Synthesis and characterisation of some iridium-carbonyl-fluoride complexes. Crystal structures of $[IrF(CO)\{P(C_6H_4\text{-}2\text{-}CH_3)_3\}_2]$ and $[IrF_2(COD)py_2][BF_4]$†

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Received 3rd March 2010, Accepted 16th April 2010
First published as an Advance Article on the web 25th May 2010
DOI: 10.1039/c0dt00066c

Two routes to iridium(III) fluorocomplexes are described. The direct reaction of tetrairidium dodecacarbonyl with elemental fluorine in aHF offers a clean, convenient, large scale route to $[IrF_3(CO)_3]$; addition of phosphines to $[IrF_3(CO)_3]$ in THF affords *mer*-$[IrF_3(CO)L_2]$ or $[IrF(CO)L_2]$. Alternatively, cationic $[IrF_2(COD)L_2]^+$ and $[IrF_2(CO)_2L_2]^+$ (L = phosphine, pyridine; $L_2 = \alpha$-diimine) are accessible *via* the oxidation of the iridium(I) precursors with xenon difluoride.

Introduction

Although the number of coordination or organometallic complexes of the platinum group metals with fluoride ligands is much smaller than those containing the heavier halides, the synthetic challenges and potential applications, such as in aryl-F bond formation, of such metal fluoride complexes have resulted in growing interest in this field. Recent notable examples include palladium(II) {*trans*-$[PdF_2py_2]$,[1] $[PdF_2(t\text{-Bubpy})]$[2] and $[PdF(4\text{-}C_6H_4F)(t\text{-Bubpy})]$[3]} and platinum(II) {$[PtF_2(PR_3)_2]$[4,5]} complexes prepared by halide exchange with AgF, ruthenium(II) {$[Ru_2(\mu\text{-}F)_3(PEt_3)_6]^+$[6]} and rhodium(I) {$[RhF(PR_3)_3]$[7,8]} complexes prepared by protonation with TREAT-HF, the iridium(I) species {$[IrF(PPh_3)(COD)]$[9]} formed by protonation with HF, and the platinum(IV) complex {$[PtF_2(Ph)_2(PPh_3)_2]$[5]} and the palladium(IV) complexes {$[PdF_2$(benzoquinolinyl)(pyridyl-sulfonamide)$]$[10] and $[PdF_2(FHF)(4\text{-}C_6H_4F)(t\text{-Bubpy})]$[3]} prepared by oxidation with XeF_2.

In comparison, however, relatively few Ir(III) fluorocomplexes have been reported. Sporadic reports on the oxidative addition chemistry of *trans*-$[IrF(CO)(PPh_3)_2]$ have afforded a modest number of such species,[11,12] the oxidative addition of NSF_3, SF_4, SeF_4 or TeF_4 to $[IrCl(CO)(PEt_3)_2]$ generates a number of iridium(III) monofluorides,[13,14] the related $[IrF(COF)(CO)_2(PEt_3)_2][BF_4]$ is formed in the reaction of XeF_2 with the iridium(I) salt $[Ir(CO)_3(PEt_3)_2][BF_4]$[15] and $[Ir(H)_2F(P^tBu_2Ph)_2]$,[16] $[Ir(H)(F)(bq\text{-}NH_2)(PPh_3)_2]$,[17] $[Ir(F)(Cp^*)(Ph)(PMe_3)]$[18] and $[Ir(F)(Cp^*)(Rf)(PMe_3)]$ {Rf = CF_3, CF_2CF_3, $CF_2CF_2CF_3$, $CF(CF_3)_2$, $CF(CF_3)(CF_2CF_3)$}[19] have been reported more recently. Herein, we describe two strategies for the synthesis of iridium(III) centres with more than one fluoride ligand. Route 1 extends our synthetic strategy[20] for the synthesis of ruthenium and osmium ternary fluorides, whereby the fluorine originates from the metal complex not from any additional fluorine-containing reagent, to *mer*-$[IrF_3(CO)L_2]$, including an improved synthesis of $[IrF_3(CO)_3]$ (**1**). Route 2 extends the brief report of the synthesis of $[IrF_2(dppe)_2]^+[BF_4]^-$,[11] generated by the low temperature oxidation of $[Ir(dppe)_2]^+[BF_4]^-$ with XeF_2 in DCM, to a range of iridium(III) difluorocations.

Results and discussion

Previously, $[IrF_3(CO)_3]$ (**1**) had been prepared by us by the low temperature oxidation of tetrairidium dodecacarbonyl with xenon difluoride in anhydrous HF,[21] but (**1**) is sensitive to over oxidation in the presence of excess XeF_2 and this is not a particularly attractive synthetic route since it generates large volumes of waste xenon. We have now found that (**1**) can be prepared on a large scale (5–10 g) using elemental fluorine as the oxidant for $Ir_4(CO)_{12}$ in HF solution by adapting our previously described procedure for the synthesis of $[MF_2(CO)_3]_4$ (M = Ru, Os).[22] It is straightforward to monitor the oxidation tensimetrically through the uptake of fluorine gas, since there are no side products generated, and to establish when the reaction is finished since, at room temperature in aHF, (**1**) is stable to further reaction even under prolonged (weeks) exposure to fluorine gas.

