

Trifluoromethyl, difluorocarbene and tetrafluoroethylene complexes of iridium and the crystal structures of $\text{IrI}(\text{CH}_3)(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$, $\text{Ir}(\text{CF}_3)(\text{C}_2\text{F}_4)(\text{CO})(\text{PPh}_3)_2$ and $\text{Ir}(\text{CF}_3)(=\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ *

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(Received December 22nd, 1989)

Abstract

A trifluoromethyl iridium(I) complex $\text{Ir}(\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (**1**) has been prepared by the reaction of $\text{Hg}(\text{CF}_3)_2$ with $\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$, or by thermal decomposition of $\text{Ir}(\text{COCF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (**3**), which is produced from $(\text{CF}_3\text{CO})_2\text{O}$ and a reduced iridium(-I) species. Either the reaction of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ with $\text{Hg}(\text{CF}_3)_2$ or the reversible thermal decarbonylation of **1** yields the coordinatively unsaturated complex $\text{Ir}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (**2**). Derivatives $\text{Ir}(\text{CF}_3)\text{L}(\text{CO})(\text{PPh}_3)_2$ ($\text{L} = \text{C}_2\text{F}_4$ (**4**), $\text{L} = \text{C}_2\text{H}_4$ (**5**), $\text{L} = \text{O}_2$ (**6**)) result from treatment of **1** with tetrafluoroethylene, or **2** with ethylene or oxygen, respectively. Both **1** and **2** undergo oxidative addition of Cl_2 , I_2 , HCl , H_2 and CH_3I to give trifluoromethyl iridium(III) complexes $\text{IrCl}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (**7**), $\text{IrI}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (**8**), $\text{IrHCl}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (**9**), *cis*- $\text{IrH}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (**10**) and $\text{IrI}(\text{CH}_3)(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (**11**), respectively. The iodo ligand in **11** is labile and can be replaced by an acetonitrile ligand to yield $[\text{Ir}(\text{CH}_3)(\text{CF}_3)(\text{L})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ ($\text{L} = \text{CH}_3\text{CN}$ (**12**)). This ligand can in turn be replaced by *p*-tolylisocyanide ($\text{L} = \text{CN-}p\text{-C}_6\text{H}_4\text{CH}_3$ (**13**)) or Cl^- to give $\text{IrCl}(\text{CH}_3)(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (**14**). Complexes **1** and **9** each react with AlCl_3 to give the difluoromethyl species $\text{IrCl}_2(\text{CF}_2\text{H})(\text{CO})(\text{PPh}_3)_2$ (**15**). A difluorocarbene iridium(I) complex, $\text{IrCl}(\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ (**16**), has been prepared by thermal decarbonylation of $\text{Ir}(\text{COCF}_2\text{Cl})(\text{CO})_2(\text{PPh}_3)_2$ (**18**), and a complex containing both CF_3 and CF_2 ligands, $\text{Ir}(\text{CF}_2)(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (**17**), has been made by treatment of either $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, **2** or **16** with $\text{Cd}(\text{CF}_3)_2 \cdot \text{glyme}$. Both **16** and **17** are hydrolysed to give carbonyl species $\text{IrCl}(\text{CO})_2(\text{PPh}_3)_2$ and **1**, respectively, while **16** reacts with *t*-butylamine to give an isocyanide complex, $\text{IrCl}(\text{CN-}t$

* This paper is dedicated to Professor Gordon Stone F.R.S. on the occasion of his 65th birthday.

$C_4H_9)(CO)(PPh_3)_2$ (**20**). Addition of HCl to **16** or **17** produces **15** or **9**, respectively. Complexes **4**, **11** and **17** have been characterised by X-ray diffraction studies.

Introduction

Transition metal mediated interconversions of alkyl, alkylidene and alkene ligands are at the heart of organometallic chemistry, but the chemistry of the corresponding fluorocarbon ligands is still at a formative stage. Even so, fluoroalkyl [1], fluorocarbene [2], and fluoroalkene [3] complexes have already made a significant contribution to organometallic chemistry. The issues surrounding the interpretation of the bonding and reactivity of trifluoromethyl complexes have enhanced our understanding of metal-carbon σ bonds, and group 8 difluorocarbene complexes of ruthenium and osmium have provided examples of both electrophilic and nucleophilic reactivity in late transition metal carbene complexes. Tetrafluoroethylene complexes represent one extreme in the continuum between σ -donor/ π -acceptor and metallacyclopropane formulations of metal alkene complexes.

The trifluoromethyl and difluorocarbene complexes of the group 8 metals ruthenium and osmium have exhibited a particularly rich chemistry [2,4,5]. In extending this chemistry to the group 9 metal iridium, the first goal was to investigate the chemistry of iridium trifluoromethyl complexes, which might prove to be useful precursors to difluorocarbene species, by analogy with the results of the group 8 chemistry. In addition, other reagents which were effective for the direct introduction of a CF_2 fragment into the ruthenium or osmium coordination sphere might also be useful in iridium chemistry.

Previous work established the oxidative addition of CF_3I to $IrCl(CO)(PPh_3)_2$ as a route to the d^6 iridium(III) complex $IrCl(CF_3)(CO)(PPh_3)_2$ [6]. The chemistry of this complex was elaborated by forming a number of iridium(III) derivatives all containing the CF_3 ligand [7]. However, all attempts to reduce these complexes chemically to d^8 trifluoromethyl iridium(I) species were unsuccessful. Although a difluorocarbene ruthenium(II) complex, $RuCl_2(=CF_2)(CO)(PPh_3)_2$, could be formed by HCl- or $(CH_3)_3SiCl$ -mediated abstraction of fluoride from the ruthenium(II) precursor $RuCl(CF_3)(CH_3CN)(CO)(PPh_3)_2$ [8,9], attempts to abstract fluoride from an iridium(III) CF_3 complex using boron trihalide reagents resulted not in an isolable difluorocarbene species but in cyclometallated products [10]. These were presumably formed by electrophilic attack of a cationic difluorocarbene intermediate at the *ortho* position of a PPh_3 phenyl ring. Finally, although reaction of $Hg(CCl_3)_2$ with $IrHCl_2(PPh_3)_3$ was successful as a route to the dichlorocarbene iridium(III) complex $IrCl_3(=CCl_2)(PPh_3)_2$ [11], reaction of iridium(III) substrates with either $Hg(CF_3)_2$ or $Cd(CF_3)_2 \cdot glyme$ did not result in transfer of CF_2 or CF_3 fragments to the metal. Both the mercury and cadmium reagents were effective for these types of transformations in reactions with suitable ruthenium and osmium substrates [4,5].

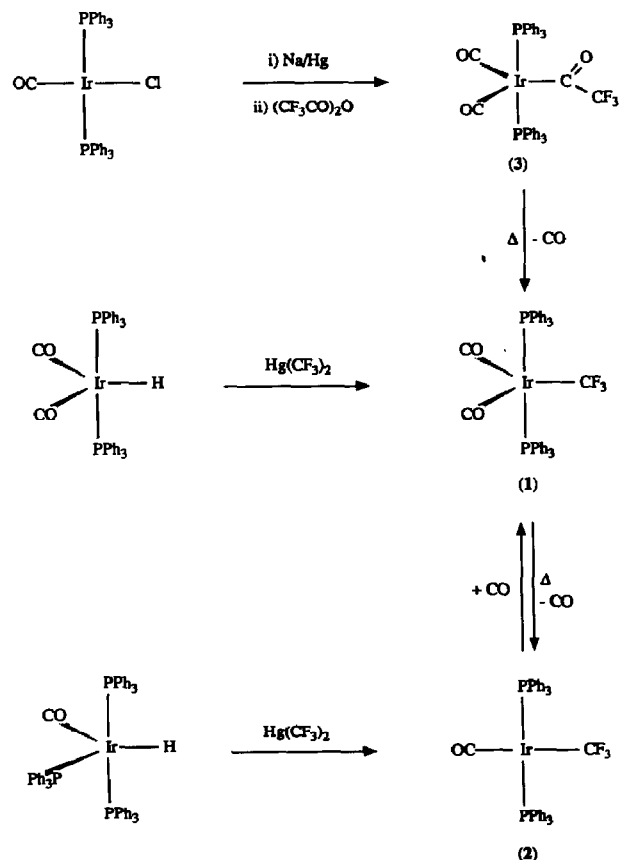
These results suggest that although trifluoromethyl iridium(III) complexes are accessible, they are not useful as precursors to either trifluoromethyl iridium(I) or difluorocarbene iridium complexes. This paper describes the development of successful routes to both difluorocarbene and trifluoromethyl iridium(I) complexes, by employing an appropriate iridium(I) substrate with the cadmium and mercury

trifluoromethyl reagents. Subsequently, alternate routes to the new complexes were developed utilizing a reduced iridium(-I) precursor with difluoro- and trifluoroacetic anhydrides. Tetrafluoroethylene also proved to be useful as a ligand in this chemistry, further elaborating the range of fluorocarbon ligands bonded to iridium(I). The new complexes include the trifluoromethyl analogue of Vaska's complex, $\text{Ir}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$, and a novel species containing both CF_2 and CF_3 ligands, $\text{Ir}(\text{CF}_3)(=\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$. The preparation and chemistry of these new difluorocarbene, trifluoromethyl, and tetrafluoroethylene iridium(I) complexes will be described below, including X-ray crystal structure determinations of a representative complex containing each ligand type.

Results and discussion

Preparation of trifluoromethyl iridium(I) complexes

In contrast to the unproductive reaction of either iridium(III) precursors or $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ with $\text{Hg}(\text{CF}_3)_2$, the reaction of $\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$ with $\text{Hg}(\text{CF}_3)_2$ in refluxing benzene produced in moderate yield the first trifluoromethyl iridium(I) complex, $\text{Ir}(\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (**1**). An attempt to decarbonylate complex **1** in



Scheme 1. Preparation of trifluoromethyl iridium(I) complexes.

refluxing *m*-xylene resulted in decomposition of the trifluoromethyl ligand, producing $\text{IrF}(\text{CO})(\text{PPh}_3)_2$. However, thermal decarbonylation of a finely divided solid sample of **1** (48 h at 120–135 °C) produced the trifluoromethyl analogue of Vaska's complex, $\text{Ir}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (**2**). Complex **2** could be prepared directly from reaction of $\text{Hg}(\text{CF}_3)_2$ with $\text{IrH}(\text{CO})(\text{PPh}_3)_3$, although the reactive nature of the product resulted in low yields of poor purity, rendering the decarbonylation method preferable as a route to **2** (Scheme 1).

