	1356(2)	44.1(10)
C(34)	−4445(3)	1491(2)	2365(2)	38.0(8)
N(4)	−2000(2)	1951(2)	2607.9(14)	23.2(5)
N(5)	−762(2)	2294(2)	2733.2(14)	20.7(5)
C(6)	−373(3)	2638(2)	3385(2)	23.8(6)
C(7)	932(3)	2922(2)	3519(2)	21.1(6)
C(8)	1506(3)	3296(2)	4193(2)	27.6(7)
C(9)	2783(3)	3506(2)	4310(2)	30.8(7)
C(10)	3480(3)	3335(2)	3752(2)	28.9(7)
C(11)	2903(3)	2981(2)	3074(2)	25.4(7)
C(12)	1635(3)	2756(2)	2938(2)	21.0(6)
F(8)	822(2)	3457.8(14)	4734.1(10)	39.0(5)
F(9)	3350(2)	3879.3(15)	4953.4(11)	43.9(6)
F(10)	4724(2)	3534.2(14)	3865.0(12)	41.6(5)
F(11)	3656(2)	2857.7(13)	2549.8(11)	35.6(5)
C(13)	1846(3)	2242(2)	1408(2)	25.9(6)
O(13)	2624(2)	2238(2)	1054.1(13)	41.1(6)
C(1s)	7103(5)	3682(3)	521(3)	67.2(14)
Cl(1s)	5784(2)	3550(2)	949.3(9)	125.5(8)
Cl(2s)	6839(2)	3476.7(13)	−449.5(9)	101.2(6)

[a] $U_{eq} = 1/3 \times$ trace of the orthogonalised U_{ij} matrix.

$\Sigma[w(F_o{}^2-F_c{}^2)^2]/(n-p)]^{1/2}\}=1.052$; max. $\Delta/\sigma=0.001$, mean $\Delta/\sigma=0.000$.

3. Results and discussion

We have found that the azine phosphines, *Z*,*E*-$PPh_2CH_2C(Bu^t)=N–N=CH(C_6H_4X$-2) (X = H, Br, Cl or F), derived from benzaldehyde or 2-halobenzaldehydes, when treated with $[IrCl(CO)_2$(*p*-toluidine)] underwent facile, selective C–H bond activation reaction to give cyclometallated iridium(III) hydrides of type $[IrHCl(CO)\{PPh_2CH_2C(Bu^t)=N–N=CH(C_6H_3X\text{-}2)\}]$ [23]. Treatment of pentafluorobenzaldehyde azine phosphine **2** [22] with $[IrCl(CO)_2$(*p*-toluidine)] in benzene

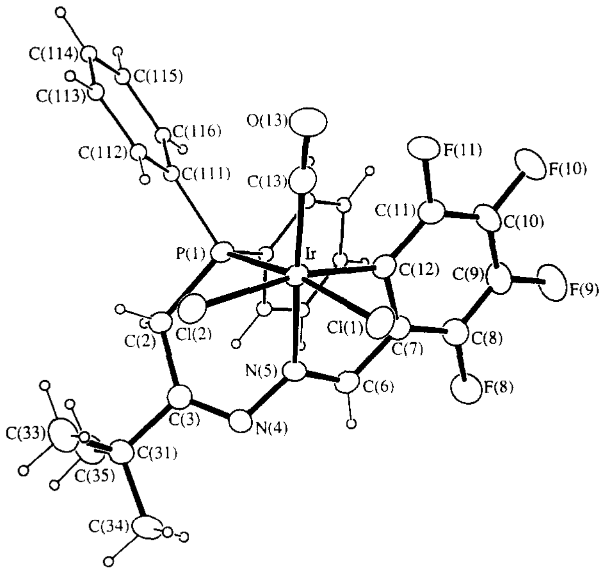


Fig. 1. ORTEP [31] representation of the molecular structure of compound **4**. Ellipses are shown at the 50% probability level. In the interest of clarity both phenyl carbon atoms and hydrogen atoms are drawn as circles each with an arbitrary small radius.

Table 2
Selected bond lengths (Å) and angles (°) for **4** with e.s.d.s in parentheses

