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Tetrafluoroethyl complexes of iridium(III) derived from a tetrafluoroethylene complex of iridium(I). A study of α-fluoride abstraction and determination of the structure of $IrCl_2(CF_2CF_2Cl)(CO)(PPh_3)_2$

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Abstract

Treatment of the tetrafluoroethylene complex, $IrCl(\eta^2\text{-}C_2F_4)(PPh_3)_2$, (1), with HCl or Cl_2 gives $IrCl_2(CF_2CF_2H)(PPh_3)_2$ (2) or $IrCl_2(CF_2CF_2Cl)(PPh_3)_2$ (3), respectively. These coordinately unsaturated complexes react with various neutral ligands to give stable, six-coordinate, tetrafluoroethyl and halotetrafluoroethyl complexes. The single crystal X-ray structure of one of these compounds, the carbonyl derivative of (3), $IrCl_2(CF_2CF_2Cl)(CO)(PPh_3)_2$ (15) was determined. The acetonitrile derivative of (2), $IrCl_2(CF_2CF_2H)(CH_3CN)(PPh_3)_2$ (17) undergoes a reaction with HCl that proceeds through the intermediate fluorocarbene complex, $[IrCl_2(=CFCF_2H)(CH_3CN)(PPh_3)]^+$ (18), to give, upon hydrolysis, $IrCl_2(C[O]CF_2H)(CH_3CN)(PPh_3)_2$ (19). The acetonitrile ligand, by virtue of its position *trans* to the acyl group, can be thermally displaced from (19) to give $IrCl_2(C[O]CF_2H)(PPh_3)_2$ (20). The vacant coordination site in (20) can be filled by other neutral ligands. Thermal treatment of any of the acyl complexes results finally in a reverse migration process and formation of $IrCl_2(CF_2H)(CO)(PPh_3)_2$ (23).

Key words: Iridium; Fluoroalkyl; Crystal structure; Fluorine

1. Introduction

As part of our continuing involvement with the chemistry of transition metal complexes which contain fluorocarbons as ligands [1–10], we continue to develop convenient procedures for the synthesis of such compounds. The difficulties associated with the introduction of fluorinated ligands to a transition metal complex are well documented [11,12]. Tetrafluoroethylene complexes have been successfully employed as precursors of tetrafluoroethyl complexes in several cases [13–16]. Treatment of $RhCl(\eta^2\text{-}C_2F_4)(PPh_3)_2$ with HCl gives $RhCl_2(CF_2CF_2H)(PPh_3)_2$ [13], but this rhodium (III) tetrafluoroethyl complex is reported to be very sensitive towards hydrolysis, which limits its further reaction chemistry. We considered that extension of this chemistry to iridium might provide improved stability of the fluorocarbon complexes. Examination of accounts of the previously reported iridium tetrafluorethylene complexes [17–22] indicated that $IrCl(\eta^2\text{-}C_2F_4)(PPh_3)_2$ (1) [17] was the most useful as a ready source of tetrafluoroethyl complexes. We describe below the synthesis and further reactions including several examples of α-fluorine abstraction, of $IrCl_2(CF_2CF_2H)(PPh_3)_2$ (2), $IrCl_2(CF_2CF_2Cl)(PPh_3)_2$ (3), and derivatives of (2) and (3). The crystal structure of a derivative of (3). $IrCl_2(CF_2CF_2Cl)(CO)(PPh_3)_2$, (15), has been determined.

2. Results and discussion

Several iridium tetrafluoroethylene complexes have been described previously. Examples include, $Ir(CF_3)(\eta^2\text{-}C_2F_4)(CO)(PPh_3)_2$ (5) [10], $IrCl(\eta^2\text{-}C_2F_4)(PPh_3)_2$ (1) [17], and $IrCl(\eta^2\text{-}C_2F_4)(CO)(PPh_3)_2$ (4) [18]. (A further example, $IrCl(\eta^2\text{-}C_2F_4)(CN\text{-}p\text{-tolyl})(PPh_3)_2$ (6), was prepared in the present study by addition of *p*-tolyl isocyanide to (1).) During investiga-

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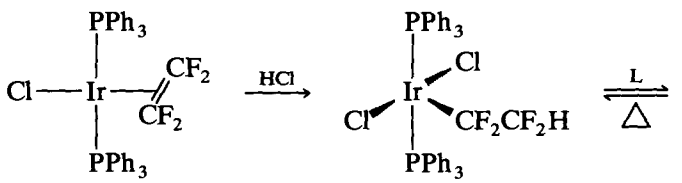
tion of these complexes, in respect of their usefulness as tetrafluoroethyl precursors marked difference in reactivity became apparent. The coordinatively saturated tetrafluoroethylene complexes (**4**), (**5**) and (**6**), were recovered unchanged after attempted reactions with acids or halogens. In contrast, complex (**1**) reacts instantly with HCl in dichloromethane, to give $IrCl_2(CF_2CF_2H)(PPh_3)_2$ (**2**). Complex (**2**) when prepared by this method is relatively stable in solution, but proved to be too sensitive to isolate as a pure solid. It was, however, possible to characterise (**2**) by multinuclear NMR spectroscopy and by subsequent preparation of derivatives (Eq. (1)).

Difficulties associated with the isolation of the tetrafluoroethyl complex could be easily overcome by treatment of the red solution of (**2**) with a potential ligand. For example, when carbon monoxide was bubbled through the red solution the colour was immediately lost. The resulting complex, $IrCl_2(CF_2CF_2H)(CO)(PPh_3)_2$ (**7**), was sufficiently stable to allow isolation and complete characterisation. Similar reactions with *p*-tolylisocyanide, or acetonitrile also gave a corresponding loss of colour and enabled the isolation of $IrCl_2(CF_2CF_2H)(L)(PPh_3)_2$ (L = CNR (**8**), or L = CH_3CN (**9**)). The complexes (**7**), (**8**), and (**9**) are stable crystalline solids, which can be interconverted by heating in benzene in the presence of the appropriate ligand. The lability of the neutral coordinated ligand in complexes (**7**), (**8**), and (**9**) is due to the location of the ligand *trans* to the tetrafluoroethyl group. This lability was turned to advantage in the isolation of solid samples of (**2**). Heating under vacuum of the acetonitrile complex (**9**) eventually gave a red solid, which had NMR properties identical to those of (**2**).