Table 1

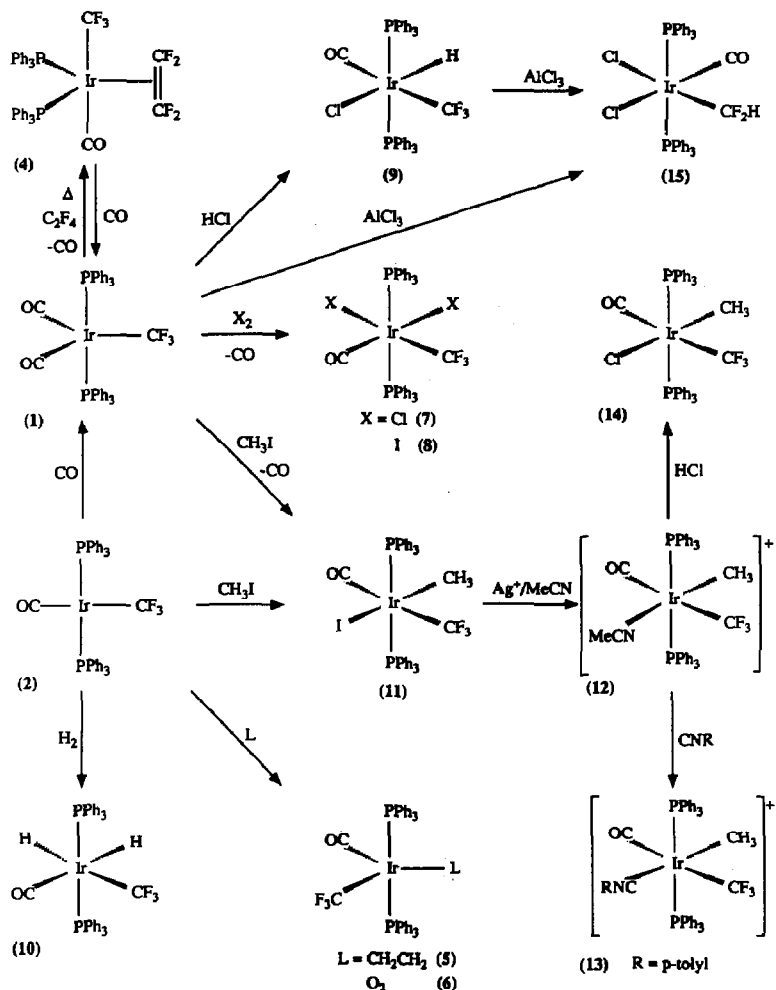
Infrared spectroscopic data (cm^{-1})^a

| | $\nu(\text{CO})$ | $\nu(\text{CF})$ | Other bands |
|--|---|--|---|
| 1 $\text{Ir}(\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ | 1991, 1937 | 1088, 1005 | |
| 2 $\text{Ir}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ | 1978 | 997, 981, 962 | |
| 3 $\text{Ir}(\text{COCF}_3)(\text{CO})_2(\text{PPh}_3)_2$ | 1991, 1941, 1634 | 1238, 1995, 1115, 1090, 875 | |
| 4 $\text{Ir}(\text{CF}_3)(\text{C}_2\text{F}_4)(\text{CO})(\text{PPh}_3)_2$ | 2064 | 1115, 1044, 1028, 1009, 807 | |
| 5 $\text{Ir}(\text{CF}_3)(\text{C}_2\text{H}_4)(\text{CO})(\text{PPh}_3)_2$ ^b | | | |
| 6 $\text{Ir}(\text{CF}_3)(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$ | 2004 | 1096, 1082, 1016 | $\nu(\text{O}_2)$ 840m |
| 7 $\text{IrCl}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ | 2094 | 1100, 1037, 1025, 1012 | $\nu(\text{IrCl})$ 329, 296w |
| 8 $\text{IrI}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ | 2069 | 1088, 1031, 1017 | |
| 9 $\text{IrHCl}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (H <i>trans</i> to Cl) | 2040 | 1024, 999 | $\nu(\text{IrH})$ 2236, 863, 850, 823 |
| 9 $\text{IrHCl}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ ^c (H <i>trans</i> to CF_3) | 2076 | 1082, 1006, 995 | $\nu(\text{IrH})$ 2031, 851w |
| 10 <i>cis</i> - $\text{IrH}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ | 2107 | 1003, 988 | $\nu(\text{IrH})$ (2228, 2208) ^d $\nu(\text{IrH})$ 1954, 849, 825w |
| <i>trans</i> - $\text{IrH}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ ^c | (2096, 2041) ^d 2049 ^e | 1019, 1076, 1008, 1001, 984, 973 | $\nu(\text{IrH})$ 1781, 831, 815w |
| 11 $\text{IrI}(\text{CH}_3)(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ | 2043 | 1009, 998, 968 | |
| 12 $[\text{Ir}(\text{CH}_3)(\text{CF}_3)(\text{CH}_3\text{CN})-$ $(\text{CO})(\text{PPh}_3)_2]^+$ | 2065 | 1045, 1020, 999, 800 | |
| 13 $[\text{Ir}(\text{CH}_3)(\text{CF}_3)(\text{CN}-p\text{-C}_6\text{H}_4\text{CH}_3)-$ $(\text{CO})(\text{PPh}_3)_2]^+$ | 2088 | 1099, 1088, 1041, 1013, 1001, 818 | $\nu(\text{CN})$ 2214 |
| 14 $\text{IrCl}(\text{CH}_3)(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ | 2049 | 1090, 1010 | |
| 15 $\text{IrCl}_2(\text{CF}_2\text{H})(\text{CO})(\text{PPh}_3)_2$ | 2073 | 1093, 1010, 961 | |
| 16 $\text{IrCl}(\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ | 1950 | 1168, 1096, 1155, 1043 | |
| 17 $\text{Ir}(\text{CF}_3)(\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ | 1976 (1998, 2047) ^e | 1184, 1196, 1175, 1157, 1088, 1066, 1012 | |
| 18 $\text{Ir}(\text{COCF}_2\text{Cl})(\text{CO})_2(\text{PPh}_3)_2$ | 1991, 1942, 1652 | 1168, 1131, 1093, 940, 812 | |
| 19 $\text{IrI}(\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ | 1970 | 1170, 1060 | |
| 20 $\text{IrCl}(\text{CN}-t\text{-C}_4\text{H}_9)(\text{CO})(\text{PPh}_3)_2$ | 2008 | | $\nu(\text{CN})$ 2078 |

^a Spectra recorded as nujol mull between KBr or CsI discs and calibrated with polystyrene. m = medium, w = weak. ^b Stable only under C_2H_4 pressure; IR spectrum not recorded. ^c Ref. 7. ^d Multiple bands attributed to solid state splitting. ^e Solution spectrum (CH_2Cl_2).

Trifluoromethyl complexes of Mo, Mn, Fe, and Co have been prepared by nucleophilic attack of an anionic transition metal complex on CF_3COCl or $(\text{CF}_3\text{CO})_2\text{O}$, producing a metal trifluoroacetyl complex which is subsequently decarbonylated [1,12]. This route offers an alternative synthesis of 1. Sodium amalgam reduction of Vaska's complex [13] followed by treatment with trifluoroacetic anhydride yields the new trifluoroacetyl complex $\text{Ir}(\text{COCF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (3), which can be thermally decarbonylated in refluxing benzene to form $\text{Ir}(\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (1) (Scheme 1). This proved to be a more convenient route for the preparation of 1 in good yield, and obviates the need for the trifluoromethyl mercury reagent which is itself produced using trifluoroacetic acid [14].

The ^{31}P NMR solution spectra of complexes 1 and 2 each demonstrated the presence of only a single isomer containing equivalent triphenylphosphine ligands. The ^{13}C NMR spectra show the *ipso* carbon atoms of the PPh_3 phenyl groups as a single resonance split into a triplet by interaction with the strong virtual coupling between the *trans* phosphorus atoms, confirming the assignment of the PPh_3 ligands as mutually *trans* in each case.



Scheme 2. Reactions of trifluoromethyl iridium complexes.

Table 2
NMR spectroscopic data ^a

| | ³¹ P NMR ^{b,c} | | Other nuclei ^d | |
|--|------------------------------------|-------------------------|--|-------------------------|
| | δ (ppm) | ³ J(PF) (Hz) | nucleus | δ (ppm) |
| 1 Ir(CF ₃) ₂ (CO) ₂ (PPh ₃) ₂ | -1.52 q | 31.4 | | |
| 2 Ir(CF ₃) ₂ (CO)(PPh ₃) ₂ | 21.56 q | 14.2 | | |
| 3 Ir(CO)(CF ₃) ₂ (CO) ₂ (PPh ₃) ₂ | -3.22 s | | ¹⁹ F | -75.4 s |
| 4 Ir(CF ₃) ₂ (C ₂ F ₅) ₂ (CO)(PPh ₃) ₂ | -10.30 m | | ¹ H C ₂ H ₄ | 0.88 t |
| 5 Ir(CF ₃) ₂ (C ₂ H ₅) ₂ (CO)(PPh ₃) ₂ | -5.35 q | 11.8 | | ³ J(HP) 7.24 |
| 6 Ir(CF ₃) ₂ (CO) ₂ (CO)(PPh ₃) ₂ | 7.11 q | 9.9 | | |
| 7 IrCl ₂ (CF ₃) ₂ (CO)(PPh ₃) ₂ | -20.37 q | 11.6 | ¹⁹ F | 2.0 t |
| 8 IrI ₂ (CF ₃) ₂ (CO)(PPh ₃) ₂ | -34.92 q | 11.9 | | ³ J(PF) 11.6 |
| 9 IrHCl(CF ₃) ₂ (CO)(PPh ₃) ₂ (H <i>trans</i> to Cl) | -6.55 | e | ¹ H IrH | -16.82 m |
| IrHCl(CF ₃) ₂ (CO)(PPh ₃) ₂ (H <i>trans</i> to CF ₃) | -4.62 | e | ¹ H IrH | -9.06 m |
| | -4.72 | e | ¹ H IrH | -10.56 m |
| 10 <i>cis</i> -IrH ₂ (CF ₃) ₂ (CO)(PPh ₃) ₂ | -9.56 | e | ¹ H IrH | -10.85 m |
| | | | | -7.64 dq |
| <i>trans</i> -IrH ₂ (CF ₃) ₂ (CO)(PPh ₃) ₂ | | | | ² J(HP) 15 |
| | | | | ³ J(HF) 10 |
| 11 Ir(CH ₃) ₂ (CF ₃) ₂ (CO)(PPh ₃) ₂ | -12.57 q | 12.7 | ¹ H CH ₃ | 0.21 t |
| | | | ¹⁹ F | -8.79 t |
| | | | | ² J(HP) 4.7 |
| | | | | ³ J(PF) 12.7 |

| | | | | | |
|--|--------------------|--------------|--|----------------------------|---|
| $\text{r}(\text{CH}_3)_2\text{CF}_3(\text{CH}_3\text{CN})\text{-CO}(\text{PPh}_3)_2]^+$ | -8.91 q | 13.1 | ^1H IrCH_3 | 0.42 t | $^3J(\text{HP})$ 5.3 |
| $\text{r}(\text{CH}_3)_2\text{CF}_3(\text{CN-}i\text{-C}_6\text{H}_4\text{CH}_3)\text{-CO}(\text{PPh}_3)_2]^+$ | -11.51 q | 12.6 | ^1H IrCH_3 C_6H_4 | 2.20 s 0.40 t 7.02 d | $^3J(\text{HP})$ 3.9 $^3J(\text{HH}')$ 8.2 7.12 d |
| $\text{r}(\text{CH}_3)_2\text{CF}_3(\text{CO})(\text{PPh}_3)_2$ | -16.58 dd | 17.5 19.4 | ArCH_3 ^1H IrCH_3 ^{19}F | s 0.18 t -57.77 ddd | 2.33 $^3J(\text{HP})$ 5.0 $^3J(\text{FH})$ 54.5 $^3J(\text{PF})$ 17.5 $^3J(\text{PF})$ 19.4 |
| $\text{r}(\text{CF}_3)_2\text{CO}(\text{PPh}_3)_2$ | 8.19 dd | 21.6 27.4 | | | |
| $i\text{-Ir}(\text{CF}_3)_2\text{CF}_2(\text{CO})(\text{PPh}_3)_2$ | 8.21, m -0.91 m | | | | |
| $\text{trans-Ir}(\text{CF}_3)_2\text{CF}_2(\text{CO})(\text{PPh}_3)_2$ | 2.75 m | | | | |
| $\text{r}(\text{COCF}_2\text{Cl})(\text{CO})_2(\text{PPh}_3)_2$ | -3.15 s | | | | |
| $\text{r}(\text{CF}_3)_2\text{CO}(\text{PPh}_3)_2$ | 1.15 dd | 23.7 | | | |
| $\text{r}(\text{CN-}i\text{-C}_4\text{H}_9)_2\text{CO}(\text{PPh}_3)_2$ | | 29.3 | ^1H C_4H_9 | 1.63 s | |

^1H NMR data observed at 162 MHz with chemical shifts (δ) reported in ppm downfield from external 85% H_3PO_4 . ^c Multiplicity: XCl_3 solutions, 21 °C. ^b $^{31}\text{P}\{^1\text{H}\}$ NMR data observed at 162 MHz with chemical shifts (δ) reported in ppm downfield from external 85% H_3PO_4 . ^c Multiplicity: singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, etc. ^d ^1H data observed at 400 MHz with chemical shifts reported downfield from TMS; ^e ^1H data observed at 84.6 MHz with chemical shifts reported downfield from external CFCl_3 . ^f Incompletely proton decoupled.

The CO stretching frequency of **2**, $\text{Ir}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$, appears at 1978 cm^{-1} , approximately 30 cm^{-1} higher than that of Vaska's complex, $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, reflecting the strongly electron withdrawing nature of the trifluoromethyl ligand. The $\nu(\text{CF})$ values for **1** ($> 1000\text{ cm}^{-1}$) and **2** ($997\text{--}962\text{ cm}^{-1}$) reflect the lower electron density at the iridium centre in **1**, arising from the presence of an additional electron-withdrawing CO ligand, and the resulting strengthening of the C–F_α bonds.

All new complexes were characterised by elemental analysis, except where specified. Important IR and NMR data are collected in Tables 1 and 2, respectively. Attempts to observe fluoroalkyl or fluorocarbene carbon resonances in the ^{13}C NMR were unsuccessful.

Reactivity of trifluoromethyl iridium(I) complexes

Complexes **1** and **2** exhibit the reactivity typical of saturated and unsaturated iridium(I) species, respectively. The five-coordinate complex **1** can undergo substitution of a CO ligand by another neutral ligand, while the unsaturated complex **2** will coordinate a fifth ligand. Both **1** and **2** are suitable substrates for oxidative addition reactions. This reactivity is summarised in Scheme 2.