On reaction of (**1**) with two equivalents of triphenylphosphine in dry thf carbon monoxide is evolved and the new air-sensitive iridium(III) carbonyl phosphine fluoride complex, *mer*-$[IrF_3(CO)(PPh_3)_2]$ (**2**) is formed in high yield. The complex is readily characterised in solution by NMR spectroscopy: The ^{19}F NMR spectrum consists of two mutually-coupled resonances, a doublet of triplets at δ –451.2 and a lower field triplet of triplets at δ –280.9. The high field resonance is typical of an F-*trans*-F interaction across Ir(III)[13,21] and is, therefore, assigned to the two *trans* fluorines (F_A; Scheme 1). The remaining resonance is typical of an F-*trans*-CO moiety across Ir(III) (F_B).[15,21,23,24] The $^{31}P\{^1H\}$ NMR spectrum exhibited a doublet of triplets at δ –5.9 which exhibited mutual coupling to the resonances in the ^{19}F NMR spectrum. Comparable *in situ* spectroscopic data (Table 1) were obtained for the products *mer*-$[IrF_3(CO)(PR_3)_2]$ {PR_3 = PMe_3 (**3**), PEt_3 (**4**), PMe_2Ph (**5**), $PMePh_2$ (**6**), $PEtPh_2$ (**7**), PCy_3 (**8**)} from the reaction of (**1**) with a range of other monodentate ligands (Scheme 1). In contrast to our previously reported air- and moisture-stable ruthenium(II) and osmium(II) carbonyl phosphine fluoride complexes,[20] these iridium(III) complexes are extremely

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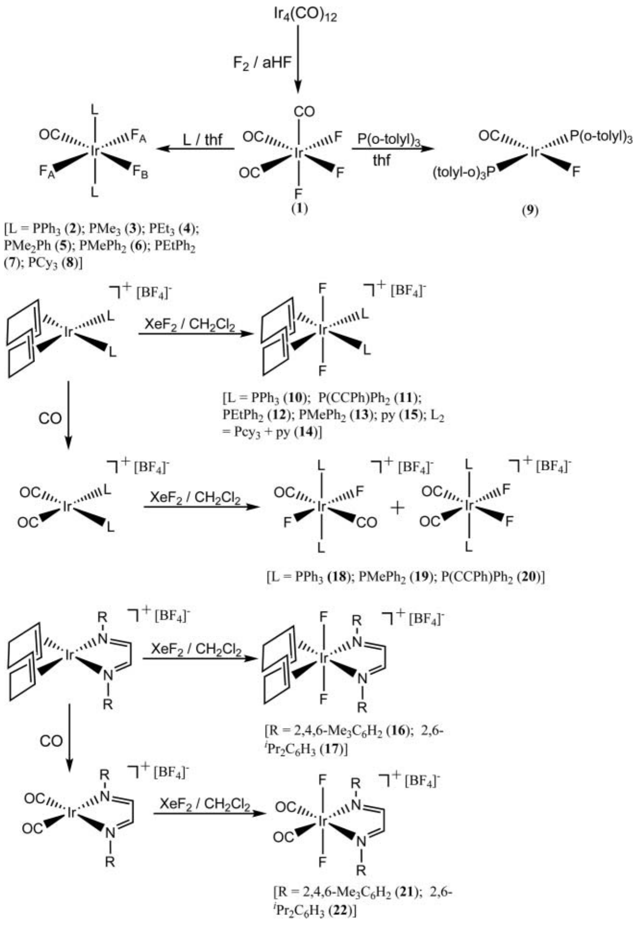
† CCDC reference numbers 720281 and 720282. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00066c

Table 1 ^{19}F and ^{31}P{^{1}H} NMR data for *mer*-[$IrF_3(CO)L_2$]

L	$\delta(F_A)^a$/ ppm	$\delta(F_B)^b$/ ppm	δ(P)/ ppm	$^2J(F_AF_B)$/ Hz	$^2J(PF_A)$/ Hz	$^2J(PF_B)$/ Hz
PPh_3	−451.2	−280.9	−5.9	97	20	29
PMe_3	−470.6	−285.0	−12.0	97	23	38
PEt_3	−470.1	−286.8	−8.6	99	21	31
$PMePh_2$	−460.2	−283.9	−9.5	99	20	36
$PEtPh_2$	−454.6	−282.0	−1.4	101	19	32
PMe_2Ph	−463.2	−280.6	−11.9	98	22	37
Pcy_3	−458.4	−281.1	−7.4	98	14	27

[a] F-*trans*-F. [b] F-*trans*-CO.



Scheme 1

air- and moisture-sensitive. In addition, although these complexes are stable in thf, even in the presence of excess ligand, on the addition of chlorinated solvents, there is rapid decomposition with the generation of a number of iridium-fluoride-phosphine species. It is tempting to presume that these products arise from halide exchange with the solvent, as reported previously for iridium(III) carbonyl phosphine fluoride complexes,[13] but these decomposition reactions were never reproducible and we were unable to definitively identify the reaction products.