Ir(1)–C(13)	1.878(3)	Ir(1)–C(12)	2.033(3)
Ir(1)–N(5)	2.092(2)	Ir(1)–P(1)	2.2803(8)
Ir(1)–Cl(1)	2.4164(8)	Ir(1)–Cl(2)	2.4279(8)
P(1)–C(121)	1.811(3)	P(1)–C(111)	1.814(3)
P(1)–C(2)	1.822(3)	C(2)–C(3)	1.520(4)
C(3)–N(4)	1.284(4)	C(3)–C(31)	1.531(4)
N(4)–N(5)	1.406(3)	N(5)–C(6)	1.293(4)
C(6)–C(7)	1.439(4)	C(7)–C(8)	1.391(4)
C(7)–C(12)	1.413(4)	C(8)–F(8)	1.339(3)
C(8)–C(9)	1.378(5)	C(9)–F(9)	1.346(4)
C(9)–C(10)	1.376(5)	C(10)–F(10)	1.340(4)
C(10)–C(11)	1.384(4)	C(11)–F(11)	1.356(3)
C(11)–C(12)	1.374(4)	C(13)–O(13)	1.130(4)
C(13)–Ir(1)–C(12)	96.36(12)	C(13)–Ir(1)–N(5)	173.75(11)
C(12)–Ir(1)–N(5)	78.72(11)	C(13)–Ir(1)–P(1)	99.25(10)
C(12)–Ir(1)–P(1)	95.48(9)	N(5)–Ir(1)–P(1)	77.57(7)
C(13)–Ir(1)–Cl(1)	89.64(10)	C(12)–Ir(1)–Cl(1)	85.02(9)
N(5)–Ir(1)–Cl(1)	93.72(7)	P(1)–Ir(1)–Cl(1)	170.97(3)
C(13)–Ir(1)–Cl(2)	91.68(10)	C(12)–Ir(1)–Cl(2)	169.83(8)
N(5)–Ir(1)–Cl(2)	93.64(7)	P(1)–Ir(1)–Cl(2)	89.34(3)
Cl(1)–Ir(1)–Cl(2)	88.82(3)	C(2)–P(1)–Ir(1)	105.97(10)
C(3)–C(2)–P(1)	121.1(2)	N(4)–C(3)–C(2)	127.7(3)
N(4)–C(3)–C(31)	116.2(3)	C(2)–C(3)–C(31)	116.1(3)
C(3)–N(4)–N(5)	116.7(2)	C(6)–N(5)–N(4)	116.8(2)
C(6)–N(5)–Ir(1)	116.2(2)	N(4)–N(5)–Ir(1)	127.0(2)
N(5)–C(6)–C(7)	115.5(3)	C(8)–C(7)–C(12)	121.1(3)
C(8)–C(7)–C(6)	122.9(3)	C(12)–C(7)–C(6)	115.9(3)
F(8)–C(8)–C(9)	119.4(3)	F(8)–C(8)–C(7)	120.3(3)
C(9)–C(8)–C(7)	120.3(3)	F(9)–C(9)–C(10)	119.8(3)
F(9)–C(9)–C(8)	121.1(3)	C(10)–C(9)–C(8)	119.0(3)
F(10)–C(10)–C(9)	119.1(3)	F(10)–C(10)–C(11)	120.1(3)
C(9)–C(10)–C(11)	120.7(3)	F(11)–C(11)–C(12)	121.4(3)
F(11)–C(11)–C(10)	116.5(3)	C(12)–C(11)–C(10)	122.1(3)
C(11)–C(12)–C(7)	116.7(3)	C(11)–C(12)–Ir(1)	130.0(2)
C(7)–C(12)–Ir(1)	113.1(2)	O(13)–C(13)–Ir(1)	178.1(3)

gave $[IrCl_2(CO)\{PPh_2CH_2C(Bu^t)=N-N=CH(C_6F_4)\}]$ (**4**) as yellow crystals (Scheme 1) in 48% yield based on iridium and 96% based on chlorine. The mother liquor contained phosphorus containing compounds which we could not isolate or identify. When this reaction was carried out in the presence of chloride ion, i.e. Adogen-464 {methyltrialkyl(C_8–C_{10})ammonium chloride} it gave a complex mixture with very little **4**. Complex **4** was characterised by microanalysis, mass spectrometry, and by proton, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ NMR spectroscopy, and the molecular structure was confirmed by an X-ray crystal structure determination (Fig. 1, see below). The elemental analytical data were in agreement with the composition $C_{26}H_{22}Cl_2F_4IrN_2OP$. An IR band at 2080 cm^{-1} was similar to literature values reported for iridium(III) carbonyl complexes [32–34]. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance at 161.3 ppm with $^2J(PC)=8.7$ and $^5J(FC)=5.5$ Hz was assigned to the carbon of the carbonyl ligand. The low δ_C value of 26.4 ppm observed for the CH_2 carbon agreed well with the values reported for CH_2 carbons in six-membered rings in similar complexes [24,34–36]. In the proton NMR spectrum the methylene protons were non-equivalent with $^2J(HH)=18.8$ Hz, as expected for a *fac*-geometry. Possibly, this cyclometallation process proceeds via a labile iridium(III) fluoride intermediate $[IrFCl(CO)\{PPh_2CH_2C(Bu^t)=N-N=CH(C_6F_4)\}]$ (**3**) and subsequent chlorination by disproportionation with $[IrCl(CO)_2(p\text{-toluidine})]$. Other workers also found that it was impossible to avoid chlorination of such metal fluoride intermediates [20,37]. Furthermore, we have observed rapid chloride transfer between iridium(I) and iridium(III) complexes previously [38].

3.1. Crystal structure of $[IrCl_2(CO)\{PPh_2CH_2C(Bu^t)=N-N=CH(C_6F_4)\}]$ (4)

The iridium(III) complex **4** was crystallised from dichloromethane/methanol as monoclinic yellow crystals in the space group $P2_1/c$. The molecular structure of **4** is shown in Fig. 1 with atom coordinates in Table 1, and selected bond lengths and angles in Table 2. The iridium atom is six-coordinated in a distorted octahedral coordination sphere. The structure showed that the distances and angles were similar to those found in other azine ligand [39–41] and iridium complexes [41–45]. The Ir–C_6F_4 bond distance of 2.033(3) Å is close to those observed previously (2.03(1)–2.081(17) Å) [19,43,44]. The Ir–P distance of 2.2803(8) Å falls within the range of 2.22–2.36 Å normally observed for other iridium complexes [42–46].

Acknowledgements

We thank the SERC for a fellowship (to S.D.P.) and for other support, and Johnson Matthey for the generous loan of platinum metal salts.

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