Treatment of complex **1** with tetrafluoroethylene at 90° for 72 h results in displacement of CO and coordination of C_2F_4 , producing $\text{Ir}(\text{CF}_3)(\text{CF}_2\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ (**4**). The ^{31}P NMR spectrum indicates the presence of two equivalent triphenylphosphine ligands, while the ^{13}C NMR shows that the *ipso* phenyl carbon atoms appear only as a doublet. The relatively unusual arrangement of *cis* triphenylphosphine ligands is consistent with the NMR data. An X-ray crystal structure determination (discussed in more detail in a later section) confirms this stereochemistry, in contrast to complexes **1** and **2** which exhibit the more common arrangement of *trans* PPh_3 ligands. Complex **4** is very stable, losing tetrafluoroethylene only at elevated temperature and under high pressure of CO, returning $\text{Ir}(\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (**1**). In contrast, $\text{IrCl}(\text{CF}_2\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$, prepared by the reaction of Vaska's complex with tetrafluoroethylene, loses C_2F_4 at room temperature in solution and slowly even in the solid state [3]. Both $\text{Ir}(\text{CF}_3)(\text{CF}_2\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ and $\text{IrCl}(\text{CF}_2\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$, however, are similar in that they display reactivity characteristic of iridium(III) rather than iridium(I) species. For example, complex **4** does not undergo oxidative addition reactions with HCl, Cl_2 or I_2 . The CO stretching frequency (2064 cm^{-1}) and ^{31}P NMR chemical shift (-10.30 ppm) observed for **4** compare more closely with those of the iridium(III) complex $\text{IrCl}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (2094 cm^{-1} , -20.37 ppm) than with those of the iridium(I) complex $\text{Ir}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (1978 cm^{-1} , 21.56 ppm).

The four-coordinate complex **2**, in contrast to the robust Vaska's complex, $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, is very air sensitive. Dioxygen and ethylene adducts, $\text{Ir}(\text{CF}_3)(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$ (**5**) and $\text{Ir}(\text{CF}_3)(\text{CH}_2\text{CH}_2)(\text{CO})(\text{PPh}_3)_2$ (**6**), were characterized by IR and NMR spectroscopy. The dioxygen adduct **5** is prepared in the solid state and has only limited stability in solution, while the ethylene complex **6**, prepared in solution, exists only in an atmosphere of ethylene, and loses the alkene ligand to reform **2** in the absence of excess ethylene. Both complexes were assigned solution structures with mutually *trans* PPh_3 ligands with the O_2 or C_2H_4 ligand coordinated in the equatorial plane of a distorted trigonal bipyramidal structure. Treatment of **2** with CO returns the five coordinate complex **1**. No further carbonylation occurs, even under vigorous conditions, indicating that the decarbonylation of **3**,

$\text{Ir}(\text{COCF}_3)(\text{CO})_2(\text{PPh}_3)_2$, the reaction by which **1** is first prepared, must be irreversible.

Oxidative addition of Cl_2 and I_2 to complex **1**, $\text{Ir}(\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$, occurs in a *cis* fashion. The product of Cl_2 addition, $\text{IrCl}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (**7**), had been previously prepared by oxidative addition of CF_3I to $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, followed by substitution of I^- by Cl^- [7]. The I_2 addition product **8** was characterized spectroscopically, by comparison with the data for the dichloro congener (**7**).

The addition of HCl to **1** produces $\text{IrHCl}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (**9**), which has been shown spectroscopically to contain H *trans* to Cl . This product is thus an isomer of the complex with H *trans* to CF_3 prepared previously by the action of LiBEt_3H on $[\text{IrCl}(\text{CF}_3)(\text{CH}_3\text{CN})(\text{CO})(\text{PPh}_3)_2]^+$ [7]. Oxidative addition of hydrogen to **2** produces the *cis*-dihydrido-iridium(III) complex $\text{IrH}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (**10**). This complex is an isomer of the *trans*-dihydrido complex formed by the reaction of NaBH_4 with $[\text{IrCl}(\text{CF}_3)(\text{CH}_3\text{CN})(\text{CO})(\text{PPh}_3)_2]^+$ [7]. Both **9** and **10**, the mono- and dihydrido complexes prepared from **1** and **2**, respectively, can be distinguished from their isomeric counterparts by examination of the ^1H and ^{31}P NMR spectra, where both chemical shifts and coupling constants vary with geometry (Table 2). The new complexes are apparently stable with respect to isomerization.

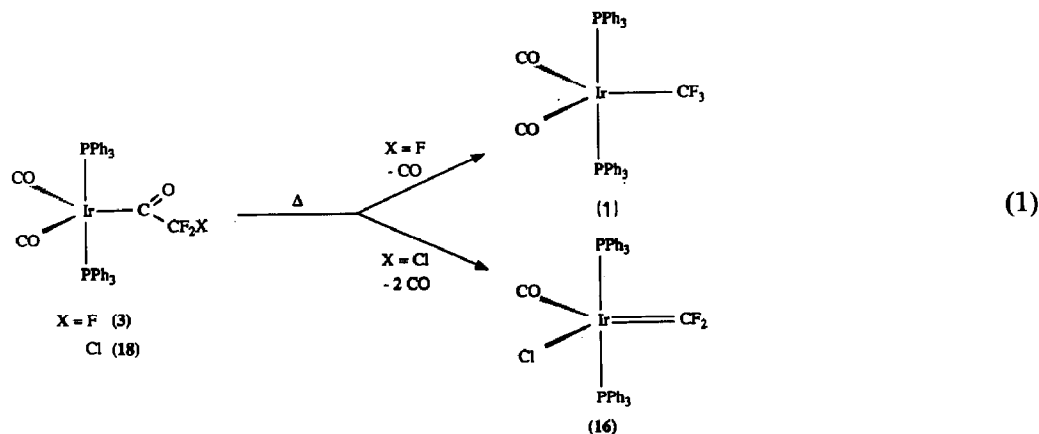
Oxidative addition of CH_3I to **2** occurs with CH_3 and I fragments adding in *trans* positions, producing a novel compound containing both methyl and trifluoromethyl ligands. This compound may be more conveniently produced by the reaction of CH_3I with **1**, with concomitant loss of CO . The product, $\text{Ir}(\text{CH}_3)(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (**11**), offered the possibility of internal comparison of the CH_3 and CF_3 ligands, and was characterized by X-ray crystallography. The structure, which contains *trans* phosphine ligands, will be discussed in detail below. Treatment of complex **11** with AgClO_4 in acetonitrile produces a cationic species $[\text{Ir}(\text{CH}_3)(\text{CF}_3)(\text{CH}_3\text{CN})(\text{CO})(\text{PPh}_3)_2]^+$ (**12**), in which the iodo ligand has been replaced by coordinated CH_3CN . The CH_3CN ligand can in turn be substituted by *p*-tolylisocyanide, yielding a further cationic trifluoromethyl complex $[\text{Ir}(\text{CH}_3)(\text{CF}_3)(\text{CN}-p\text{-C}_6\text{H}_4\text{CH}_3)(\text{CO})(\text{PPh}_3)_2]^+$ (**13**). The acetonitrile ligand in complex **12** is not displaced by a CO ligand even after prolonged periods under CO pressure. However, the acetonitrile complex **12** (but not the isocyanide complex **13**) reacts with HCl , resulting in coordination of a chloro ligand to produce $\text{IrCl}(\text{CH}_3)(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (**14**), which was characterised only by ^{31}P NMR, and by comparison with the closely related complex **11**.

Halide abstraction from trihalomethyl complexes has proved in particular cases to be a means of preparing dihalocarbene complexes. For example, treatment of $\text{RuCl}(\text{CF}_3)(\text{CH}_3\text{CN})(\text{CO})(\text{PPh}_3)_2$ with dry HCl or $(\text{CH}_3)_3\text{SiCl}$ forms, after fluoride abstraction, $\text{RuCl}_2(=\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ [8]. Similarly, $[\text{CpFe}(=\text{CF}_2)(\text{CO})_2]\text{BF}_4$ can be formed by BF_3 -mediated fluoride abstraction from $\text{CpFe}(\text{CF}_3)(\text{CO})_2$ [15]. In an attempt to prepare a difluorocarbene iridium(I) complex from $\text{Ir}(\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (**1**), this substrate was treated with AlCl_3 . The product, rather than a difluorocarbene species, was a difluoromethyl complex, $\text{IrCl}_2(\text{CF}_2\text{H})(\text{CO})(\text{PPh}_3)_2$ (**15**). This product could be rationalised by the formation of an intermediate difluorocarbene complex which subsequently reacts with HCl generated by the hydrolysis of excess AlCl_3 during work-up. When the reaction was monitored by ^{31}P NMR, a triplet at -1.3 ppm with $J(\text{PF})$ 24.58 Hz was observed, which is consistent with a difluorocarbene intermediate. Over a longer period of time the spectrum of the neutral

The solid state and solution structures will be discussed in more depth below. The preparation and reactions of new fluorocarbene complexes are outlined in Scheme 3.

The utility of the reduced iridium(-I) species with trifluoroacetic anhydride as a source of trifluoromethyl iridium(I) complexes suggested that chlorodifluoroacetic anhydride may be a useful source of the CF_2 fragment. One other precedent for this proposal came from a previous report of the preparation of the difluoromethyl complex **15** [16] by the reaction of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ with $\text{CF}_2\text{ClCOO}^- \text{Na}^+$ in diglyme. In addition, previous work in our laboratory has implicated the intermediacy of difluorocarbene complexes in reactions producing difluoromethyl products. The sodium salt $\text{CF}_2\text{ClCOO}^- \text{Na}^+$ has been utilized by organic chemists as a difluorocarbene source.

Reaction of the anionic iridium species (produced in situ from Na/Hg reduction of Vaska's complex [13]) with $(\text{CF}_2\text{ClCO})_2\text{O}$ gave $\text{Ir}(\text{COCF}_2\text{Cl})(\text{CO})_2(\text{PPh}_3)_2$ (**18**), the chlorodifluoroacetyl analogue of the trifluoroacetyl complex **3**. However, whereas the product of thermolysis of **3** was the trifluoromethyl species $\text{Ir}(\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (**1**), thermal decarbonylation of **18** produced a new difluorocarbene complex, $\text{IrCl}(\text{=CF}_2)(\text{CO})(\text{PPh}_3)_2$ (**16**). A CF_2Cl complex analogous to **1** would be expected to form as an intermediate in the thermal reaction of **18**, but facile chloride migration with concomitant CO loss can be invoked to rationalise the formation of the product **16**. In contrast, migration of a fluoride atom from the CF_3 group of complex **1** is much less facile and no further rearrangement of this complex occurs (eq. 1). This result reflects the stronger C-F relative to the C-Cl bond strengths.



Treatment of complex **16** with $\text{Cd}(\text{CF}_3)_2 \cdot \text{glyme}$ serves as an additional preparation of $\text{Ir}(\text{CF}_3)(\text{=CF}_2)(\text{CO})(\text{PPh}_3)_2$ (**17**). Thus the cadmium reagent serves as a source of both CF_3 and CF_2 fragments when the substrate is Vaska's complex, or as a source of either CF_3 when the substrate already contains CF_2 (complex **16**), or as a source of CF_2 when the complex already contains CF_3 (complex **1** or **2**). In one further example of the use of this reagent, reaction of the iodo Vaska's analogue $\text{IrI}(\text{CO})(\text{PPh}_3)_2$ with $\text{Cd}(\text{CF}_3)_2 \cdot \text{glyme}$ in refluxing benzene produces **17**, but at ambient temperature only CF_2 is transferred, resulting in a new complex, $\text{IrI}(\text{=CF}_2)(\text{CO})(\text{PPh}_3)_2$ (**19**). This species was characterized by NMR and IR spectroscopy and by comparison with the closely related complex **16**.

Both the NMR data and the solution IR data for $\text{Ir}(\text{CF}_3)(=\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ (**17**) support the presence of two geometrical isomers in solution. However, ^{31}P and ^{13}C NMR data for $\text{IrCl}(=\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ (**16**) indicate that only the isomer with *trans*, equivalent phosphine ligands is present in solution. These structures will be examined in a later section. The IR data for both difluorocarbene complexes **17** and **16** show $\nu(\text{CF})$ values in the region $1155\text{--}1184\text{ cm}^{-1}$, significantly higher than the $\nu(\text{CF})$ stretch observed for the iridium(I) trifluoromethyl complexes **1** ($1000\text{--}1100\text{ cm}^{-1}$) and **2** ($< 1000\text{ cm}^{-1}$). This indicates stronger C–F bonds in the carbenoid fluorocarbon ligands relative to the saturated fluoroalkyl ligands. Complex **17**, which contains a CF_3 ligand in addition to the difluorocarbene ligand, shows an additional set of $\nu(\text{CF})$ vibrations in the region $1000\text{--}1100\text{ cm}^{-1}$.

Reactivity of difluorocarbene iridium(I) complexes

The nature and rationalization of the reactivity of transition metal carbene complexes has been a subject of debate for at least a decade. Originally, the nucleophilic reactivity of early transition metal carbenes and the electrophilic reactivity of the late metal carbenes were thought to be chemically distinct phenomena. However, it has been recently demonstrated that group 8 methylene and difluorocarbene complexes in the +2 oxidation state exhibited electrophilic behaviour typical of the later metals, where d^8 , zerovalent complexes of the same metals containing the same carbene ligands are remarkable in that they show nucleophilic reactivity [2,4]. This has led to a rationalization of the diverse reactivity of transition metal carbene complexes [17].