In contrast to the synthesis of (**2–8**), reaction between [$IrF_3(CO)_3$] and bulky phosphines {*e.g.* trisnaphthylphosphine or tris-*o*-tolylphosphine} did not afford *mer*-[$IrF_3(CO)_2L_2$]. For trisnaphthylphosphine, the starting materials were recovered unchanged. For tris-*o*-tolylphosphine, NMR experiments on the crude reaction mixture reveal a doublet at δ 26.2 and a mutually-coupled triplet in the ^{19}F NMR spectrum at δ −253.2 that indicate reduction of the iridium(III) centre and formation of *trans*-[$IrF(CO)\{P(C_6H_4\text{-}2\text{-}CH_3)_3\}_2$] (**9**). In addition, resonances in the NMR spectra that can be assigned to tris-*o*-tolylphosphineoxide and HF that arise from oxidation of the ligand and reaction with adventitious water. The phosphine oxide is readily removed by recrystallization from methanol. It is assumed that the steric demands made by the bulkier $P(C_6H_4\text{-}2\text{-}CH_3)_3$ prevent formation of the expected Ir(III) complex. Confirmation of this assignment comes from a single crystal structure determination; the molecular structure and selected bond distances and angles are shown in Fig. 1. The geometry around the metal centre is approximately square planar, with little deviation from ideality [C(1)–Ir(1)–P(1) 87.89(6)°]. There is scrambling between the F and CO sites. The disorder could not be resolved and the data was modelled to give Ir–F = 2.028(9) Å and Ir–C = 1.749(15) Å distances. Similar X/CO disorder has been observed previously in the related complex *trans*-[$IrCl(CO)\{P(C_6H_4\text{-}2\text{-}CH_3)_3\}_2$].[25]

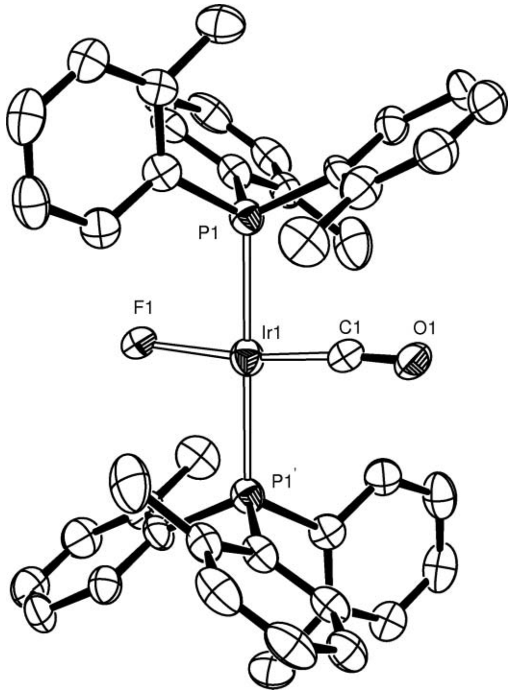


Fig. 1 Molecular structure of (**9**) with 50% displacement ellipsoids. H atoms are omitted for clarity. The Ir atom is located on a centre of symmetry and primed atoms are generated by 1–x, 1–y, –z. The CO and F sites indicate 50 : 50 disorder of these positions. The disordered site of the C1 and F1 could not be resolved and was modelled. The disorder is assumed from the oxidation state of the Ir and the electron density of the C/F site with respect to the carbonyl oxygen site (~2 : 1). Ir(1)–F(1), 2.028(9), Ir(1)–P(1), 2.3334(17), Ir(1)–C(1), 1.749(15), C(1)–O(1), 1.156(15), C(1)–Ir(1)–P(1), 93.6(16), P(1)–Ir(1)–F(1), 86.1(6).

An alternative route to iridium(III) fluorides is oxidation. A series of [$Ir(COD)L_2]^+[BF_4]^-$ complexes (L = PPh_3, PPh_2CCPh, PPh_2Et) have been prepared following a literature procedure.[26] The addition of one aliquot of XeF_2 to deep red solutions of these species in dry dichloromethane, even at −80 °C, liberated xenon gas and the solutions changed to a pale straw yellow colour. The colour change was sufficiently dramatic that it was possible to

Table 2 Selected ^{19}F and ^{31}P NMR data for iridium difluoride cations

	trans-,cis-$[IrF_2L_2(COD)]^+$			*trans*-$[IrF_2L_2(CO)_2]^+$			*cis-,trans*-$[IrF_2L_2(CO)_2]^+$		
L	δ(F)/ppm	δ(P)/ppm	^2J(PF)/Hz	δ(F)/ppm	δ(P)/ppm	^2J(PF)/Hz	δ(F)/ppm	δ(P)/ppm	^2J(PF)/Hz
PPh_3	−501.0	−28.1	12	−508.0	−12.6	18	−343.3	−3.3	31
PPh_2CCPh	−491.1	−31.0	21	−514.1	−25.3	—	−331.2	5.2	32
$PMePh_2$	−496.5	−28.2	18	−510.6	−33.0	—	−304.0	−19.9	38
$PEtPh_2$	−483.4	−11.7	15						
py	−378.5	—	—						
L_2									
py/PCy_3	−448.3	−10.3	14						
RNCHCHNR[a]	−433.4	—	—	−460.0	—	—			
RNCHCHNR[b]	−427.6	—	—	−456.5	—	—			