The NMR characteristics of all of the tetrafluoroethyl complexes described here are very similar. The ^{31}P NMR spectra all have signals which appear as triplets resulting from $^3J(PF)$ coupling only. In the ^1H NMR spectra the proton of the tetrafluoroethyl ligand is apparent as a triplet of triplets at 5–6 ppm. The signals for the fluorides, in complexes (**7**), (**8**), and (**9**), appear at two distinct chemical shifts in the ^{19}F NMR. Both of the fluoride signals in the ^{19}F spectrum display coupling to the proton, but no fluorine–fluorine coupling is evident.



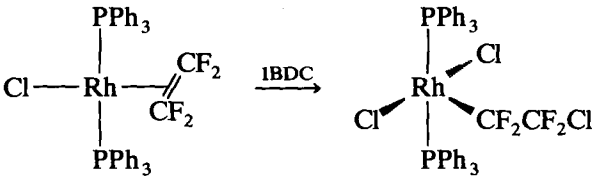
(**1**) (**2**)

(1)

(**7**) L = CO
(**8**) L = CN-*p*-tolyl
(**9**) L = $NCCH_3$

2.1. Formation of Halotetrafluoroethyl complexes

Prior to this work no attempts to react tetrafluoroethylene complexes with halogens had been reported. Following the successful synthesis of the tetrafluoroethyl complexes, described above, the reactions of (**1**) with halogens were also investigated. Exploratory reactions using $RhCl(\eta^2\text{-}C_2F_4)(PPh_3)_2$ (**10**) [23] proved promising. Treatment of (**10**) with iodobenzene dichloride (IBDC), used as the source of chlorine, resulted in rapid formation of the chlorotetrafluoroethyl complex, $RhCl_2(CF_2CF_2Cl)(PPh_3)_2$ (**11**), (eqn. (2)).



(**10**) (**11**)

(2)

This complex is only fairly stable in solution, decomposing over time to give $RhCl_3(PPh_3)_2$ (**12**). Unfortunately (**11**) did not form a stable adduct with CO, and its sensitivity in solution prevented a more complete elaboration of its chemistry. The iridium compound, (**1**), proved to be a more useful starting material for the production of stable halotetrafluoroethyl complexes. Treatment of (**1**) with halogens (or IBDC) gave rise to the five coordinate complexes $IrClX(CF_2CF_2X)(PPh_3)_2$ (X=Cl, (**3**); Br, (**13**); and I, (**14**); respectively). As in the case of the iridium compounds containing the CF_2CF_2H ligand, it was not possible to isolate as solids, coordinatively unsaturated complexes containing the halotetrafluoroethyl ligand, *i.e.* complexes (**3**), (**13**), and (**14**). In fact, the bromide and iodide complexes, (**13**) and (**14**), while evident in the NMR spectra of reactions carried out in NMR tubes, could not be fully characterised. It was possible to characterise (**3**) by spectroscopy and the isolation of its derivatives. In chemistry similar to that described above for (**2**), neutral donor molecules such as CO, isocyanide and CH_3CN gave stable, isolable, complexes $IrCl_2(CF_2CF_2Cl)(L)(PPh_3)_2$ (L=CO, (**15**); CNR, (**16**); and CH_3CN, (**17**)) respectively, (eqn. (3)).

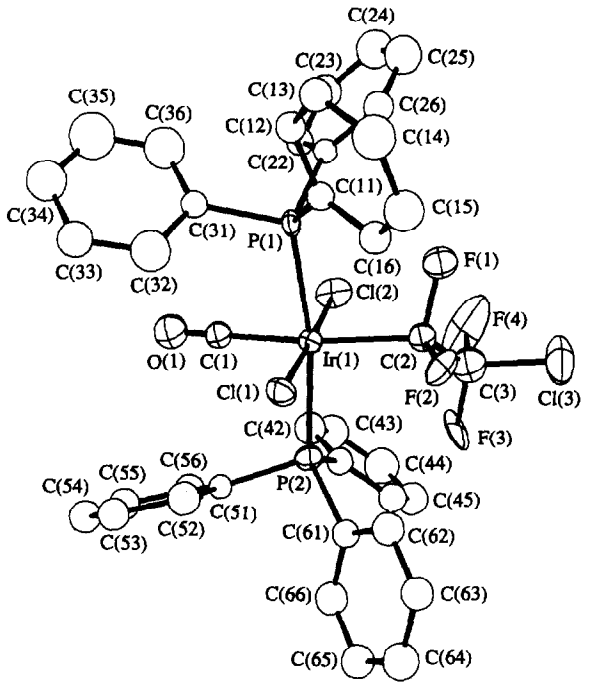


Fig. 1. Molecular structure of $IrCl_2(CF_2CF_2Cl)(CO)(PPh_3)_2$ (**15**).

TABLE 1. Selected bond lengths (Å) and angles [deg] for $IrCl_2(CF_2CG_2Cl)$ (CO) $(PPh_3)_2$

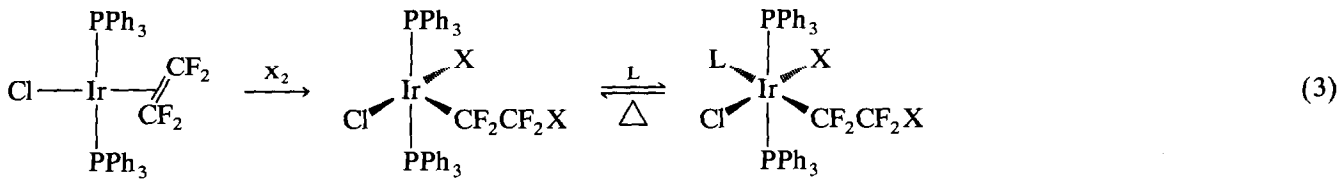
Ir–C(1)	1.94(4)
Ir–C(2)	2.25(4)
Ir–Cl(2)	2.367(9)
Ir–Cl(1)	2.386(8)
Ir–P(1)	2.437(6)
Ir–P(2)	2.457(7)
Cl(3)–C(3)	1.83(5)
F(1)–C(2)	1.43(4)
F(2)–C(2)	1.32(4)
F(3)–C(3)	1.32(4)
F(4)–C(3)	1.41(5)
O(1)–C(1)	1.06(4)
C(2)–C(3)	1.41(6)
C(1)–Ir–C(2)	172 (2)
C(1)–Ir–Cl(2)	83.4(13)
C(2)–Ir–Cl(2)	88.5(12)
C(1)–Ir–Cl(1)	96.1(13)
C(2)–Ir–Cl(1)	91.9(12)
Cl(2)–Ir–Cl(1)	177.7(2)
C(1)–Ir–P(1)	86.7(10)
C(2)–Ir–P(1)	91.6(6)
Cl(2)–Ir–P(1)	90.6(3)
Cl(1)–Ir–P(1)	87.1(3)
C(1)–Ir–P(2)	85.6(10)
C(2)–Ir–P(2)	96.8(6)
Cl(2)–Ir–P(2)	94.7(3)
Cl(1)–Ir–P(2)	87.5(3)
P(1)–Ir–P(2)	170.1(3)
F(2)–C(2)–C(3)	106 (2)
F(2)–C(2)–F(1)	106 (2)
C(3)–C(2)–F(1)	106 (4)
F(2)–C(2)–Ir	112 (3)
C(3)–C(2)–Ir	121 (2)
F(1)–C(2)–Ir	105 (2)
F(3)–C(3)–F(4)	105 (3)
F(3)–C(3)–C(2)	114 (4)
F(4)–C(3)–C(2)	114 (3)
F(3)–C(3)–Cl(3)	106 (2)
F(4)–C(3)–Cl(3)	103 (3)
C(2)–C(3)–Cl(3)	114 (3)