The d^6 dichlorocarbene iridium(III) complex $\text{IrCl}_3(\text{CCl}_2)(\text{PPh}_3)_2$ behaves, as expected, in an electrophilic fashion, reacting with substrates like H_2O , H_2S , amines and thiols to produce CO, CS, aminocarbene or thiocarbene products, respectively [11]. It was of considerable interest to observe whether the d^8 difluorocarbene iridium(I) complexes **17** and **16** would exhibit any nucleophilic traits, as do their d^8 ruthenium(0) and osmium(0) counterparts.

The difluorocarbene ligands in both complexes **17** and **16** can be hydrolysed to carbonyl ligands. Complex **16**, $\text{IrCl}(=\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$, is extremely sensitive toward hydrolysis, quickly forming $\text{IrCl}(\text{CO})_2(\text{PPh}_3)_2$ in solvents containing moisture. This behaviour is in contrast to $\text{Ir}(\text{CF}_3)(=\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ (**17**), which is only hydrolysed to $\text{Ir}(\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ at higher temperature (refluxing benzene) or in the presence of acid. Although the more electron withdrawing CF_3 ligand in complex **17** (relative to the Cl ligand in complex **16**) might be expected to enhance the electrophilic nature of the carbene ligand, the ease of hydrolysis of **16** may be related to the lability of metal-halide substituents in saturated d^8 iridium(I) complexes. For example, addition of isocyanide to $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ results not in simple adduct formation, but in both Cl and CO loss, yielding $[\text{Ir}(\text{CN-}p\text{-C}_6\text{H}_4\text{CH}_3)_3(\text{PPh}_3)_2]^+$ [18].

Reaction of $\text{Ir}(\text{CF}_3)(=\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$, (**17**) with other nucleophilic reagents like primary amines, thiolates or alkyl lithium reagents resulted in hydrolysis and decomposition. However, the reaction of $\text{IrCl}(=\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ (**16**) with *t*-butylamine resulted in attack at the carbene ligand to form an isocyanide complex, $\text{IrCl}(\text{CN-}t\text{-C}_4\text{H}_9)(\text{CO})(\text{PPh}_3)_2$ (**20**), identified by IR and NMR spectroscopy. This complex cannot be formed directly by isocyanide addition to Vaska's complex, as outlined above [18].

Both the hydrolysis and amine reactions are clear evidence for electrophilic behaviour at the carbene ligand. However, the difluorocarbene complexes also display weakly nucleophilic reactivity. For example, reaction of $\text{Ir}(\text{CF}_3)(=\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ with ${}^n\text{Bu}_4\text{NAuI}_2$ gave a product, observed spectroscopically and presumed to be $\text{Ir}(\text{CF}_3)(\text{CF}_2\text{-Au-I})(\text{CO})(\text{PPh}_3)_2$, where the electrophilic gold centre is coordinated to the carbene $\text{Ir}=\text{C}$ bond. This kind of adduct has been prepared for nucleophilic zerovalent Ru and Os difluorocarbene, methylene and carbyne complexes [4]. In this iridium example, however, the gold adduct is of limited stability in solution.

Protonation at the carbene carbon atom can be considered attack by an electrophilic reagent on a carbene with nucleophilic character. The reaction of dry HCl with $\text{IrCl}(\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ (**16**) gave the difluoromethyl complex $\text{IrCl}_2(\text{CF}_2\text{H})(\text{CO})(\text{PPh}_3)_2$ (**15**) presumably by protonation at the metal centre followed by hydride transfer to the carbene. The formation of **15** from the difluorocarbene species **16** is evidence for difluorocarbene intermediates in the formation of the same difluoromethyl complex **15** from the reaction of AlCl_3 with either $\text{Ir}(\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (**1**) or $\text{IrHCl}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (**9**) as outlined above.

The reaction of $\text{Ir}(\text{CF}_3)(=\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ (**17**), however, with aqueous HCl yields $\text{IrHCl}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (**9**) resulting from hydrolysis of the carbene ligand. In this case, the hydrolysis of a postulated cationic intermediate, $[\text{IrH}(\text{CF}_3)(=\text{CF}_2)(\text{CO})(\text{PPh}_3)_2]^+$, must compete favourably with hydride migration. Attempts to prevent hydrolysis and thus prepare a mixed trifluoromethyl difluoromethyl complex by reaction of **17** with dry HCl were unsuccessful, resulting in mixtures of products which may include geometric isomers of the desired product.

Thus although the iridium carbenes do show some weakly nucleophilic behaviour, the predominant reactivity at the carbene centre is electrophilic. The nucleophilic reactivity of the zerovalent, d^8 Ru and Os difluorocarbene complexes has been rationalized by the electron rich nature of the metal centre, resulting in very efficient metal to ligand π back-bonding [2,17], and although the iridium carbene complexes also have a d^8 configuration, the higher formal charge on iridium (+1 versus 0) must be sufficient to reduce the electron density at the metal centre and so reduce the tendency towards nucleophilic behaviour.

*Crystal structures of $\text{IrI}(\text{CH}_3)(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (**11**), $\text{Ir}(\text{CF}_3)(\text{C}_2\text{F}_4)(\text{CO})(\text{PPh}_3)_2$ (**4**) and $\text{Ir}(\text{CF}_3)(=\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ (**17**)*

Representative complexes containing each of the three important fluorocarbon ligand types, trifluoromethyl, tetrafluoroethylene, and difluorocarbene, have been examined by X-ray crystallography. The data for each structure were collected at room temperature, resulting in large thermal parameters for the fluorine atoms due to thermal motion. Interpretation of the bond lengths and angles involving fluorine atoms are consequently limited by the associated large estimated standard deviation values. Supplementary data which consist of atomic thermal parameters and observed and calculated structure factors for compounds **4**, **11**, and **17** are available from the authors.

Crystals of $\text{IrI}(\text{CH}_3)(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (**11**) contain one disordered molecule of THF per unit cell, which contributes to the poor convergence of the structure ($R = 0.058$, $R_w = 0.062$). The complex displays a distorted octahedral geometry (Fig. 1) with mutually *trans* triphenylphosphine ligands and the methyl and iodo

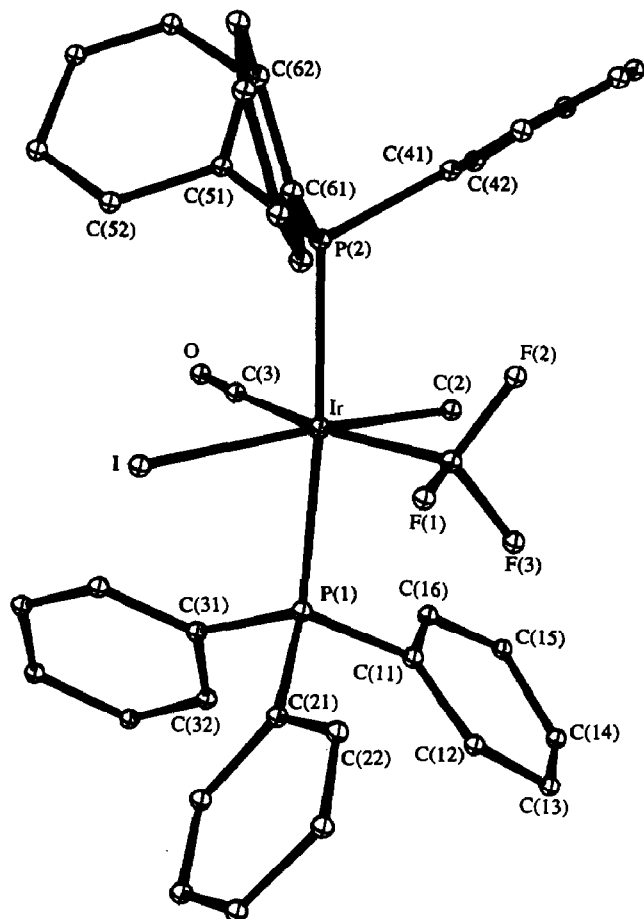


Fig. 1. Molecular geometry for $\text{IrI}(\text{CH}_3)(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (11).

ligands also *trans*, confirming the stereochemistry of addition of methyl iodide. Important bond lengths and angles are given in Table 3, and the final atomic positions are given in Table 4. The iridium–carbon bond lengths for the methyl (2.12(3) Å) and trifluoromethyl (2.15(2) Å) ligands are not significantly different, although the relative electron donating and withdrawing properties of these ligands might be expected to be quite different. However, it is difficult to make comparisons since each is *trans* to a different ligand (CH_3 *trans* to I; CF_3 *trans* to CO). The Ir–C bond of the trifluoromethyl ligand is within the range observed for other iridium σ -fluorocarbon bonds (Table 5).

The tetrafluoroethylene complex, $\text{Ir}(\text{CF}_3)(\text{C}_2\text{F}_4)(\text{CO})(\text{PPh}_3)_2$ (4) crystallised as colourless cubic crystals from dichloromethane/ethanol solution. The unit cell contains two crystallographically independent molecules, related approximately by (x, z) and $(x + \frac{1}{2}, -z)$. The structure of 4 (Fig. 2) is a distorted trigonal bipyramid with CO and CF_3 ligands in the axial positions. The resulting *cis*, equatorial arrangement of the two triphenylphosphine ligands is unusual in five-coordinate d^8 complexes. The in-plane geometry of the tetrafluoroethylene ligand is in accord with maximum π overlap in the equatorial plane [19].

Table 3

Selected bond lengths and angles for $\text{IrI}(\text{CH}_3)(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (11)

| Bond length (Å) | | Bond angle (°) | |
|-----------------|----------|----------------|----------|
| Ir–C(1) | 2.15(2) | P(1)–Ir–P(2) | 175.3(2) |
| Ir–C(2) | 2.12(3) | P(1)–Ir–I | 86.4(2) |
| Ir–C(3) | 1.95(3) | P(1)–Ir–C(1) | 92.9(6) |
| Ir–I | 2.785(2) | P(1)–Ir–C(2) | 92.1(8) |
| Ir–P(1) | 2.404(7) | P(1)–Ir–C(3) | 88.7(9) |
| Ir–P(2) | 2.402(7) | P(2)–Ir–C(1) | 90.7(6) |
| C(1)–F(1) | 1.35(3) | P(2)–Ir–C(2) | 91.5(8) |
| C(1)–F(2) | 1.32(3) | P(2)–Ir–C(3) | 88.5(9) |
| C(1)–F(3) | 1.32(3) | I–Ir–C(1) | 97.0(6) |
| C(3)–O | 1.06(4) | I–Ir–C(2) | 176.9(8) |
| | | I–Ir–C(3) | 97.5(8) |
| | | C(1)–Ir–C(2) | 80 (1) |
| | | C(1)–Ir–C(3) | 166 (1) |
| | | C(2)–Ir–C(3) | 85 (1) |

Important bond lengths and angles are listed in Table 6, and final atomic positions are listed in Table 7. The metal–carbon bond lengths are not significantly different for the σ -bonded trifluoromethyl and π -bonded tetrafluoroethylene ligands. An alkene complex can be represented by two extreme resonance forms, in this case as an iridium(I) π -alkene complex or as an iridium(III) σ -metallacyclopropane complex. The presence of the strongly electron withdrawing fluoro substituents should enhance the π -back-bonding capability of a π -alkene complex to the point where it may be more reasonably represented as a σ -metallacyclopropane complex. The IR and NMR data, and the chemical reactivity of 4 as presented above were not typical of an iridium(I) complex and the structural data also seems to indicate that a σ -bonding component is important in the tetrafluoroethylene Ir–C bonds. The efficient π -acceptor property of the tetrafluoroethylene ligand is illustrated by the very high $\nu(\text{CO})$ value of 2064 cm^{-1} for this complex, compared with 2094 cm^{-1} for an iridium(III) complex, $\text{IrCl}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$, and 1978 cm^{-1} for the iridium(I) species $\text{Ir}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$. The Ir– CF_3 bond length is within the range observed for other iridium(I) and iridium(III) σ -fluorocarbon bond lengths (Table 5) [16,20,21].

Complex 17, $\text{Ir}(\text{CF}_3)(=\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$, adopts a distorted trigonal bipyramidal structure, and again demonstrates unusual stereochemistry with *cis* triphenylphosphine ligands (Fig. 3). One occupies an axial site *trans* to the CF_3 ligand, while the other shares the equatorial plane with the CO and difluorocarbene ligands. This is a different arrangement from the tetrafluoroethylene complex 4 which also exhibits unusual geometry with *cis* triphenylphosphine ligands (but with both contained in the equatorial plane). Complex 17 also contrasts with the d^8 , group 8 difluorocarbene complexes (Table 8) which all contain mutually *trans* triphenylphosphine ligands.