[a] R = 2,4,6-$Me_3C_6H_2$. [b] R = 2,6-$^iPr_2C_6H_3$.

judge accurately the end point of the reaction by sequentially subliming small aliquots of XeF_2 into the solutions. Confirmation of the identities of the products was obtained by multinuclear NMR spectroscopic studies, recorded at −60 °C, which revealed mutually-coupled triplets in both the ^{19}F and ^{31}P spectra (Table 2). The ^{19}F NMR resonances, at *ca.* δ −500, are in the region diagnostic of F-*trans*-F on iridium(III) centres,[13,21] which confirm the formulation of the products as *trans-,cis*-$[IrF_2L_2(COD)]^+[BF_4]^-$ (**10–12**; Scheme 1). As expected for such a conformation, the four olefinic resonances on the COD ligand are equivalent, but at *ca.* δ 5.6 are substantially shifted from those for the iridium(I) starting materials (*ca.* δ 4.2) in line with the greater Lewis acidity of the iridium(III) metal centre. Extremely air- and moisture-sensitive orange solids were obtained on removal of the solvent, which were further characterised by mass spectrometry, infrared spectroscopy and, for selected examples, elemental analysis. Unfortunately, the products were also temperature sensitive and decomposed rapidly in the solid state or in solution above −60 °C. In marked contrast, no colour change occurred on the addition of XeF_2 to a solution of $[Ir(COD)(PPh_2Me)_2]^+[BF_4]^-$ at low temperature and NMR spectra revealed only resonances associated with the starting materials. However, slow reaction did occur at room temperature, with xenon evolution, and the NMR spectra for the product, *trans-,cis*-$[IrF_2(PPh_2Me)_2(COD)]^+[BF_4]^-$ (**13**) (Table 2), were comparable to those obtained for the other iridium(III) cations, whilst the orange product, was thermally stable and could be stored at room temperature without evidence of decomposition. The reason for the anomalous behaviour in this particular reaction is unclear, but others have reported the resistance of complexes incorporating the PPh_2Me ligand to undergo oxidation with XeF_2.[23]

Similarly, oxidation of the pyridine-substituted iridium(I) cations {$[Ir(py)(PCy_3)(COD)]^+[BF_4]^-$, and $[Ir(py)_2(COD)]^+[BF_4]^-$} with XeF_2 afforded the analogous *trans-,cis*-$[IrF_2(py)(PCy_3)(COD)]^+[BF_4]^-$ (**14**) and $[IrF_2(py)_2(COD)]^+[BF_4]^-$ (**15**), which were characterised by multinuclear NMR (Table 2), mass spectrometry and elemental analysis. For the former, inequivalence of the olefinic COD protons is clearly evident in two 2H multiplets in the ^{1}H NMR spectrum, whilst the high frequency shift in the ^{19}F NMR resonances (δ −448 and −378 respectively) reflect the changes observed between phosphorus- and nitrogen-donors in $[RuF_2(CO)_2L_2]$ complexes.[20] Single crystals of $[IrF_2(py)_2(COD)]^+[BF_4]^-$ (**15**) suitable for structural characterisation were grown by slow diffusion of hexane into a saturated dichloromethane solution at 0 °C; the molecular structure, which confirms the geometry suggested from the spectroscopic data, in particular the F-*trans*-F arrangement, is shown in Fig. 2 and selected bond lengths and bond angles are reported in Table 3. This represents the first structurally characterised iridium complex containing two fluoride ligands and only the second structurally characterised iridium-COD fluoride complex.[9] The Ir–F bond lengths (2.003(6) Å) are towards the lower end of the range of reported Ir(III)–F bond lengths {1.998(3)[15] to 2.143(4)[17] Å}, consistent with the presence

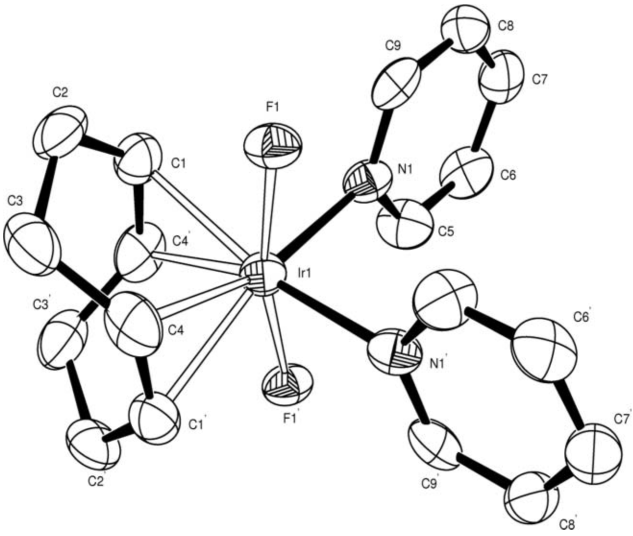


Fig. 2 Molecular structure of the cation of (**15**) with 50% displacement ellipsoids. H-atoms and the counter-ion (BF_4^-) are omitted for clarity. Symmetry transformation used to generate equivalent atoms: −x+1/2, y, −z.