Like the tetrafluoroethyl complexes described above, the chlorotetafluoroethyl complexes could be interconverted by heating in benzene with an excess of the appropriate ligand. Also, solid samples of (**3**) could be obtained by the vacuum pyrolysis of the acetonitrile complex (**17**).

The complexes (**3**), (**15**), (**16**) and (**17**) show ^{31}P NMR patterns which are unlike the tetrafluoroethyl complexes in that a triplet of triplets pattern is observed, (*e.g.* for $IrCl_2(CF_2CF_2Cl)(PPh_3)_2$, $^3J(PF) = 29.2$ Hz, $^4J(PF) = 5.4$ Hz). The carbonyl complex (**15**) was obtained as well-formed crystals and a single crystal X-ray analysis was undertaken.

2.2. *Structure of $IrCl_2(CF_2CF_2Cl)(CO)(PPh_3)_2$ (15)*

The structure (Fig. 1) is a distorted octahedron with mutually *trans* triphenylphosphine groups and *trans* chloride ligands. The relevant bond angles and lengths are given in Table 1 with the atomic coordinates presented in Table 2. The carbonyl ligand occupies the coordination site *trans* to the chlorotetrafluoroethyl group. Although the CO ligand is easily displaced by other coordinating groups the Ir–Cl bond is not significantly longer than typical Ir–CO distances (Table 1). The Ir–C2 bond is well within the range expected for iridium–carbon σ-bonds [10]. The difference between the α-fluorine–carbon bond lengths (av. = 1.38(4) Å)



(3)

(**1**)

(**3**) X = Cl
(**13**) X = Br
(**14**) X = I

(**15**) L = CO, X = Cl
(**16**) L = CN-*p*-tolyl, X = Cl
(**17**) L = $NCCH_3$, X = Cl

and the β-fluorine–carbon bond lengths (av. = 1.37(4) Å) is not significant.

2.3. Reactivity of tetrafluoroethyl complexes towards Lewis acids

The enhanced reactivity of the α-fluorines in fluorinated alkyl transition metal complexes is well documented [25–28]. Reactions of the trifluoromethyl ligand with BCl_3 are known to give highly reactive dichlorocarbene intermediates [1]. In some cases less reactive Lewis acids may also give rise to stable dihalocarbene complexes [4]. The reactivity of transition metal fluorocarbon complexes towards Lewis acids is apparently restricted to the α-fluorines [26]. This observation is true for the iridium tetrafluoroethyl and halotetrafluoroethyl complexes reported here. These complexes, however, demonstrated an unusual lack of reactivity towards Lewis acids.

Treatment of the coordinatively unsaturated complexes (**2**) and (**3**) with HCl gas gave no observable reaction, while the strong Lewis acids BCl_3 and BBr_3 resulted only in decomposition. The six coordinate complexes were remarkably robust, showing almost no reactivity towards Lewis acids. The complexes (**7**) and (**8**) were recovered unchanged from concentrated solutions of BCl_3 at room temperature even after one hour. Only the acetonitrile complex, (**9**), displayed any reactivity towards Lewis acids. Monitoring the reaction of (**9**) with BCl_3 provided evidence for the possibility of a carbene intermediate. When the reaction was carried out in an NMR tube and the solution examined by ^{31}P NMR spectroscopy a doublet pattern was observed at −19.3 ppm ($^3J(PF) = 37.4$ Hz), which possibly comes from a fluorocarbene complex, $[IrCl_2(=CF(CF_2H))(CH_3CN)(PPh_3)_2]^+$ (**18**), (eqn. (4)).

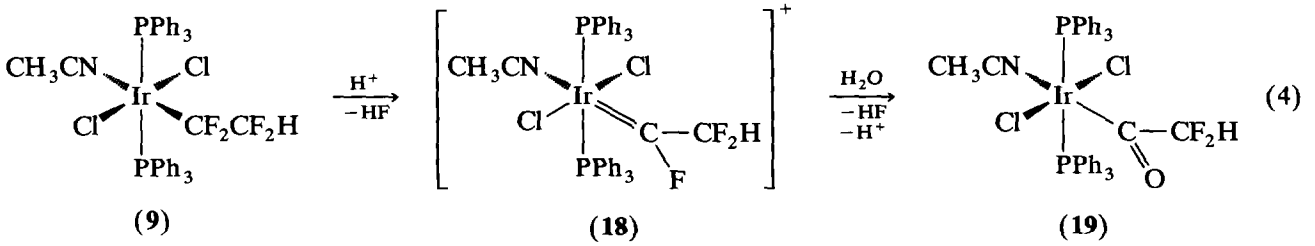
This cationic complex (**18**), unfortunately proved to be too moisture sensitive for isolation. The only product isolated from reactions of (**9**) with Lewis acids (such as HCl) was the difluoroacetyl complex, $IrCl_2(C[O]CF_2H)(CH_3CN)(PPh_3)_2$ (**19**). As in the case of the precursor complex (**9**) the acetonitrile ligand could be displaced thermally from (**19**) to give the coordinatively unsaturated complex, $IrCl_2(C[O]CF_2H)(PPh_3)_2$ (**20**), or replaced in the presence of CO or CN-tolyl-*p* to give $IrCl_2(C[O]CF_2H)(CO)(PPh_3)_2$ (**21**) or $IrCl_2(C[O]CF_2H)(CN\text{-}p\text{-}tolyl)(PPh_3)_2$ (**22**). All of these difluoroacyl complexes could be thermally converted to $IrCl_2(CF_2H)(CO)(PPh_3)_2$ (**23**), (eqn. (5)).