Important bond lengths and angles are shown in Table 9, and final atomic positions are given in Table 10. The axial PPh_3 ligand is bent away from the equatorial PPh_3 by 10° (relative to ideal trigonal bipyramidal geometry), probably a

consequence of the steric bulk of these ligands. The CF_2 ligand is oriented perpendicular to the equatorial plane, again in accord with maximum π overlap in this plane. [19] The carbene Ir–C bond length (1.874(7) Å) is within the range observed for the d^8 ruthenium and osmium carbene complexes shown in Table 8, but is significantly shorter than the trifluoromethyl Ir–C bond group (2.095(8) Å) in the same molecule. This bond length in turn is in the range observed for iridium σ -fluorocarbon bond lengths (Table 5). The Ir–C bond lengths of the carbene and carbonyl ligands are approximately the same, illustrating the multiple character of the iridium–carbene bond.

Comparison of the structures of $\text{Ir}(\text{CF}_3)\text{L}(\text{CO})(\text{PPh}_3)_2$ ($L = \text{CO}$ (1), CF_2 (17), C_2F_4 (4))

Geometrical isomerism is common in four and six coordinate metal complexes, but is unusual in five coordinate complexes where the barrier to inconversion via the Berry pseudo-rotation mechanism is very low. However, slow interconversion of stereoisomers in a d^8 , five-coordinate complex has been reported in one example [22]. The three complexes $\text{Ir}(\text{CF}_3)\text{L}(\text{CO})(\text{PPh}_3)_2$ show a change in geometry as L varies from CO to CF_2 and C_2F_4 . The latter two were characterised by X-ray crystallography, while for all three complexes ^{31}P , ^{13}C and ^{19}F NMR data allow assignments of the solution structures. The variations in geometry reflect an interplay of steric and electronic demands.

In $\text{Ir}(\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (1, $L = \text{CO}$) the phosphine ligands take up the least sterically demanding *trans* geometry. This structure is confirmed in solution by the presence of a single quartet in the ^{31}P NMR spectrum and a single triplet in the ^{19}F NMR spectrum, each with $^3J(\text{PF})$ 31.4 Hz, and the triplet pattern for the *ipso* carbon atoms of the PPh_3 phenyl groups, which is consistent only with strong virtual coupling between mutually *trans* phosphorus atoms.

The carbene complex $\text{Ir}(\text{CF}_3)(=\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ (17, $L = \text{CF}_2$) exists as two isomers in solution, in approximately equal amounts. The ^{31}P NMR spectrum shows a complex multiplet at 2.75 ppm assigned to two equivalent phosphorus atoms, while the second isomer results in two multiplets at 8.21 and -0.91 ppm. This latter isomer is believed to correspond to the isomer observed in the solid state structure, in which the two phosphine ligands are chemically inequivalent. The former isomer, with equivalent phosphine ligands, is assigned to a structure with these coordinated mutually *trans* in axial sites, on the basis of a triplet pattern for the *ipso* phenyl carbon atoms in the ^{13}C NMR spectrum.

The third complex, $\text{Ir}(\text{CF}_3)(\text{C}_2\text{F}_4)(\text{CO})(\text{PPh}_3)_2$ (4, $L = \text{C}_2\text{F}_4$) exhibits a single multiplet in the ^{31}P NMR, and a doublet in the ^{13}C NMR for the *ipso* phenyl carbon atoms, corresponding to equivalent, mutually *cis* phosphine ligands, and indicating that the solution and solid state geometries are the same.

In comparing the structures of the three complexes 1, 17, and 4 shown below, only the first of these, complex 1 with $L = \text{CO}$, adopts the least sterically demanding geometry with mutually *trans* phosphine ligands. Substituting the CO ligand with the more strongly π -accepting CF_2 and C_2F_4 ligands result in increasingly unfavorable configurations with first one, then two PPh_3 ligands occupying equatorial sites in order to reduce competition for electron density in this plane. This illustrates a delicate balance between steric and electronic factors, with the difluorocarbene complex 17 near the crossover point, evidenced by the existence in solution of isomers of both the sterically (complex 17a) and the electronically (complex 17b)

Table 4

Atomic coordinates for $\text{IrI}(\text{CH}_3)(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (11)

| Atom | x | y | z |
|-------|------------|------------|------------|
| Ir | 0.43023(7) | 0.52487(6) | 0.11390(3) |
| I | 0.4567(1) | 0.4316(1) | 0.05307(5) |
| P(1) | 0.6164(5) | 0.5046(4) | 0.1268(2) |
| P(2) | 0.2480(5) | 0.5459(4) | 0.0957(2) |
| O | 0.489(2) | 0.665(1) | 0.0765(6) |
| C(1) | 0.380(2) | 0.445(1) | 0.1539(6) |
| C(2) | 0.413(2) | 0.591(2) | 0.1621(8) |
| C(3) | 0.469(2) | 0.614(2) | 0.0881(8) |
| F(1) | 0.380(2) | 0.375(1) | 0.1430(5) |
| F(2) | 0.283(2) | 0.454(1) | 0.1671(6) |
| F(3) | 0.441(1) | 0.443(1) | 0.1841(5) |
| C(11) | 0.659(2) | 0.534(1) | 0.1737(6) |
| C(12) | 0.661(2) | 0.607(1) | 0.1814(7) |
| C(13) | 0.693(2) | 0.631(2) | 0.2158(8) |
| C(14) | 0.744(3) | 0.582(2) | 0.2411(9) |
| C(15) | 0.742(3) | 0.507(2) | 0.2348(8) |
| C(16) | 0.702(2) | 0.485(2) | 0.1999(7) |
| C(21) | 0.667(2) | 0.413(1) | 0.1226(6) |
| C(22) | 0.624(2) | 0.355(2) | 0.1394(8) |
| C(23) | 0.662(3) | 0.280(2) | 0.136(1) |
| C(24) | 0.764(3) | 0.273(2) | 0.118(1) |
| C(25) | 0.811(2) | 0.331(2) | 0.1031(8) |
| C(26) | 0.769(2) | 0.403(1) | 0.1051(7) |
| C(31) | 0.706(2) | 0.557(1) | 0.0958(7) |
| C(32) | 0.802(2) | 0.583(1) | 0.1093(7) |
| C(33) | 0.876(2) | 0.619(2) | 0.0856(8) |
| C(34) | 0.852(2) | 0.624(2) | 0.0468(9) |
| C(35) | 0.756(2) | 0.594(1) | 0.0327(7) |
| C(36) | 0.688(2) | 0.560(1) | 0.0573(7) |
| C(41) | 0.160(2) | 0.582(1) | 0.1341(8) |
| C(42) | 0.176(2) | 0.653(2) | 0.1458(8) |
| C(43) | 0.108(3) | 0.681(2) | 0.176(1) |
| C(44) | 0.033(2) | 0.635(2) | 0.1901(9) |
| C(45) | 0.015(2) | 0.566(2) | 0.1780(8) |
| C(46) | 0.082(2) | 0.535(1) | 0.1489(7) |
| C(51) | 0.236(2) | 0.614(1) | 0.0584(7) |
| C(52) | 0.296(3) | 0.602(2) | 0.0236(9) |
| C(53) | 0.287(2) | 0.650(2) | -0.0059(8) |
| C(54) | 0.210(2) | 0.714(2) | -0.0012(8) |
| C(55) | 0.153(2) | 0.722(1) | 0.0299(7) |
| C(56) | 0.161(2) | 0.673(1) | 0.0608(7) |
| C(61) | 0.168(2) | 0.468(1) | 0.0770(6) |
| C(62) | 0.078(2) | 0.489(1) | 0.0560(7) |
| C(63) | 0.012(2) | 0.434(2) | 0.0426(9) |
| C(64) | 0.039(2) | 0.363(2) | 0.0481(8) |
| C(65) | 0.128(2) | 0.342(1) | 0.0682(7) |
| C(66) | 0.197(2) | 0.400(2) | 0.0820(8) |
| S(1') | 0.114(5) | 0.191(3) | 0.683(2) |
| S(2') | 0.019(6) | 0.169(4) | 0.677(2) |
| S(3') | -0.058(6) | 0.162(4) | 0.713(2) |
| S(4') | 0.014(6) | 0.183(4) | 0.751(2) |
| S(5') | 0.145(5) | 0.220(3) | 0.723(2) |

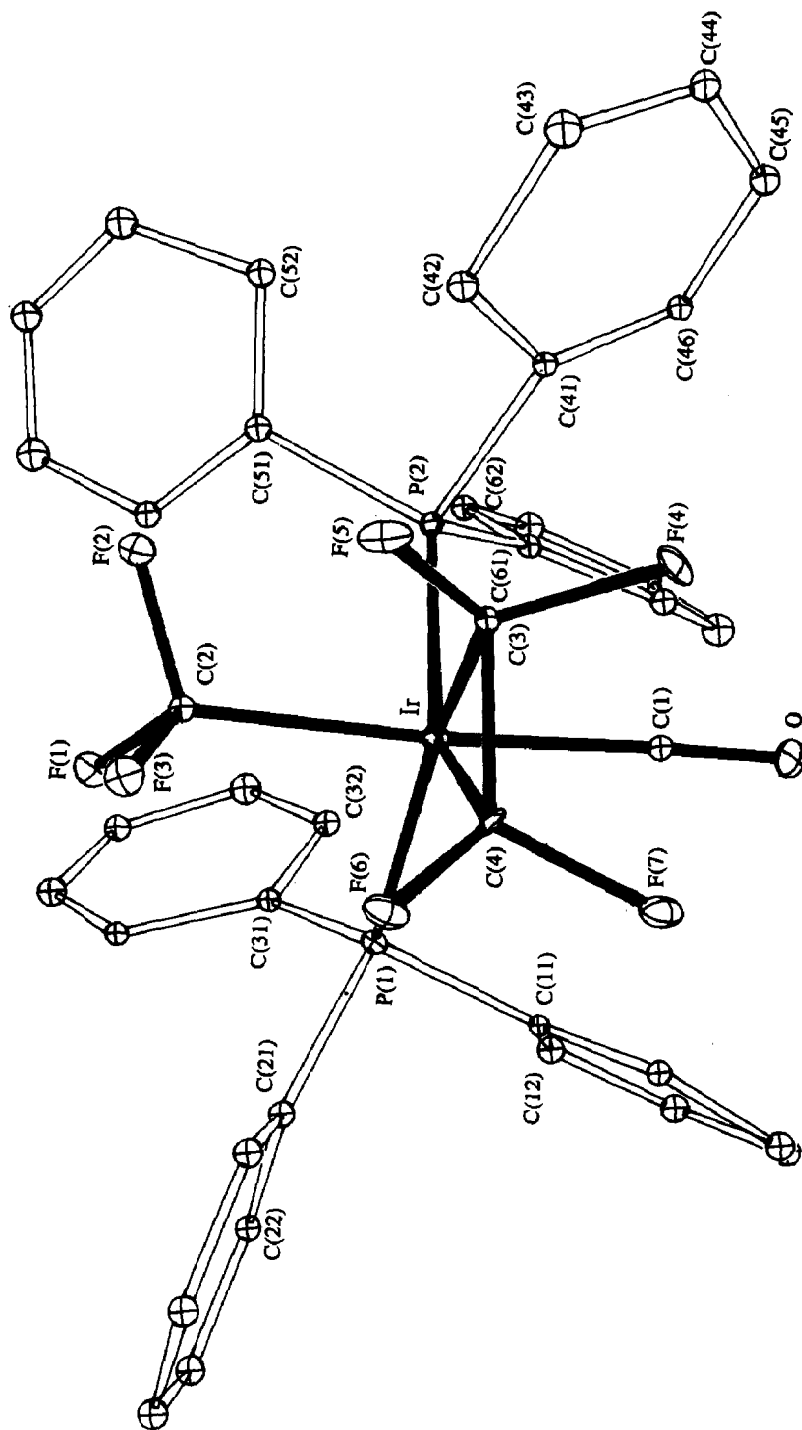


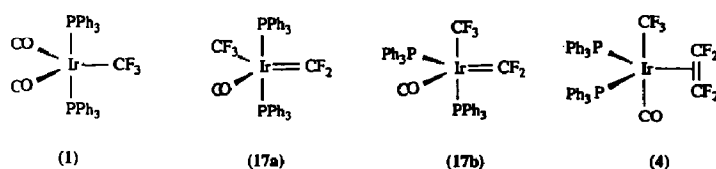
Fig. 2. Molecular geometry for $\text{Ir}(\text{CF}_3)_2(\text{C}_2\text{F}_4)_2(\text{CO})(\text{PPh}_3)_2$ (4).

Table 5

Iridium-carbon bond lengths in complexes containing fluoroalkyl ligands

| | Bond length (Å) | Ref. |
|--|-----------------|------|
| $\text{Ir}(\text{CF}_2\text{CF}_2\text{H})(\text{CO})_2(\text{PPh}_3)_2$ | 2.144(8) | 20 |
| $\text{IrCl}_2(\text{CF}_2\text{CF}_2\text{Cl})(\text{CO})(\text{PPh}_3)_2$ | 2.24(4) | 20 |
| $\text{IrCl}(\text{CF}_2\text{H})(\text{O}_2\text{CCF}_2\text{Cl})(\text{CO})(\text{PPh}_3)_2$ | 2.09(2) | 21 |
| $\text{IrCl}_2(\text{CF}_2\text{H})(\text{CO})(\text{PPh}_3)_2$ | 2.19(3) | 16 |

favoured geometries. The single isomer isolated in the solid state (17b) may simply be the least soluble of the two.