Table 3 Selected bond lengths (Å) and angles (°) for bis(pyridine)(cycloocta-1,5-diene)iridiumdifluoride tetrafluoroborate, $[IrF_2py_2(COD)][BF_4]$, (**15**)

Ir(1)–F(1)	2.003(6)	F(1)–Ir(1)–F(1′)	167.0(3)
Ir(1)–N(1)	2.124(9)	F(1)–Ir(1)–N(1)	85.7(3)
Ir(1)–C(4)	2.237(11)	N(1)–Ir(1)–N(1′)	88.6(4)
Ir(1)–C(1)	2.242(11)	F(1)–Ir(1)–C(4)	75.8(4)
N(1)–C(9)	1.303(14)	F(1)–Ir(1)–C(1)	77.4(4)
N(1)–C(5)	1.344(14)	C(5)–N(1)–Ir(1)	120.0(8)
		C(9)–N(1)–Ir(1)	119.7(8)

of two fluoride ligands and a cationic metal centre. However, the Ir–C distances associated with the coordinated COD ligand are unusually long (2.240 Å) in comparison with those for the parent iridium(I) COD cation (2.120 Å)[26] or the recently characterised [IrF(PPh_3)(COD)] (2.135 Å).[9]

In a parallel study, we have prepared a couple of iridium(I) α-diimine cationic complexes, *e.g.* [Ir(COD)(RN=CH–CH=NR)]$^+$[BF_4]$^-$ { R = 2,4,6-$Me_3C_6H_2$, 2,6-$^iPr_2C_6H_3$},[27] and these can similarly be oxidised with XeF_2 in solution to afford [IrF_2(COD)(RN=CH-CH=NR)]$^+$[BF_4]$^-$ (**16**,**17**; Scheme 1), which have been characterised by multinuclear NMR spectroscopy, mass spectrometry and elemental analysis. These are room temperature stable examples of this group of difluoroiridium(III) cations and the first α-diimine metal fluoride complexes. These species have ν_{CN} stretches shifted to slightly lower frequencies than those for the starting materials in keeping with the change in oxidation state of the metal. The low frequency ^{19}F NMR resonances for these complexes (Table 2) are diagnostic of the F-*trans*-F arrangement on iridium(III) centres and are observed at an intermediate field between those for [$IrF_2(py)_2$(COD)]$^+$ and [$IrF_2(phosphine)_2$(COD)]$^+$.

The potential applicability of these COD-derivatised iridium(III) difluorocations is severely restricted by their limited stability. It has been noted previously[11] that the presence of Lewis acidic co-ligands tends to increase the stability of the M-F bond and, indeed, the majority of late transition metal fluoride complexes contain CO or NO co-ligands. Displacement of COD by CO in the iridium(I) starting materials described above is facile and the resulting complexes [$Ir(CO)_2L_2$]$^+$[BF_4]$^-$ (L = PPh_3, PPh_2Me, PPh_2CCPh; L_2 = RN=CH-CH=NR {R = 2,4,6-$Me_3C_6H_2$, 2,6-$^iPr_2C_6H_3$})[27,28] could be similarly oxidised with XeF_2 in dichloromethane at −80 °C. Significantly, in line with our intentions, the products are stable in the solid state at room temperature. Unfortunately, for the monodentate phosphine complexes, the stereochemical rigidity of the COD-complexes is lost such that the desired iridium(III) difluoride complexes were formed as approximately 1 : 1 mixtures of the all-*trans* and *cis*-difluoride complexes [$IrF_2(CO)_2L_2$]$^+$[BF_4]$^-$ (**18–20**) (Scheme 1; Table 2). For the all-*trans* isomers, the ^{19}F NMR resonances occur at substantially lower frequencies and the $^2J_{PF}$ coupling constants are larger than those for the *cis*-difluoride isomers, as expected for the F-*trans*-F and F-*cis*-F arrangements.[13,21–24] In the oxidations of the α-diimine complexes, the corresponding iridium(III) difluoride cations are formed as the single F-*trans*-F isomers, *trans*-,*cis*-[$IrF_2(CO)_2$(L-L)]$^+$[BF_4]$^-$ (**21**,**22**) (Scheme 1; Table 2), for which the shifts in δ_F to low frequency, in comparison to those for the related COD-complexes, mirror those for the related pairs of monodentate phosphine complexes.

Conclusions

Tricarbonyliridium trifluoride, readily prepared by the treatment of [$Ir_4(CO)_{12}$] in aHF with elemental fluorine, is a convenient reagent for iridium(III) fluorine chemistry. Reaction with phosphines affords highly reactive *mer*-[$IrF_3(CO)L_2$] or *trans*-[$IrF(CO)L_2$]. Alternatively, a range of cationic [$IrF_2(COD)L_2$]$^+$, [IrF_2(COD)(L-L)]$^+$, [$IrF_2(CO)_2L_2$]$^+$ or [$IrF_2(CO)_2$(L-L)]$^+$ can be prepared by reaction of iridium(I) precursors with XeF_2. Although the COD-derivatised complexes have limited solution and solid-state stability, the CO-derivatised species can be stored in the solid-state at room temperature. Throughout, these iridium fluoride complexes reveal highly diagnostic very low frequency resonances in their ^{19}F NMR spectra.