3. Conclusions

The unexpected lack of reactivity of the α-fluorines in these tetrafluoroethyl and chorotetrafluoroethyl complexes contrasts with the reactivity of those in the related trifluoromethyl complex $IrCl_2(CF_3)(CO)(PPh_3)_2$ [1]. Until recently it was reasonable to assume that all transition metal bound α-fluorines were activated towards abstraction reactions by Lewis acids [25–28]. This has turned out not to be the case with complexes such as $Fe(CF_2)_4(CO)_4$ [28] and now with the tetrafluoroethyl and halotetrafluoroethyl complexes studied in this work. The most obvious reason for this unexpected lack of reactivity would be steric protection offered by the β-fluorine atoms. However, the differences in reactivities between complexes such as (**7**) and (**9**), which should have similar steric properties, indicates that this is not the only reason. The most satisfactory explanation for the variations in reactivity of the α-fluorines in these cases must be an electronic one. A comparison of the reactivity of the complexes (**7**), (**8**), and (**9**) indicates that the relative electronic properties of the ligand *trans* to the tetrafluoroethyl ligand is the most significant feature. With the π-accepting ligands, CO and CNR, there is no activation of the α-fluorines, while the more electron releasing acetonitrile donates sufficient electron density to the metal to activate the α-fluorines. It is likely that modification of the metal centre, *via* variation of the ancillary ligands, will provide systems in which the α-fluorines are activated and any subsequent carbene complexes that might be formed could be stabilised.

4. Experimental details

Standard Schlenk techniques were used for all manipulations involving oxygen- or moisture-sensitive compounds. Solvents used were freshly distilled over appropriate drying agents prior to use. When procedures involved materials that were not air-sensitive, solvents were purified by chromatography on alumina



(4)

(**9**) (**18**) (**19**)

(Spence type H, 100-200 mesh) or filtered prior to use. In these cases, solvent removal under reduced pressure was achieved using a rotary evaporator. Routine recrystallisations were achieved by the following method; the sample was dissolved in a low boiling point solvent and a higher boiling point solvent, in which the compound was insoluble, was added. Evaporation at reduced pressure effected gradual crystallisation.

Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer Model 597 double-beam spectrophotometer calibrated with polystyrene film. All spectra were recorded as Nujol mulls between KBr plates or as a dichloromethane solution in KBr cells. Far-infrared spectra (400–200 cm^{-1}) were recorded as concentrated Nujol mulls between CsI plates. ^1H NMR were recorded on a Bruker AM-400 spectrometer operating at 400-MHz and are quoted in ppm down field from TMS. $^{31}P\{^1H\}$ NMR were recorded on a Bruker AM-400 at 162 MHz and are quoted relative to 85% phosphoric acid solution (external). ^{19}F NMR were recorded on a Jeol FX-90 spectrometer at 84.6 MHz and are reported relative to $CFCl_3$. Melting points were determined on a Reichert microscope hot stage and are uncorrected.

$RhCl(\eta^2\text{-}C_2F_4)(PPh_3)_2$ and $IrCl(\eta^2\text{-}C_2F_4)(PPh_3)_2$ (**1**) were prepared as described in refs. 13 and 17 respectively.

4.1. $IrCl_2(CF_2CF_2H)(PPh_3)_2$ (2)

(i) A solution of $IrCl(\eta^2\text{-}C_2F_4)(PPh_3)_2$ (**1**) (200 mg, 0.23 mmol) in dichloromethane (10 ml) was prepared and dry HCl gas was bubbled through for 5 s. The solution immediately became deep red. This product could not be isolated but was characterised by NMR measurements and the products of subsequent reactions.

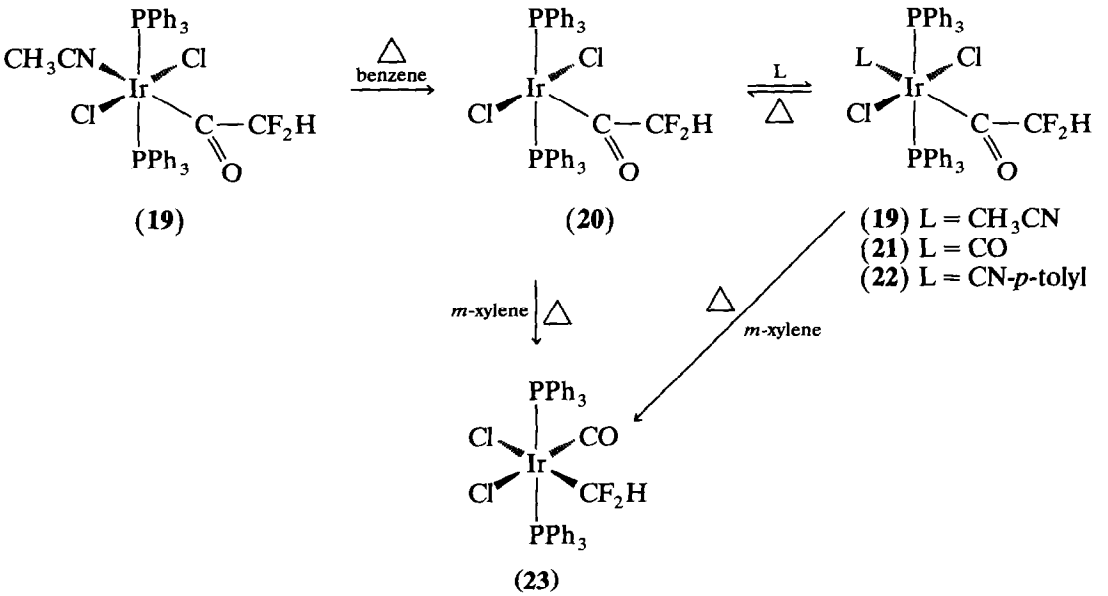
(ii) A solid sample of $IrCl_2(CF_2CF_2H)(CH_3CN)(PPh_3)_2$ (**9**) (100 mg, 0.1 mmol) was heated to 100°C under vacuum for 10 h, during which the colour changed from white to red. IR (Nujol, cm^{-1}): ν(CF) 1174, 1094, 998, 801; ^1H NMR ($CDCl_3$, ppm): 6.01 (tt, 1, $^2J(HF) = 54.0$ Hz, $^3J(HF) = 4.2$ Hz, $-CF_2H$); ^{31}P NMR ($CDCl_3$, ppm): 1.92 (t, $^3J(PF) = 26.50$); ^{19}F ($CDCl_3$, ppm): −57.10 (m, $-CF_2-$), −127.7 (dt, $^2J(FH) = 54$ Hz, $^3J(FH) = 8.2$ Hz).