This allows the addition of both tetrafluoroethylene and difluorocarbene ligands to the ranking of π -acceptor capabilities derived from studies of group 8 and 9 complexes:

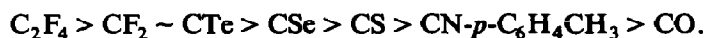


Table 6

Selected averaged bond lengths and angles for $\text{Ir}(\text{CF}_3)(\text{C}_2\text{F}_4)(\text{CO})(\text{PPh}_3)_2$ (4)

| Bond length (Å) | | Bond angle (°) | |
|-----------------|----------|------------------------|----------|
| C(1)–Ir | 1.94(4) | P(1)–Ir–P(2) | 101.7(3) |
| C(2)–Ir | 2.14(4) | C(1)–Ir–P(1) | 92.0(1) |
| C(3)–Ir | 2.13(4) | C(2)–Ir–P(1) | 91.2(9) |
| C(4)–Ir | 2.10(4) | C(3)–Ir–P(1) | 154.0(1) |
| P(1)–Ir | 2.43(1) | C(4)–Ir–P(1) | 119.5(8) |
| P(2)–Ir | 2.429(8) | C(1)–Ir–P(2) | 91.0(1) |
| C(3)–C(4) | 1.59(5) | C(2)–Ir–P(2) | 92.0(1) |
| C(1)–O | 1.12(5) | C(3)–Ir–P(2) | 105.0(1) |
| C(2)–F(1) | 1.35(5) | C(4)–Ir–P(2) | 147.0(1) |
| C(2)–F(2) | 1.36(4) | C(1)–Ir–C(2) | 175.0(1) |
| C(2)–F(3) | 1.37(4) | C(1)–Ir–C(3) | 83.0(2) |
| C(3)–F(4) | 1.36(5) | C(1)–Ir–C(4) | 89.0(1) |
| C(3)–F(5) | 1.23(5) | C(2)–Ir–C(3) | 92.0(1) |
| C(4)–F(6) | 1.35(5) | C(2)–Ir–C(4) | 87.0(2) |
| C(4)–F(7) | 1.40(5) | C(3)–Ir–C(4) | 44.0(1) |
| | | Ir–C(2)–F ^a | 114.0(2) |
| | | Ir–C(3)–F ^b | 123.0(3) |
| | | Ir–C(4)–F | 120.0(3) |

^a Average of F(1), F(2) and F(3). ^b Average of F(4) and F(5).

Table 7

Atomic coordinates for Ir(CF₃)(C₂F₄)(CO)(PPh₃)₂ (4) with two independent molecules in the unit cell (see text)

| Molecule 1 | | | | Molecule 2 | | | |
|------------|------------|------------|-----------|------------|------------|-----------|-------------|
| Atom | x | y | z | Atom | x | y | z |
| Ir | 0.38246(8) | 0.1620(1) | 0.1169(5) | Ir' | 0.12049(8) | 0.5413(1) | -0.11451(4) |
| P(1) | 0.4696(5) | -0.0038(8) | 0.1394(3) | P(1') | 0.0318(4) | 0.3781(8) | -0.1367(2) |
| P(2) | 0.2699(4) | 0.0513(7) | 0.1153(2) | P(2') | 0.2319(5) | 0.4270(8) | -0.1118(2) |
| O | 0.372(2) | 0.095(3) | 0.033(1) | O' | 0.131(1) | 0.490(2) | -0.0304(8) |
| F(1) | 0.409(1) | 0.137(2) | 0.2004(6) | F(1') | 0.097(1) | 0.516(2) | -0.1986(6) |
| F(2) | 0.318(1) | 0.257(2) | 0.1801(6) | F(2') | 0.189(1) | 0.636(2) | -0.1774(6) |
| F(3) | 0.424(1) | 0.327(2) | 0.1832(6) | F(3') | 0.079(1) | 0.706(2) | -0.1835(6) |
| F(4) | 0.321(1) | 0.362(2) | 0.0587(7) | F(4') | 0.183(1) | 0.743(2) | -0.0609(5) |
| F(5) | 0.327(1) | 0.432(2) | 0.1206(6) | F(5') | 0.174(1) | 0.804(2) | -0.1166(5) |
| F(6) | 0.474(1) | 0.412(2) | 0.1258(6) | F(6') | 0.042(1) | 0.711(2) | -0.0686(7) |
| F(7) | 0.460(1) | 0.323(2) | 0.0681(7) | F(7') | 0.030(1) | 0.787(2) | -0.1256(5) |
| C(1) | 0.374(2) | 0.117(4) | 0.064(1) | C(1') | 0.123(2) | 0.501(3) | -0.062(1) |
| C(2) | 0.385(2) | 0.223(3) | 0.174(1) | C(2') | 0.122(2) | 0.603(3) | -0.1711(8) |
| C(3) | 0.345(3) | 0.335(4) | 0.095(1) | C(3') | 0.148(2) | 0.738(3) | -0.0981(9) |
| C(4) | 0.433(2) | 0.328(3) | 0.105(1) | C(4') | 0.068(2) | 0.710(3) | -0.102(1) |
| C(11) | 0.498(1) | -0.093(2) | 0.1014(8) | C(11') | 0.002(2) | 0.295(3) | -0.099(1) |
| C(12) | 0.508(2) | -0.220(3) | 0.099(1) | C(12') | -0.007(2) | 0.161(3) | -0.096(1) |
| C(13) | 0.530(2) | -0.284(4) | 0.068(1) | C(13') | -0.030(2) | 0.104(4) | -0.066(1) |
| C(14) | 0.549(2) | -0.208(3) | 0.039(1) | C(14') | -0.051(2) | 0.183(4) | -0.038(1) |
| C(15) | 0.547(2) | -0.078(3) | 0.042(1) | C(15') | -0.046(2) | 0.316(3) | -0.039(1) |
| C(16) | 0.518(2) | -0.019(3) | 0.0712(9) | C(16') | -0.021(2) | 0.372(3) | -0.067(1) |
| C(21) | 0.555(2) | 0.055(3) | 0.1637(9) | C(21') | -0.054(2) | 0.438(3) | -0.1622(8) |
| C(22) | 0.611(2) | -0.034(3) | 0.178(1) | C(22') | -0.111(2) | 0.346(3) | -0.173(1) |
| C(23) | 0.679(2) | 0.004(3) | 0.193(1) | C(23') | -0.179(2) | 0.393(3) | -0.192(1) |
| C(24) | 0.694(2) | 0.132(3) | 0.196(1) | C(24') | -0.193(2) | 0.520(3) | -0.197(1) |
| C(25) | 0.645(2) | 0.221(3) | 0.183(1) | C(25') | -0.139(2) | 0.607(3) | -0.185(1) |
| C(26) | 0.575(2) | 0.180(3) | 0.168(1) | C(26') | -0.071(2) | 0.571(3) | -0.169(1) |
| C(31) | 0.447(2) | -0.127(3) | 0.169(1) | C(31') | 0.054(1) | 0.254(2) | -0.1695(8) |
| C(32) | 0.401(2) | -0.224(3) | 0.156(1) | C(32') | 0.098(2) | 0.152(3) | -0.153(1) |
| C(33) | 0.379(2) | -0.326(4) | 0.182(1) | C(33') | 0.116(2) | 0.055(3) | -0.180(1) |
| C(34) | 0.406(2) | -0.316(3) | 0.219(1) | C(34') | 0.092(2) | 0.068(4) | -0.218(1) |
| C(35) | 0.450(2) | -0.217(4) | 0.234(1) | C(35') | 0.025(2) | 0.264(3) | -0.208(1) |
| C(36) | 0.472(2) | -0.123(3) | 0.2107(8) | C(36') | 0.044(2) | 0.167(3) | -0.231(1) |
| C(41) | 0.204(1) | 0.149(3) | 0.0832(8) | C(41') | 0.300(2) | 0.516(3) | -0.078(1) |
| C(42) | 0.191(2) | 0.264(3) | 0.101(1) | C(42') | 0.316(2) | 0.641(3) | -0.089(1) |
| C(43) | 0.134(2) | 0.349(4) | 0.074(1) | C(43') | 0.366(2) | 0.718(4) | -0.066(1) |
| C(44) | 0.102(2) | 0.315(3) | 0.042(1) | C(44') | 0.393(2) | 0.665(4) | -0.029(1) |
| C(45) | 0.118(2) | 0.202(3) | 0.028(1) | C(45') | 0.377(2) | 0.541(3) | -0.018(1) |
| C(46) | 0.165(2) | 0.114(3) | 0.049(1) | C(46') | 0.329(2) | 0.468(3) | -0.042(1) |
| C(51) | 0.228(2) | 0.028(3) | 0.158(1) | C(51') | 0.277(2) | 0.406(3) | -0.154(1) |
| C(52) | 0.152(2) | 0.051(3) | 0.153(1) | C(52') | 0.348(2) | 0.428(3) | -0.152(1) |
| C(53) | 0.124(2) | 0.010(4) | 0.191(1) | C(53') | 0.382(2) | 0.408(4) | -0.183(1) |
| C(54) | 0.167(3) | -0.044(4) | 0.220(1) | C(54') | 0.345(2) | 0.353(3) | -0.215(1) |
| C(55) | 0.235(2) | -0.063(4) | 0.222(1) | C(55') | 0.268(2) | 0.325(3) | -0.217(1) |
| C(56) | 0.267(2) | -0.030(3) | 0.190(1) | C(56') | 0.230(2) | 0.355(3) | -0.185(1) |
| C(61) | 0.257(2) | -0.102(3) | 0.092(1) | C(61') | 0.243(1) | 0.266(2) | -0.0932(8) |
| C(62) | 0.226(2) | -0.204(3) | 0.1104(9) | C(62') | 0.282(2) | 0.175(3) | -0.108(1) |
| C(63) | 0.218(2) | -0.325(4) | 0.093(1) | C(63') | 0.289(2) | 0.047(3) | -0.094(1) |
| C(64) | 0.240(2) | -0.346(3) | 0.060(1) | C(64') | 0.259(2) | 0.018(3) | -0.064(1) |
| C(65) | 0.274(2) | -0.259(4) | 0.043(1) | C(65') | 0.217(2) | 0.109(4) | -0.048(1) |
| C(66) | 0.277(2) | -0.130(3) | 0.058(1) | C(66') | 0.207(2) | 0.232(3) | -0.066(1) |

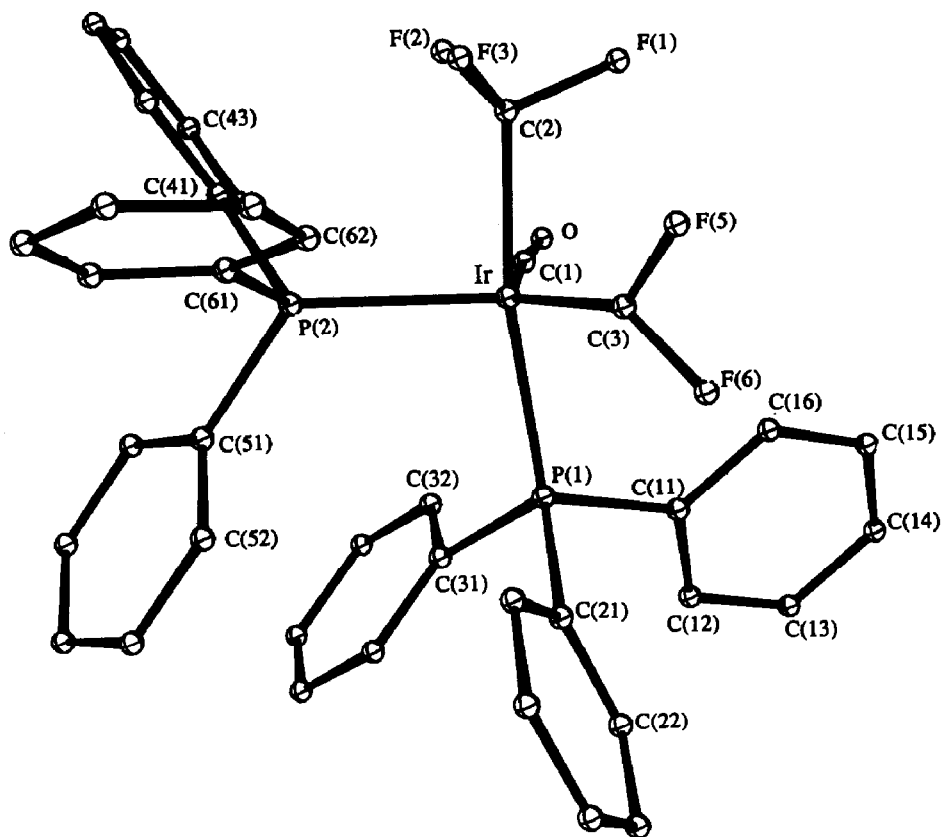


Fig. 3. Molecular geometry for $\text{Ir}(\text{CF}_3)(=\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ (17).