Experimental

General remarks

All reactions, unless otherwise stated, were carried out under an atmosphere of dry, oxygen-freed nitrogen, using standard Schlenk line or metal vacuum line techniques or in a nitrogen purged dry box. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use.[29] ^1H, ^{19}F and ^{31}P NMR spectroscopies were carried out on a Bruker DPX300 spectrometer at 300.14, 282.41 and 121.50 MHz respectively or a Bruker DRX400 spectrometer at 400.13, 376.46 and 161.98 MHz respectively and were referenced to external $SiMe_4$ (^1H), external $CFCl_3$ (^{19}F) and to external H_3PO_4 (^{31}P) using the high frequency positive convention. Spectra were recorded at −60 °C, unless otherwise stated. Abbreviations for NMR spectral multiplicities are as follows: *s* = singlet, *d* = doublet, *m* = multiplet. *J* values are given in Hz. Elemental analyses were performed by the Elemental Analysis Service at the University of North London. Mass spectra were recorded on a Kratos Concept 1H mass spectrometer. IR spectra were recorded as solid samples on a Perkin Elmer Spectrum One FT-IR spectrometer.

Syntheses. *fac*-Iridiumtricarbonyltrifluoride (**1**)[21]. Tetrairidiumdodecacarbonyl (1 g, 0.9 mmol) was dissolved in aHF (2 cm^3) in a 10 mm O.D., 1.5 mm wall thickness pre-passivated FEP vessel fitted with a PTFE valve. Aliquots of elemental fluorine were metered into the reaction vessel, to a total pressure of 2 atm, whilst cooling the solution to −78 °C. After each addition, the reaction mixture was allowed to warm to room temperature and stirred for 16 h. The reaction was judged to have finished when fluorine stopped being consumed. The solvent was then removed *in vacuo* and to give the product as a yellow solid (0.290 g, 96%), which was stored in pre-passivated FEP containers in a dry box.

Bis(triphenylphosphine)carbonyliridiumtrifluoride (**2**). Triphenylphosphine (126 mg, 0.48 mmol) and *fac*-[$IrF_3(CO)_3$] (75 mg, 0.23 mmol) were stirred in dry thf (50 cm^3) under nitrogen for 16 h. The solvent was removed *in vacuo* and the resulting powder recrystallized from methanol to give the product as an air-sensitive yellow powder (110 mg, 60%). Found: C, 55.6; H, 3.9. Calc. for $C_{37}H_{30}F_3IrOP_2$: C, 55.4; H, 3.75%. ν_{max}/cm^{-1} 3924br, 3053br, 2966br, 2011 s, 1479 s, 1432 s, 1262 s, 1094 s, 797 s, 744 s, 685s. δ_H ($CDCl_3$) 7.40-7.20 (30H, m, Ph). δ_F ($CDCl_3$) −451.2 (dt, $^2J_{FF}$ 97, $^2J_{PF}$ 20, Ir*F*-*trans*-F), −280.9 (tt, $^2J_{FF}$ 97, $^2J_{PF}$ 29, Ir*F*-*trans*-CO). δ_P ($CDCl_3$) −5.9 (dt, $^2J_{PF}$ 29, $^2J_{PF}$ 20, IrP_2).

The other iridium(III) complexes (**3–8**) were prepared similarly but not isolated and their NMR spectra recorded (Table 1).

Bis{tris(*o*-tolyl)phosphine}carbonyliridiumfluoride (**9**) was prepared similarly and obtained as an air-sensitive yellow solid (68 mg, 35%). *m*/*z* (FAB) 848 ([M]$^+$), 829 ([M-F]$^+$). ν_{max}/cm^{-1} 1936 s, 1561br, 1443br, 1273br, 1029 m, 747 s, 713s. δ_H (C_6D_6) 8.20 (3H, m, Ph), 7.20-7.08 (9H, m, Ph), 2.63 (9H, s, C*H*$_3$). δ_F (C_6D_6) −253.2 (t,$^2J_{PF}$ 36, Ir*F*). δ_P (C_6D_6) 26.2 (d, $^2J_{PF}$ 36, IrP_2).