4.2. $IrCl_2(CF_2CF_2Cl)(PPh_3)_2$ (3)

(i) To a solution of $IrCl(\eta^2\text{-}C_2F_4)(PPh_3)_2$ (**1**) (200 mg, 0.23 mmol) in dichloromethane (10 ml) was added IBDC (66 mg, 0.23 mmol). The mixture immediately became deep red. This product could not be isolated but was characterised by ^{31}P NMR and by subsequent reactions. IR (Nujol, cm^{-1}): ν(CF) 1119, 1160, 1092, 1047, 1001, 857; ^{31}P NMR ($CDCl_3$, ppm): −0.13 (tt, $^3J(FP) = 26.16$ Hz, $^3J(FP) = 5.42$ Hz). (b) A solid sample of $IrCl_2(CF_2CF_2Cl)(CH_3CN)(PPh_3)_2$ (**15**) (100 mg, 0.1 mmol) was heated to 100°C under vacuum for 10 h, during which the sample changed colour from white to red.

4.3. $IrCl(\eta^2\text{-}C_2F_4)$(p-tolylisocyanide)$(PPh_3)_2$ (6)

To a solution of $IrCl(\eta^2\text{-}C_2F_4)(PPh_3)_2$ (**1**) (100 mg, 0.11 mmol) in dichloromethane (10 ml) was added *p*-tolylisocyanide (13 mg, 0.12 mmol). The mixture was stirred for 5 minutes. Ethanol (20 ml) was then added and the dichloromethane was removed under reduced pressure to give the product as pale yellow crystals (109 mg, 96%). m.p. 180–185°C. Anal. Calcd. for $C_{46}H_{37}$-



(5)

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $IrCl_2(CF_2CF_2Cl)(CO)(PPh_3)_2$ [a]

	x	y	z	U_{eq}
Ir	4894(1)	1334(1)	1781(1)	22(1)
Cl(1)	4641(5)	1169(4)	536(4)	29(2)
Cl(2)	5221(5)	1500(5)	3023(4)	41(3)
Cl(3)	3435(7)	3779(6)	1714(7)	68(3)
P(1)	6864(5)	1564(4)	1897(5)	20(2)
P(2)	2962(5)	904(5)	1576(5)	26(2)
F(1)	5516(13)	2875(12)	1939(13)	42(7)
F(2)	4168(11)	2692(10)	950(11)	35(5)
F(3)	2693(13)	2513(11)	1733(14)	46(7)
F(4)	4011(20)	2819(18)	2686(15)	108(12)
O(1)	5578(16)	−171(17)	2235(14)	46(8)
C(1)	5334(25)	355(23)	2057(23)	41(12)
C(2)	4479(21)	2509(22)	1630(24)	26(12)
C(3)	3690(24)	2825(24)	1932(25)	27(13)
C(12)	8391(12)	2031(13)	1186(12)	26(7)
C(13)	8769(11)	2443(14)	710(12)	32(8)
C(14)	8034(16)	2899(16)	235(14)	53(10)
C(15)	6920(15)	2942(15)	236(15)	51(10)
C(16)	6542(11)	2530(13)	712(13)	32(8)
C(11)	7277(12)	2075(13)	1187(12)	20(7)
C(22)	8123(14)	2683(11)	2700(10)	32(8)
C(23)	8747(15)	3024(9)	3319(13)	56(10)
C(24)	8941(15)	2683(13)	3975(11)	64(11)
C(25)	8509(15)	2000(13)	4012(9)	43(9)
C(26)	7885(13)	1659(9)	3394(12)	29(8)
C(21)	7692(12)	2000(11)	2738(9)	17(6)
C(32)	7192(13)	264(12)	1265(10)	46(9)
C(33)	7723(16)	−379(12)	1203(11)	41(8)
C(34)	8660(16)	−595(11)	1743(14)	67(11)
C(35)	9066(15)	−169(14)	2346(12)	90(15)
C(36)	8535(16)	474(14)	2408(10)	76(12)
C(31)	7598(15)	690(10)	1868(12)	20(7)
C(42)	2885(13)	698(11)	2980(12)	42(9)
C(43)	2435(16)	785(13)	3547(10)	56(10)
C(44)	1488(17)	1209(14)	3466(10)	62(10)
C(45)	991(14)	1546(12)	2818(12)	54(10)
C(46)	1441(14)	1459(12)	2252(10)	39(8)
C(41)	2388(15)	1036(12)	2332(11)	36(8)
C(52)	3191(13)	−314(11)	804(10)	44(9)
C(53)	3307(13)	−1039(12)	671(9)	37(8)
C(54)	3183(14)	−1552(10)	1158(12)	38(8)
C(55)	2941(14)	−1340(12)	1779(11)	46(8)
C(56)	2825(13)	−615(13)	1912(9)	51(10)
C(51)	2949(13)	−102(10)	1425(11)	20(7)
C(62)	1980(11)	1719(11)	321(11)	36(8)
C(63)	1124(15)	1894(11)	−289(11)	41(9)
C(64)	111(12)	1525(12)	−449(9)	45(9)
C(65)	−46(11)	982(11)	0(11)	36(8)
C(66)	810(13)	808(10)	610(10)	37(8)
C(61)	1823(11)	1177(11)	770(9)	30(7)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

ClF_4IrNP_2: C, 59.16; H, 3.99; F, 8.14. Found: C, 58.48; H, 4.16; F, 7.53%. IR (Nujol, cm^{-1}): ν(CN) 2182, ν(CF)1401, 1090, 1037, 809; ^{31}P NMR ($CDCl_3$, ppm): −12.40 (m).