Table 8

Metal–carbene bond lengths for dihalocarbene complexes

| | Bond length (Å) | Ref. |
|---|-----------------|------|
| $\text{Ru}(\text{CF}_2)(\text{CO})_2(\text{PPh}_3)_2$ | 1.83(1) | 9 |
| $\text{Os}(\text{CF}_2)(\text{CO})_2(\text{PPh}_3)_2$ | 1.92(2) | 5 |
| $\text{OsCl}(\text{CF}_2)(\text{NO})(\text{PPh}_3)_2$ | 1.967(6) | 4 |
| $\text{IrCl}_3(\text{CCl}_2)(\text{PPh}_3)_2$ | 1.872(7) | 11 |

Table 9

Selected bond lengths and angles for $\text{Ir}(\text{CF}_3)(\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ (17)

| Bond length (Å) | | Bond angle (°) | |
|---------------------|----------|------------------------|----------|
| Ir–C(1) | 1.874(7) | P(1)–Ir–P(2) | 100.0(1) |
| Ir–C(2) | 2.095(8) | P(1)–Ir–C(1) | 88.8(2) |
| Ir–C(3) | 1.874(7) | P(1)–Ir–C(2) | 169.7(2) |
| Ir–P(1) | 2.374(2) | P(1)–Ir–C(3) | 90.6(2) |
| Ir–P(2) | 2.408(2) | P(2)–Ir–C(1) | 105.8(3) |
| C(2)–F ^a | 1.37(1) | P(2)–Ir–C(2) | 90.0(2) |
| C(3)–F ^b | 1.30(1) | P(2)–Ir–C(3) | 121.1(2) |
| C(1)–O | 1.139(9) | C(1)–Ir–C(2) | 85.9(3) |
| | | C(1)–Ir–C(3) | 132.4(4) |
| | | C(2)–Ir–C(3) | 86.4(3) |
| | | Ir–C(2)–F ^a | 116.5(6) |
| | | Ir–C(3)–F ^b | 134.8(8) |

^a Average of F(1), F(2) and F(3). ^b Average of F(4) and F(5).

Experimental

Standard Schlenk techniques were used for all manipulations involving oxygen- or moisture-sensitive compounds. Infrared spectra ($4000\text{--}200\text{ cm}^{-1}$) were recorded

Table 10

Atomic coordinates for $\text{Ir}(\text{CF}_3)(=\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$ (17)

| Atom | <i>x</i> | <i>y</i> | <i>z</i> |
|-------|------------|------------|------------|
| Ir | 0.13062(2) | 0.23178(1) | 0.27683(2) |
| P(1) | 0.9043(2) | 0.2217(1) | 0.2048(2) |
| P(2) | 1.1616(1) | 0.2984(1) | 0.0803(2) |
| F(1) | 1.3582(5) | 0.1865(4) | 0.4861(7) |
| F(2) | 1.3577(6) | 0.1745(5) | 0.2777(7) |
| F(3) | 1.4199(5) | 0.2938(4) | 0.3969(9) |
| F(4) | 1.103(1) | 0.3159(5) | 0.5261(8) |
| F(5) | 1.277(1) | 0.3227(6) | 0.5790(8) |
| O | 1.0689(6) | 0.0457(4) | 0.1878(8) |
| C(3) | 1.1708(7) | 0.2943(5) | 0.4588(8) |
| C(2) | 1.3263(7) | 0.2252(5) | 0.3654(8) |
| C(1) | 1.0898(7) | 0.1166(5) | 0.2141(8) |
| C(11) | 0.8330(7) | 0.1421(4) | 0.2913(7) |
| C(12) | 0.6993(8) | 0.1043(5) | 0.227(1) |
| C(13) | 0.646(1) | 0.0474(5) | 0.300(1) |
| C(14) | 0.727(1) | 0.0285(5) | 0.433(1) |
| C(15) | 0.858(1) | 0.0640(5) | 0.495(1) |
| C(16) | 0.9146(8) | 0.1223(4) | 0.4270(7) |
| C(21) | 0.8543(6) | 0.3144(4) | 0.2505(6) |
| C(22) | 0.7362(8) | 0.3076(4) | 0.2581(8) |
| C(23) | 0.6964(8) | 0.3778(5) | 0.2927(8) |
| C(24) | 0.7827(9) | 0.4572(5) | 0.3216(8) |
| C(25) | 0.9003(8) | 0.4651(5) | 0.3147(8) |
| C(26) | 0.9396(7) | 0.3937(4) | 0.2801(7) |
| C(31) | 0.7970(6) | 0.1854(4) | 0.0093(7) |
| C(32) | 0.7906(7) | 0.1066(5) | -0.0522(8) |
| C(33) | 0.7099(8) | 0.0765(6) | -0.2009(9) |
| C(34) | 0.6060(7) | 0.1270(5) | -0.2899(8) |
| C(35) | 0.7258(6) | 0.2353(4) | -0.0773(7) |
| C(36) | 0.6435(7) | 0.2041(5) | -0.2281(8) |
| C(41) | 1.2376(6) | 0.2405(4) | -0.0077(7) |
| C(42) | 1.1731(7) | 0.1562(5) | -0.0735(9) |
| C(43) | 1.228(1) | 0.1110(6) | -0.145(1) |
| C(44) | 1.349(1) | 0.1490(7) | -0.145(1) |
| C(45) | 1.412(1) | 0.2286(6) | -0.080(1) |
| C(46) | 1.3591(8) | 0.2760(5) | -0.006(1) |
| C(51) | 1.0258(6) | 0.3185(4) | -0.0781(6) |
| C(52) | 0.9721(6) | 0.3834(4) | -0.0570(7) |
| C(53) | 0.8740(7) | 0.4057(5) | -0.1725(8) |
| C(54) | 0.8271(8) | 0.3608(5) | -0.3142(8) |
| C(55) | 0.8784(8) | 0.2959(6) | -0.3365(8) |
| C(56) | 0.9768(7) | 0.2741(5) | -0.2223(7) |
| C(61) | 1.2699(6) | 0.4045(4) | 0.1347(7) |
| C(62) | 1.3323(7) | 0.4437(4) | 0.2815(7) |
| C(63) | 1.4147(8) | 0.5229(5) | 0.3198(8) |
| C(64) | 1.4376(8) | 0.5641(5) | 0.213(1) |
| C(65) | 1.3763(8) | 0.5286(5) | 0.066(1) |
| C(66) | 1.2902(7) | 0.4476(4) | 0.0267(8) |

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 ($400\text{--}200\text{ cm}^{-1}$) were recorded as concentrated Nujol mulls between CsI plates. NMR spectra were recorded on a Bruker AM-400 spectrometer operating at 400 (^1H), 162 (^{31}P), 100 (^{13}C) or 61.4 (^2D) MHz. ^{19}F NMR spectra were recorded on a Jeol FX-90 instrument at 84.6 MHz. Melting points were determined on a Reichert microscope hot stage and are uncorrected. Elemental analyses for carbon, hydrogen and fluorine were performed by Professor A.D. Campbell and associates at the University of Otago and are gratefully acknowledged. $\text{Hg}(\text{CF}_3)_2$ [14], $\text{Cd}(\text{CF}_3)_2 \cdot \text{glyme}$ [23], $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ [24] and $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ [25] were prepared by published methods. Tetrafluoroethylene was produced by vacuum pyrolysis of polytetrafluoroethylene.

$\text{Ir}(\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (1)

(a) A solution of $\text{Hg}(\text{CF}_3)_2$ (800 mg, 2.3 mmol) and $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ (1 g, 0.1 mmol) in benzene (40 ml) was heated under reflux for 30 min. The yellow solution was then cooled to room temperature and filtered through Celite. Ethanol (50 ml) was added to the filtrate and the benzene removed at reduced pressure to give white crystals of the product (470 mg, 56%). M.p. $145\text{--}147^\circ\text{C}$. Anal. Found: C, 54.09; H, 3.83; F, 6.54. $\text{C}_{39}\text{H}_{30}\text{F}_3\text{IrO}_2\text{P}_2 \cdot \text{CH}_2\text{Cl}_2$ calcd.: C, 53.65; H, 3.53; F, 6.45%.

(b) A suspension of $\text{Ir}(\text{COCF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (3) (500 mg, 0.6 mmol) in benzene (20 ml) was heated until all the solid had dissolved (approximately 30 min) and the solution was then cooled to room temperature. Ethanol (30 ml) was added and the benzene removed under reduced pressure to give the product as white crystals (485 mg, 97%).

(c) A solution of $\text{Ir}(\text{CF}_2)(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (17) (100 mg, 0.1 mmol) in benzene (10 ml) to which one drop of water had been added, was heated for 30 min. Ethanol (20 ml) was then added and the benzene removed under reduced pressure to give the product as white crystals (55 mg, 57%).

(d) Carbon monoxide was bubbled through a solution of $\text{Ir}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (2) (100 mg, 0.12 mmol) in CH_2Cl_2 (10 ml) until the colour was discharged. Ethanol (30 ml) was added and the benzene removed under reduced pressure to give the product as white crystals (100 mg, 98%).

$\text{Ir}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (2)

An amorphous sample of $\text{Ir}(\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (1) (500 mg, 0.6 mmol) was prepared by subliming the solvent from a frozen solution of the compound. The sample was heated at $120\text{--}135^\circ\text{C}$ under dynamic vacuum for 48 h. During this time the colour of the solid changed from white to yellow. The compound was allowed to cool to room temperature and dissolved in oxygen free dichloromethane (15 ml). Ethanol (20 ml) was added and the dichloromethane removed at reduced pressure to give the product as yellow crystals (440 mg, 91%). M.p. $174\text{--}178^\circ\text{C}$. Anal. Found: C, 56.49; H, 4.30; F, 6.34. $\text{C}_{38}\text{H}_{30}\text{F}_3\text{IrOP}_2$ calcd.: C, 56.08; H, 3.72; F, 7.00%.

$\text{Ir}(\text{COCF}_3)(\text{CO})_2(\text{PPh}_3)_3$ (3)

A solution of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (1 g, 1.3 mmol) dissolved in THF (50 ml) was stirred with 1% sodium amalgam (5 ml) under carbon monoxide pressure (500 kPa)

in a Fischer-Porter bottle at 80 °C for 12 h. The mixture was then cooled and the carbon monoxide vented. The solution was transferred under nitrogen to another vessel and trifluoroacetic anhydride (0.2 ml, 1.4 mmol) was added with stirring. The solution was left a further 5 min before the solvent was removed in vacuo. The crude solid was extracted with dichloromethane (30 ml) and filtered to remove insoluble sodium salts. Ethanol (50 ml) was added to the filtrate and the dichloromethane removed under reduced pressure to give the product as a pale yellow crystalline solid (948 mg, 85%). M.p. 157–160 °C. Anal. Found: C, 54.91; H, 3.78; F, 6.79. $C_{40}H_{30}F_3IrO_3P_2$ calcd.: C, 55.23; H, 3.48; F, 6.55%.

Ir(CF₃)(C₂F₄)(CO)(PPh₃)₂ (4)

A solution of $Ir(CF_3)(CO)_2(PPh_3)_2$ (1) (500 mg, 0.6 mmol) in dry benzene (10 ml) was kept under tetrafluoroethylene pressure (500 kPa) at 90 °C for 72 h in a 20 ml Carius tube. The tube was cooled and opened, and the solution filtered. Ethanol (20 ml) was added and the dichloromethane removed under reduced pressure to give the product as white crystals (500 mg, 92%). M.p. 195–197 °C. Anal. Found: C, 53.49; H, 3.75; F, 14.22. $C_{40}H_{30}F_7IrOP_2$ calcd.: C, 52.57; H, 3.31; F, 14.55%.

IrCl₂(CF₃)(CO)(PPh₃)₂ (7)

To a solution of $Ir(CF_3)(CO)_2(PPh_3)_2$ (1) (100 mg, 0.12 mmol) in dichloromethane (10 ml) was added a solution of chlorine (0.15 mmol) in dichloromethane. The solution was stirred for 10 min then ethanol (20 ml) was added and the dichloromethane removed under reduced pressure to give the product as white crystals (90 mg, 92%). This was identified by comparison with an authentic sample.

IrHCl(CF₃)(CO)(PPh₃)₂ (9)

(a) $Ir(CF_3)(CO)_2(PPh_3)_2$ (1) (100 mg, 0.12 mmol) was dissolved in dichloromethane (10 ml) and HCl gas was bubbled through the solution for 2 s. Ethanol (20 ml) was added and the dichloromethane removed under reduced pressure to give the product as white crystals (93 mg, 92%). M.p. 230–233 °C. Anal. Found: C, 53.50; H, 4.08; F, 6.30. $C_{38}H_{31}ClF_3IrOP_2$ calcd.: C, 53.68; H, 3.68; F, 6.70%.