Bis(triphenylphosphine)(cyclo-octa-1,5-diene)iridiumdifluoride tetrafluoroborate (**10**). [$Ir(PPh_3)_2$(COD)][BF_4] (50 mg, 0.055 mmol) and XeF_2 (13 mg, 0.076 mmol) were loaded into separate, passivated, FEP reaction vessels (4 mm O.D., 3 mm I.D.) linked *via* a T-union (PTFE, Production Techniques Ltd) in a dry box and connected to an all-metal vacuum line *via* a PTFE valve. The apparatus was evacuated, dichloromethane transferred onto the solids by distillation at −196 °C and the vessels warmed to ensure complete dissolution of the solids. The solution of the iridium salt was refrozen at −196 °C and the XeF_2 solution added in a single aliquot. On warming, ca −80 °C, with agitation and occasional venting to remove xenon gas, the solutions mixed and the red solution slowly turned yellow. Once the reaction was deemed complete, either the FEP vessel was heat-sealed for NMR investigations (at −60 °C) or the solvent removed *in vacuo* to leave the product as an air- and temperature-sensitive yellow powder in quantitative yield (52 mg). Found: C, 52.6; H, 4.0. Calc. for $C_{44}H_{42}BF_6IrP_2{\cdot}CH_2Cl_2$: C, 52.2; H, 4.3%. *m/z* (FAB) 755 ([M-COD-BF$_4$]$^+$). ν_{max}/cm^{-1} 3059br, 1483 s, 1432 s, 1048vs, 747 s, 688s. δ_H (CD_2Cl_2) 7.60-7.10 (30H, m, Ph), 5.65 (4H, br s, COD-CH), 2.40 (4H, m, COD-CH_2), 2.15 (4H, m, COD-CH_2). δ_F (CD_2Cl_2) −153.0 (s, $[BF_4]^-$), −501.0 (t, $^2J_{PF}$ 12, IrF_2). δ_P (CD_2Cl_2) −28.1 (t, $^2J_{PF}$ 12, IrP_2).

The other iridium difluorocations (**11–22**) were prepared similarly in quantitative yields.

Bis(phenylethynyldiphenylphosphine)(cyclo-octa-1,5-diene)-iridiumdifluoride tetrafluoroborate (**11**) as an orange powder. Found: C, 57.55; H, 4.4. Calc. for $C_{48}H_{42}BF_6IrP_2$: C, 57.8; H, 4.2%. *m/z* (FAB) 911 ([M-BF$_4$]$^+$), 803 ([M-COD-BF$_4$]$^+$). ν_{max}/cm^{-1} 3095 s, 2941w, 2174 s, 1480 s, 1438 s, 1040vs, 752 s, 688s. δ_H (CD_2Cl_2) 7.80-7.20 (30H, m, Ph), 5.67 (4H, br s, COD-CH), 2.50 (4H, m, COD-CH_2), 2.32 (4H, m, COD-CH_2). δ_F (CD_2Cl_2) −152.1 (s, $[BF_4]^-$), −491.1 (t, $^2J_{PF}$ 21 Hz, IrF_2). δ_P (CD_2Cl_2) −31.0 (t, $^2J_{PF}$ 21, IrP_2).

Bis(ethyldiphenylphosphine)(cyclo-octa-1,5-diene)iridiumdifluoride tetrafluoroborate (**12**) as a yellow powder. *m/z* (FAB) 659 ([M-COD-BF$_4$]$^+$). ν_{max}/cm^{-1} 2941w, 1483w, 1432 s, 1025vs, 742 s, 691s. δ_H (CD_2Cl_2) 7.70-7.10 (20H, m, Ph), 5.76 (4H, br s, COD-CH), 2.48 (4H, m, COD-CH_2), 2.26 (4H, m, COD-CH_2). δ_F (CD_2Cl_2) −151.1 (s, $[BF_4]^-$), −483.4 (t, $^2J_{PF}$ 15, IrF_2). δ_P (CD_2Cl_2) −11.7 (t, $^2J_{PF}$ 15, IrP_2).

Bis(methyldiphenylphosphine)(cyclo-octa-1,5-diene)iridiumdifluoride tetrafluoroborate (**13**) was prepared as a yellow powder on reaction at room temperature. Found: C, 49.4; H, 4.7. Calc. for $C_{34}H_{38}BF_6IrP_2$: C, 49.45; H, 4.6%. *m/z* (FAB) 739 ([M-BF$_4$]$^+$), 631 ([M-COD-BF$_4$]$^+$). ν_{max}/cm^{-1} 3048br, 1477 s, 1432 s, 1046vs, 741 s, 691s. δ_H (CD_2Cl_2) 7.90-7.10 (20H, m, Ph), 5.74 (4H, br s, COD-CH), 2.50-2.10 (11H, m, COD-CH_2 and CH_3). δ_F (CD_2Cl_2) −152.1 (s, $[BF_4]^-$), −496.5 (t, $^2J_{PF}$ 18, IrF_2). δ_P (CD_2Cl_2) −28.2 (t, $^2J_{PF}$ 18, IrP_2).

Pyridine(tricyclohexylphosphine)(cyclo-octa-1,5-diene)iridiumdifluoride tetrafluoroborate (**14**) as an orange solid. *m/z* (FAB) 698 ([M-BF$_4$]$^+$), 599 ([M-py-HF-BF$_4$]$^+$). ν_{max}/cm^{-1} 2924br, 2852br, 1449 s, 1039vs, 763br, 699br. δ_H (CD_2Cl_2) 9.24 (2H, s, NCHCH), 8.19 (1H, t, $^3J_{HH}$ 14, 4-CH), 7.85 (2H, m, NCH), 6.38 (2H, br s, COD-CH), 5.69 (2H, br s, COD-CH), 2.50-1.00 (41H, m, COD-CH_2 and C_6H_{11}). δ_F (CD_2Cl_2) −151.2 (s, $[BF_4]^-$), −448.3 (d, $^2J_{PF}$ 14, IrF_2). δ_P (CD_2Cl_2) −10.3 (t, $^2J_{PF}$ 14, IrP_2).