4.4. $IrCl_2(CF_2CF_2H)(CO)(PPh_3)_2$ (7)

A solution of $IrCl_2(CF_2CF_2H)(PPh_3)_2$ (2) was prepared as above and carbon monoxide was bubbled through the solution until the colour had disappeared. Ethanol (20 ml) was then added and the dichloromethane was removed under reduced pressure to give the product as white crystals (202 mg, 94%). m.p. 193–195°C. Anal. Calcd. for $C_{39}H_{31}Cl_2F_4IrOP_2$: C, 51.10; H, 3.40; F, 8.29. Found: C, 51.23; H,. 3.68; F, 8.18%. IR (Nujol, cm^{-1}): ν(CO) 2099, ν(CF) 1162, 1093 996, 942, 795, ν(IrCl) 340, 320; ^1H NMR ($CDCl_3$, ppm): 5.18 (tt, 1, ^2J(HF) = 55.3 Hz, ^3J(HF) = 4.1 Hz, $-CF_2H$); ^{31}P NMR ($CDCl_3$, ppm): −23.63 (t, ^3J(PF) = 25.0); ^{19}F ($CDCl_3$, ppm): −79.7 (m, $-CF_2-$,), −129.9 (dm, ^2J(FH) = 54 Hz).

4.5. $IrCl_2(CF_2CF_2H)$(p-tolylisocyanide)$(PPh_3)_2$ (8)

(i) A solution of $IrCl_2(CF_2CF_2H)(PPh_3)_2$ (2) was prepared as above and *p*-tolylisocyanide (13 mg, 0.12 mmol) was added. The mixture was stirred for 5 minutes. Ethanol (20 ml) was then added and the dichloromethane was removed under reduced pressure to give the products as pale yellow crystals (97 mg, 89%).

(ii) To a solution of $IrCl_2(CF_2CF_2H)(CH_3CN)(PPh_3)_2$ (9) (100 mg, 0.11 mmol) in dichloromethane (10 ml) was added *p*-tolylisocyanide (13 mg, 0.12 mmol). The mixture was stirred for 5 minutes. Ethanol (20 ml) was then added and the dichloromethane was removed under reduced pressure to give the product as pale yellow crystals (104 mg, 96%). m.p. 180–185°C. Anal. Calcd. for $C_{46}H_{38}Cl_2F_4IrNP_2$: C, 54.93; H, 3.81; N, 1.39 F, 7.55. Found: C, 56.53; H, 4.82; N, 1.23 F, 7.86%. IR (Nujol, cm^{-1}): ν(CN) 2178, ν(CF) 1156, 1090, 1075, 977, 940, 792; ^1H NMR ($CDCl_3$, ppm): 5.12 (tt, 1, ^2J(HF) = 54.67 Hz, ^3J(HF) = 7.44 Hz, $-CF_2H$), 2.28 (s, 3, $-CH_3$), 6.87, (d, 2, ^2J(HH) = 8.0 Hz, CH), 6.29, (d, 2, ^2J(HH) = 8.0 Hz, CH); ^{31}P NMR ($CDCl_3$, ppm): −26.26 (t, ^3J(PF) = 25.22).

4.6. $IrCl_2(CF_2CF_2H)(CH_3CN)(PPh_3)_2$ (9)

(i) A solution of $IrCl_2(CF_2CF_2H)(PPh_3)_2$ (2) was prepared as above and acetonitrile was added dropwise until the colour had disappeared. Ethanol (20 ml) was then added and the dichloromethane was removed under reduced pressure to give the product as cream crystals (198 mg, 91%). m.p. 160–165°C. Anal. Calcd. for $C_{40}H_{34}Cl_2F_4IrNP_2$: C, 51.67,; H, 3.69; N, 1.57 F, 8.17. Found: C, 52.84; H, 4.19; N, 1.00 F, 7.87%. IR (Nujol, cm^{-1}): ν(CN) 2012, ν(CF) 1158, 1041, 1036, 951, 940, 818, ν(IrCl) 350; ^1H NMR ($CDCl_3$, ppm): 5.58 (tt, 1, ^2J(HF) = 54.5 Hz, ^3J(HF) = 4.1 Hz, $-CF_2H$), 2.13 (s, 3, CH_3CN); ^{31}P NMR ($CDCl_3$, ppm): −21.15 (t, ^3J(PF) = 25.58 Hz).

(ii) A solution of $IrCl_2(CF_2CF_2H)(CO)(PPh_3)_2$ (7) (100 mg, 0.11 mmol) temperature in benzene : acetonitrile (1 : 1, 5 ml) was heated to reflux for 5 minutes then cooled. The solvents were removed *in vacuo* and the residue was then recrystallised from dichloromethane and ethanol to give the product (88 mg, 87%).

4.7. $RhCl_2(CF_2CF_2Cl)(PPh_3)_2$ (11)

To a solution of $RhCl(\eta^2-C_2F_4)(PPh_3)_2$ (**10**) (200 mg, 0.26 mmol) in dichloromethane (10 ml) was added IBCD (72 mg, 0.26 mmol). The mixture was stirred for 30 seconds then ethanol (40 mL) was added and the dichloromethane removed under reduced pressure to give the product as red crystals (218 mg, 73%). m.p. 185–187°C. Anal. Calcd. for $C_{38}H_{30}Cl_3F_4P_2Rh$: C, 54.73; H, 3.36; F, 9.11. Found: C, 55.10; H, 4.35; F, 8.10%. IR (Nujol, cm^{-1}): ν(CF) 1175, 1167, 1113, 1095, 1062, 1042, 1028, 933, 802; ^{31}P NMR ($CDCl_3$, ppm): 18.47 (dtt, ^1J(RhP) = 103.5, ^3J(PF) = 31.14, ^4J(PF) = 5.6 Hz).

4.8. $IrCl_2(CF_2CF_2Cl)(CO)(PPh_3)_2$ (15)

A solution of $IrCl_2(CF_2CF_2Cl)(PPh_3)_2$ (**3**) was prepared as above and carbon monoxide was bubbled through until the colour had disappeared. Ethanol (20 ml) was then added and the dichloromethane was removed under reduced pressure to give the product as white crystals (203 mg, 94%). m.p. 199–203°C. Anal. Calcd. for $C_{39}H_{33}Cl_3F_4IrOP_2$: C, 49.24; H, 3.18. Found: C, 49.50; H, 3.67°. IR (Nujol, cm^{-1}): ν(CO) 2089, ν(CF) 1190, 1109, 1052, 1007, 995; ^{31}P NMR ($CDCl_3$, ppm): −24.61 (t, ^3J(FP) = 23.44 Hz); ^{19}F NMR ($CDCl_3$, ppm): −64.33 (t, ^2J(PF) = 23.2 Hz).