(b) $Ir(CF_2)(CF_3)(CO)(PPh_3)_2$ (17) (300 mg, 0.35 mmol) was stirred in dichloromethane (10 ml) and ethanol (10 ml) with two drops of aqueous HCl added. After 5 min, ethanol (20 ml) was added and the dichloromethane removed at reduced pressure to give the product as white crystals (250 mg, 85%).

cis-IrH₂(CF₃)(CO)(PPh₃)₂ (10)

Hydrogen was bubbled through a solution of $Ir(CF_3)(CO)(PPh_3)_2$ (2) (100 mg, 0.6 mmol) in dichloromethane (10 ml) until the colour had been completely discharged. Ethanol (20 ml) was added and the dichloromethane removed under reduced pressure to give the product as white crystals (87 mmol, 90%). M.p. 212–217 °C. Anal. Found: C, 53.25; H, 4.10; F, 6.69. $C_{38}H_{32}F_3IrOP_2 \cdot \frac{1}{2}CH_2Cl_2$ calcd.: C, 53.88; H, 3.88; F, 6.64%.

IrI(CH₃)(CF₃)(CO)(PPh₃)₂ (11)

(a) Iodomethane (1 ml, 11 mmol) was added to a solution of $Ir(CF_3)(CO)(PPh_3)_2$ (4) (100 mg, 0.12 mmol) in dichloromethane (15 ml) and the solution was stirred until the colour was completely discharged. Ethanol (20 ml) was added and the

dichloromethane removed at reduced pressure to give the products as white crystals (104 mg, 89%). M.p. 180–182°C. Anal. Found: C, 47.44; H, 3.27; F, 5.67. $C_{39}H_{33}F_3IrOP_2 \cdot CH_2Cl_2$ calcd.: C, 47.53; H, 3.43; F, 5.71%.

(b) Iodomethane (3 ml, 33 mmol) was added to a solution of $Ir(CF_3)(CO)_2(PPh_3)_2$ (1) (300 mg, 0.36 mmol) in dichloromethane (20 ml) and the mixture was stirred for three hours. Ethanol (20 ml) was added and the dichloromethane removed under reduced pressure to give the product as white crystals (249 mg, 73%).

[Ir(CH₃)(CF₃)(CH₃CN)(CO)(PPh₃)₂]ClO₄ (12)

To a solution of $Ir(CH_3)(CF_3)(CO)(PPh_3)_2$ (11) (100 mg, 0.1 mmol) in dichloromethane (15 ml) was added a solution of silver perchlorate (22 mg, 0.1 mmol) in acetonitrile and the mixture was stirred for 30 min. The mixture was filtered through Celite to remove the silver salts. Ethanol (20 ml) was added and the dichloromethane removed under reduced pressure to give the product as white crystals (76 mg, 79%). Anal. Found: C, 50.68; H, 4.49; N, 1.66; F, 5.39. $C_{41}H_{36}ClF_3IrNO_5P_2$ calcd.: C, 50.80; H, 3.74; N, 1.44; F, 5.88%.

*[Ir(CH₃)(CF₃)(CN-*p*-C₆H₄CH₃)(CO)(PPh₃)₂]ClO₄ (13)*

To a solution of $[Ir(CH_3)(CF_3)(CH_3CN)(CO)(PPh_3)_2]ClO_4$ (12) (100 mg, 0.1 mmol) in dichloromethane (15 ml) was added *p*-tolylisocyanide (12 mg, 0.1 mmol). The mixture was stirred for 30 min then ethanol (20 ml) was added and the dichloromethane removed under reduced pressure to give the product as white crystals (96 mg, 92%). Anal. Found: C, 54.19; H, 4.23; N, 1.72; F, 5.39. $C_{47}H_{40}ClF_3IrNO_5P_2$ calcd.: C, 53.00; H, 4.23; N, 1.72; F, 5.45%.

IrCl₂(CF₂H)(CO)(PPh₃)₂ (15)

(a) $IrCl(CF_2)(CO)(PPh_3)_2$ (16) (100 mg, 0.12 mmol) was dissolved in dry dichloromethane (10 ml) and HCl was bubbled through the solution for 2 s. Ethanol (20 ml) was added and the dichloromethane was removed under reduced pressure to give the product as white crystals (99 mg, 95%). This was identified by comparison with an authentic sample.

(b) To a solution of $Ir(CF_3)(CO)_2(PPh_3)_2$ (1) (200 mg, 0.24 mmol) in dry dichloromethane (10 ml) was added $AlCl_3$ (50 mg, 0.4 mmol). The mixture was stirred at room temperature for 30 min and then filtered. Ethanol (20 ml) was added and the dichloromethane removed at reduced pressure to give the product as white crystals (168 mg, 82%).

IrCl(CF₂)(CO)(PPh₃)₂ (16)

A suspension of $Ir(COCF_2Cl)(CO)_2(PPh_3)_2$ (18) (200 mg, 0.73 mmol) in benzene (10 ml) was heated to reflux, then cooled to room temperature and the solvent removed in vacuo. The solid was dissolved in dry dichloromethane (10 ml) and dry ethanol (20 ml) was added. The dichloromethane was removed under reduced pressure to give the product as pale yellow crystals (127 mg, 68%). M.p. 182–187°C. Anal. Found: C, 54.80; H, 4.14. $C_{38}H_{30}ClF_2IrOP_2$ calcd.: C, 54.97; H, 3.64%.

Ir(CF₂)(CF₃)(CO)(PPh₃)₂ (17)

(a) To a solution of $IrCl(CO)(PPh_3)_2$ (1 g, 1.2 mmol) in benzene (15 ml) was added $Cd(CF_3) \cdot glyme$ (1 g, 3 mmol). The mixture was then heated under reflux for

5 min then cooled, and the benzene removed in vacuo. The solid was extracted with dichloromethane (30 ml) and the extract filtered through Celite to remove the cadmium salts. Ethanol (30 ml) was added and the dichloromethane removed under reduced pressure to give the product as a pale yellow crystalline solid (936 mg, 87%). M.p. 153–156 °C. Anal. Found: C, 54.05; H, 3.87; F, 10.63. $C_{39}H_{30}IrOP_2F_5$ calcd.: C, 54.23; H, 3.50, F, 11.00%.

(b) To a solution of $Ir(CF_3)(CO)_2(PPh_3)_2$ (**1**) (150 mg, 0.18 mmol) in benzene (10 ml) was added $Cd(CF_3)_2 \cdot glyme$ (100 mg, 0.3 mmol). The mixture was refluxed for 5 min and then cooled. The solvent was removed in vacuo, and work-up was carried out as above to give the product (103 mg, 67%).

(c) To a solution of $Ir(CF_3)(CO)(PPh_3)_2$ (**2**) (100 mg, 0.12 mmol) in benzene (10 ml) was added $Cd(CF_3)_2 \cdot glyme$ (100 mg, 0.3 mmol). The mixture was refluxed for 5 min and then cooled. The solvent was removed in vacuo, and work-up as above gave the product (78 mg, 74%).

(d) To a solution of $IrCl(CF_2)(CO)(PPh_3)_2$ (**16**) (100 mg, 0.12 mmol) in benzene (10 ml) was added $Cd(CF_3)_2 \cdot glyme$ (100 mg, 0.3 mmol). The mixture was refluxed for 5 min and then cooled. The solvent was removed in vacuo, and work-up as above gave the product (87 mg, 84%).

Ir(COCF₂Cl)(CO)₂(PPh₃)₂ (18)

A solution of $IrCl(CO)(PPh_3)_2$ (500 mg, 0.64 mmol) in THF (30 ml) was stirred with 1% sodium amalgam (5 ml) under carbon monoxide pressure (500 kPa) in a Fischer–Porter bottle at 80 °C for 12 h. The mixture was then cooled and the carbon monoxide vented. The solution was transferred under nitrogen to another vessel and freshly distilled difluorochloroacetic anhydride (0.12 ml, 0.67 mmol) was added with stirring. The solution was left for a further 5 min and the solvent then removed in vacuo. The solid was extracted with dichloromethane (30 ml) and the extract filtered to remove insoluble sodium salts. Ethanol (50 ml) was added and the dichloromethane removed under reduced pressure to give the product as a pale yellow crystalline solid (440 mg, 78%). M.p. 197–202 °C. Anal. Found: C, 54.59; H, 4.08; F, 4.16. $C_{40}H_{30}ClF_2IrO_3P_2$ calcd.: C, 54.21; H, 3.41; F, 4.29%.

X-ray crystal structure determinations of Ir(CF₃)(C₂F₄)(CO)(PPh₃)₂ (4), IrI(CH₃)(CF₃)(CO)(PPh₃)₂ (11), and Ir(CF₂)(CF₃)(CO)(PPh₃)₂ (17)

Crystals suitable for data collection were mounted on glass fibres and positioned on an Enraf-Nonius CAD-4 diffractometer. Unit cell dimensions were derived from least squares fits to the observed setting angles of 25 reflections, using monochromated Mo- K_{α} ($\lambda = 0.71069 \text{ \AA}$) radiation. Crystal alignment and decomposition were monitored throughout data collection by measuring three standard reflections every 100 measurements. No non-statistical variation was observed. The data were corrected for Lorentz and polarisation effects and equivalent reflections were averaged. Absorption corrections were applied by the empirical azimuthal method [26]. Detail of crystal data and data collection and reduction parameters are summarised in Table 11.

The structures were solved by conventional Patterson and Fourier techniques and refined by full-matrix least squares. Atoms, other than phenyl carbons, were refined anisotropically. The fluorine atoms all show high thermal motion which may indicate some disorder in their position. Atomic scattering factors used were for

Table 11

Crystal data, data collection and refinement parameters

| Atom | $\text{Ir}(\text{CF}_3)_2\text{C}_2\text{F}_4(\text{CO})(\text{PPh}_3)_2$ (4) | $\text{Ir}(\text{CH}_3)_2\text{CF}_3(\text{CO})(\text{PPh}_3)_2$ (11) | $\text{Ir}(\text{CF}_3)_2\text{CF}_2(\text{CO})(\text{PPh}_3)_2$ (17) |
|---|---|---|---|
| <i>Crystal data</i> | | | |
| formula | $\text{C}_{40}\text{H}_{30}\text{F}_7\text{IrOP}_2$ | $\text{C}_{39}\text{H}_{33}\text{F}_3\text{IrOP}_2$ | $\text{C}_{39}\text{H}_{30}\text{F}_5\text{IrOP}_2$ |
| molecular weight/g mol ⁻¹ | 913.81 | 955.76 | 863.82 |
| space group | $P2_1/c$ | $Pbca$ | $P\bar{1}$ |
| cryst system | monoclinic | orthorhombic | triclinic |
| $a/\text{Å}$ | 18.919(5) | 12.511(2) | 11.491(1) |
| $b/\text{Å}$ | 10.548(2) | 18.485(2) | 16.530(3) |
| $c/\text{Å}$ | 35.807(9) | 35.553(5) | 9.971(1) |
| $\alpha/^\circ$ | | | 93.04(1) |
| $\beta/^\circ$ | | | 113.33(1) |
| $\gamma/^\circ$ | | | 101.94(1) |
| $V/\text{Å}^3$ | 7029.3 | 8223.2 | 1682.2 |
| Z | 8 | 8 | 2 |
| $d(\text{calcd})/\text{g cm}^{-3}$ | 1.727 | 1.544 | 1.557 |
| $F(000)$ | 3584 | 3698 | 848 |
| μ/cm^{-1} | 41.9 | 43.2 | 39.9 |
| <i>Data collection and reduction</i> | | | |
| diffractometer | Enraf-Nonius Cad-4 | Enraf-Nonius Cad-4 | Enraf-Nonius Cad-4 |
| radiation | $\text{Mo-K}\alpha$ (λ 0.71069 Å) | $\text{Mo-K}\alpha$ (λ 0.71069 Å) | $\text{Mo-K}\alpha$ (λ 0.71069 Å) |
| temperature/K | 294–296 | 294–296 | 294–296 |
| scan technique | $2\theta/\omega$ | $2\theta/\omega$ | $2\theta/\omega$ |
| $2\theta(\text{min-max})/^\circ$ | 2–50 | 2–50 | 2–42 |
| scan speed $^\circ$ min ⁻¹ | 2–30 | 2–30 | 2–30 |
| no. unique obsd. reflections | 3456 | 2224 | 4708 |
| σ criterion | 3.0 | 3.0 | 3.0 |
| <i>Structure determination and refinement</i> | | | |
| R and R_w ^a | 0.074, 0.076 | 0.058, 0.062 | 0.035, 0.037 |
| weight | $0.9829/(\sigma^2(F) + 0.008331F^2)$ | $0.8185/(\sigma^2(F) + 0.004402F^2)$ | $0.6341/(\sigma^2(F) + 0.002381F^2)$ |

$$^a R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|; R_w = [\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega|F_o|^2]^{1/2}.$$

neutral atoms and final residuals are given in Table 11. Computing was carried out using the SDP suite of programmes on a PDP-11 computer for initial data processing, and SHELX-76 on an IBM 4341 computer for structure solution and refinement.

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