4.9. $IrCl_2(CF_2CF_2Cl)$(p-tolylisocyanide)$(PPh_3)_2$ (16)

(i) A solution of $IrCl_2(CF_2CF_2Cl)(PPh_3)_2$ (**3**) was prepared as above and *p*-tolylisocyanide (26 mg., 0.24 mmol) was added. The mixture was stirred for 5 min. Ethanol (20 ml) was then added and the dichloromethane was removed under reduced pressure to give the product as pale yellow crystals (215 mg, 90%)

(ii) To a solution of $IrCl_2(CF_2CF_2Cl)(CH_3CN)(PPh_3)_2$ (**17**) (100 mg, 0.1 mmol) in dichloromethane (10 ml) was added *p*-tolyl isocyanide (13 mg, 0.12 mmol). The mixture was stirred for 5 min. Ethanol (20 ml) was then added and the dichloromethane was removed under reduced pressure to give the product as pale yellow crystals (104, 96%). m.p. 180–185°C. Anal. Calcd. for $C_{46}H_{37}Cl_3F_4IrNP_2$: C, 53.11; H, 3.58; N, 1.35; F, 7.30. Found: C, 53.55; H, 4.17; N, 1.39 F, 7.23%. IR (Nujol, cm^{-1}): ν(CN) 2194, ν(CF) 1155, 1089, 1044, 985; ^1H NMR ($CDCl_3$, ppm): 2.30 (s, 3, $-CH_3$), 6.86, (d, 2, ^2J(HH) = 8.0 Hz, CH), 6.30, (d, 2, ^2J(HH) = 8.0 Hz, CH); ^{31}P NMR ($CDCl_3$, ppm): −24.13 (tt, ^3J(PF) = 23.38, ^4J(PF) = 3.18 Hz); ^{19}F NMR ($CDCl_3$, ppm): 63.71 (t, 2 ^2J(PF) = 22.6 Hz), −50.56 (s).

4.10. $IrCl_2(CF_2CF_2Cl)(CH_3CN)(PPh_3)_2$ (17)

(i) A solution of $IrCl_2(CF_2CF_2Cl)(PPh_3)_2$ (**3**) was prepared as above and acetonitrile was added drop wise until the colour had disappeared. Ethanol (20 ml) was then added and the dichloromethane was removed under reduced pressure to give the product a cream crystals (197 mg, 91%). m.p. 160–165°C. Anal. Calcd. for $C_{40}H_{33}Cl_3F_4IrNP_2$: C, 49.83; H, 3.45; N, 1.45 F, 7.88., Found: C, 49.19; H, 3.71; N, 0.91 F, 7.87%. IR (Nujol, cm^{-1}): ν(CN) 2115, ν(CF) 1190, 1160, 1043; ^{31}P NMR ($CDCl_3$, ppm): − 8.26 (tt, ^3J(FP) = 21.65, ^4J(FP) = 5.32 Hz).

(ii) A solution of $IrCl_2(CF_2CF_2Cl)(CO)(PPh_3)_2$ (**15**) (100 mg, 0.1 mmol) temperature in benzene : acetonitrile (1 : 1, 5 ml) was heated to reflux for 5 min. The solution was then cooled, the solvents removed in vacuo and the residue was recrystallised from dichloromethane and ethanol to give the product (88 mg, 87%).

4.11. $IrCl_2(C[O]CF_2H)(CH_3CN)(PPh_3)_2$ (19)

To a solution of $IrCl_2(CF_2CF_2H)(CH_3CN)(PPh_3)_2$ (**9**) (100 mg, 0.11 mmol) in dichloromethane (10 ml) was added concentrated HCl (2 drops) in acetonitrile (5 ml). The mixture was stirred for 5 min. Ethanol (20 ml) was then added and the dichloromethane was removed under reduced pressure to give the product as pale yellow crystals (74 mg, 76%). m.p. 220–225°C. Anal. Calcd. for $C_{46}H_{38}Cl_2F_2IrNOP_2$: C, 52.93; H, 3.78; N, 1.54 F, 4.19. Found: C, 52.13; H, 4.28; N, 1.14 F, 3.89%. IR (Nujol, cm^{-1}): ν(CO) 1640, ν(CF) 1185, 1094, 1037, 910, 838, ν(IrCl) 318; ^1H NMR ($CDCl_3$, ppm): 5.84 (t, 1, ^2J(HF) = 55.84 Hz, $-CF_2H$), 1.96 (s, 3, $-CH_3$); ^{31}P NMR ($CDCl_3$, ppm): −9.29 (s).

4.12. $IrCl_2(C[O]CF_2H)(PPh_3)_2$ (20)

A solution of $IrCl_2(C[O]CF_2H)(CH_3CN)(PPh_3)_2$ (**19**) (100 mg, 0.11 mmol) in benzene (10 ml) was heated to the reflux temperature for 2 min. Ethanol (20 ml) was then added and the benzene was removed under reduced pressure to give the product as orange crystals (80 mg, 84%). m.p. 222–227°C. Anal. Calcd. for $C_{38}H_{31}Cl_2F_2IrOP_2$: C, 52.66; H, 3.61; F, 4.38. Found: C, 52.17; H, 4.32; F, 4.05%. IR (Nujol, cm^{-1}): ν(CO) 1678, ν(CF) 1116, 1094, 1053, 918, 834, ν(IrCl) 312; ^1H NMR ($CDCl_3$, ppm): 5.85 (t, 1, ^2J(HF) = 55.75 Hz, $-CF_2H$); ^{31}P NMR ($CDCl_3$, ppm): −9.70 (s).

4.13. $IrCl_2(C[O]CF_2H)(CO)(PPh_3)_2$ (21)

(i) A solution of $IrCl_2(C[O]CF_2H)(CH_3CN)(PPh_3)_2$ (**19**) (100 mg, 0.11 mmol) in dichloromethane was pre-

pared and CO was bubbled through for 2 min. Ethanol (20 ml) was then added and the dichloromethane was removed under reduced pressure to give the product as white crystals (93 mg, 94%). m.p. 220–224°C. Anal. Calcd. for $C_{39}H_{31}Cl_2F_2IrO_2P_2$: C, 52.35; H, 3.49; F, 4.25. Found: C, 52.41; H, 3.98; F, 4.21%. IR (Nujol, cm^{-1}): ν(CO) 2068, 1650, ν(CF) 1097, 943, 851, ν(IrCl) 320; ^{1}H NMR ($CDCl_3$, ppm): 5.45 (t, 1, ^2J(HF) = 55.09 Hz, $-CF_2H$); ^{31}P NMR ($CDCl_3$, ppm): −19.09 (s).

(ii) Treatment of $IrCl_2(C[O]CF_2H)(PPh_3)_2$ (**20**) (100 mg, 0.12 mmol) as above gave the product (100 mg, 96%).

4.14. $IrCl_2(C[O]CF_2H)$(p-tolylisocyanide)$(PPh_3)_2$ (22)

(i) To a solution of $IrCl_2(C[O]CF_2H)(CH_3CN)(PPh_3)_2$ (**19**) (100 mg, 0.11 mmol) in dichloromethane (10 ml) was added *p*-tolyl isocyanide (13 mg, 0.12 mmol). The mixture was stirred for 5 min. Ethanol (20 ml) was then added and the dichloromethane was removed under reduced pressure to give the product as pale yellow crystals (96 mg, 88%). m.p. 197–200°C. Anal. Calcd. for $C_{46}H_{38}Cl_2F_2IrNP_2$: C, 56.16; H, 3.89; N, 1.42; F, 3.86. Found: C, 56.20; H, 4.41; N, 1.02; F, 3.64%. IR (Nujol, cm^{-1}): ν(CO) 1640, ν(CN) 2166, ν(CF) 1094, 1036, 903, 838; ^{1}H NMR ($CDCl_3$, ppm): 5.51 (t, 1, ^2J(HF) = 55.47 Hz, $-CF_2H$), 2.32 (s, 3, $-CH_3$), 6.86, (d, 2, ^2J(HH) = 8.0 Hz, CH), 6.30, (d, 2, ^2J(HH) = 8.0 Hz, CH); ^{31}P NMR ($CDCl_3$, ppm): −13.12 (s).

(ii) Similar treatment of $IrCl_2(C[O]CF_2H)(PPh_3)_2$ (**20**) (100 mg, 0.12 mmol) gave the product (110 mg, 97%).

4.15. $IrCl_2(CF_2H)(CO)(PPh_3)_2$ (23)

A solution of $IrCl_2(C[O]CF_2H)(PPh_3)_2$ (**20**) (100 mg, 0.12 mmol) in *m*-xylene (10 ml) was heated at the reflux temperature for 4 h then cooled. The xylene was removed *in vacuo* and the residue recrystallised from dichloromethane and ethanol to give the product as white crystals (84 mg, 84%). The complex was characterised by comparison with an authentic sample[10]. IR (Nujol, cm^{-1}): ν(CO) 2073, ν(CF) 1093, 1010, 961; ^{31}P NMR ($CDCl_3$, ppm): −16.58 (dd, ^3J(FP) = 17.5 Hz, ^3J(FP) = 19.4 Hz); ^{19}F NMR ($CDCl_3$, ppm): − 57.77 (ddd, ^2J(PF) = 54.5 Hz, ^3J(PF) = 17.5 Hz, ^3J(PF) = 19.4 Hz.

4.16. Crystal structure determination of $IrCl_2(CF_2CF_2Cl)(CO)(PPh_3)_2$ (15)

Crystals of complex (**15**) were grown from CH_2Cl–EtOH mixtures as colourless, cubes. Details of crystal data and intensity collection parameters are given in Table 3. Unit cell parameters were obtained from least squares fits to the four circles coordinates of 25 reflections centered on a CAD-4 diffractometer. Reflections were counted until $\sigma(I)/I$ was 0.02 or for a maximum of 60 s. Three reflections were monitored throughout the data collection as a check on crystal alignment and decomposition, no systematic trends being observed. The data were corrected for Lorentz and polarisation effects using locally written programs. The structure was solved by Patterson and Fourier techniques [29] and refined by full-matrix least squares [30]. Atomic scattering factors were for neutral atoms [31]. Absorption corrections were applied using the program DIFABS [32]. Atoms other than aromatic carbon atoms were allowed to assume anisotropic motion and the aromatic rings were refined as rigid groups with hydrogen atoms in calculated positions. Refinement converged to R = 0.049 for the 1535 observed reflections. Final refinement details are given in Table 3. A perspective view of the molecule (ORTEP) is given in Fig. 1 which also shows the atom numbering scheme. Selected interatomic distances and angles are given in Table 1 and

TABLE 3. Crystal data for $IrCl_2(CF_2CF_2Cl)(CO)(PPh_3)_2$

Formula	$C_{39}H_{30}Cl_3F_4IrOP_2$
Molecular weight	951.12
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	12.458(10)
b (Å)	18.620(4)
c (Å)	19.576(4)
β (°)	106.77(5)°
V (Å^3)	4348(4)
Z	4
d(calc) (g cm^{-3})	1.435
F(000)	1864
μ (cm^{-1})	35.2
Radiation Mo Kα (Monochromatic) λ (Å)	0.71069
Temperature (K)	173(2)
Diffractometer	Nonius CAD-4
Scan technique	$\omega/2\theta$
2θ (min–max)	5°–44°
h, k, l range	$-13 \le h \le 12, 0 \le k \le 17, 0 \le l \le 21$
No. of observed reflections	1535 $I > 2\sigma(I)$
Crystal size (mm^3)	0.37×0.28×0.22
Least squares weights	$1.0/[\sigma^2(F_o^2) + \{0.006(F_o^2 + 2F_c^2)/3\}^2]$
No. of variables in LS	199
Goodness of fit on F^2	0.575
Function minimised	$\Sigma w(F_o^2 - F_c^2)^2$
R and wR2	0.049 0.141
Peak height in final density map (min–max) (e Å^{-3})	−0.54 0.85
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	$wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

atomic coordinates in Table 2. Complete lists of bond lengths and angles and tables of anisotropic displacement parameters and hydrogen coordinates have been deposited at the Cambridge Crystallographic Data Centre.

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