Bis(pyridine)(cyclo-octa-1,5-diene)iridiumdifluoride tetrafluoroborate (**15**) as yellow crystals. Found: C, 37.05; H, 3.6; N, 4.9. Calc. for $C_{18}H_{22}BF_6IrN_2$: C, 37.05; H, 3.8; N, 4.8%. *m/z* (FAB) 497 ([M-BF$_4$]$^+$), 459 ([M-2F-BF$_4$]$^+$), 398 ([M-py-HF-BF$_4$]$^+$). ν_{max}/cm^{-1} 3125w, 1608 s, 1483 s, 1450 s, 1035vs, 762 s, 688s. δ_H (CD_2Cl_2) 8.89 (4H, m, NCHCH), 8.03 (2H, t, $^3J_{HH} = 14$ Hz, 4-CH), 7.64 (4H, m, NCH), 5.75 (4H, br s, COD-CH), 2.68 (4H, m, COD-CH_2), 2.43 (4H, m, COD-CH_2). δ_F (CD_2Cl_2) −153.4 (s, $[BF_4]^-$), −378.5 (s, IrF_2).

Glyoxal-bis-(2,4,6-trimethylphenylimine)(cyclo-octa-1,5-diene)iridiumdifluoride tetrafluoroborate (**16**) as a dark brown solid. Found: C, 46.7; H, 4.95; N, 3.8. Calc. for $C_{28}H_{36}BF_6IrN_2$: C, 46.9; H, 5.0; N, 3.9%. *m/z* (FAB) 631 ([M-BF$_4$]$^+$). ν_{max}/cm^{-1} 2919w, 1606w, 1477w, 1020vs, 850s. δ_H (CD_2Cl_2) 8.58 (2H, br s, NCHCHN), 7.18 (4H, br s, 3-CH), 5.65 (4H, br s, COD-CH), 2.50-1.80 (26H, m, COD-CH_2 and CH_3). δ_F (CD_2Cl_2) −153.0 (s, $[BF_4]^-$), −433.4 (s, IrF_2).

Glyoxal-bis-(2,6-diisopropylphenylimine)(cyclo-octa-1,5-diene)iridiumdifluoride tetrafluoroborate (**17**) as a deep red solid. Found: C, 50.8; H, 6.0; N, 3.5. Calc. For $C_{34}H_{48}BF_6IrN_2$: C, 50.9; H, 6.0; N, 3.5%. *m/z* (FAB) 715 (M-BF$_4$]$^+$), 695 ([M-HF-BF$_4$]$^+$), 677 ([M-2F-BF$_4$]$^+$). ν_{max}/cm^{-1} 2964w, 1595w, 1463br, 1032vs, 800 s, 752s. δ_H (CD_2Cl_2) 8.98 (2H, br s, NCHCHN), 7.40-7.10 (6H, m, 3-CH and 4-CH), 5.50 (4H, br s, COD-CH), 2.50 (4H, m, CH_3CH), 2.50-1.00 (32H, m, COD-CH_2 and CH_3). δ_F (CD_2Cl_2) −151.0 (s, $[BF_4]^-$), −427.6 (s, IrF_2).

Bis(triphenylphosphine)(dicarbonyl)iridiumdifluoride tetrafluoroborate (**18**) as a buff solid. Found: C, 50.7; H, 3.5. Calc. for $C_{38}H_{30}BF_6IrO_2P_2$: C, 50.8; H, 3.3%. *m/z* (FAB) 792 ([M-F-BF$_4$]$^+$), 773 ([M-2F-BF$_4$]$^+$), 745 ([M-2F-CO-BF$_4$]$^+$). ν_{max}/cm^{-1} 3059 w, 1994 s, 1480 s, 1435 s, 1040vs, 747 s, 689vs. δ_H (CD_2Cl_2) 7.65-7.25 (30H, m, Ph). δ_F (CD_2Cl_2) −152.4 (s, $[BF_4]^-$), −343.4 (t, $^2J_{PF}$ 31, IrF_2 {F-*trans*-CO}), −508.0 (t, $^2J_{PF}$ 18, IrF_2 {F-*trans*-F}). δ_P (CD_2Cl_2) −3.3 (t, $^2J_{PF}$ 31, IrP_2), −12.6 (t, $^2J_{PF}$ 18, IrP_2).

Bis (methyldiphenylphosphine) (dicarbonyl) iridiumdifluoride tetrafluoroborate (**19**) as a buff solid. Found: C, 43.5; H, 3.3. Calc. for $C_{28}H_{26}BF_6IrO_2P_2$: C, 43.5; H, 3.4%. *m/z* (FAB) 649 ([M-2F-BF$_4$]$^+$), 621 ([M-2F-CO-BF$_4$]$^+$). ν_{max}/cm^{-1} 2930 w, 2034 s, 1435 s, 1038vs, 884 s, 739 s, 691vs. δ_H (CD_2Cl_2) 7.58-7.20 (20H, m, Ph), 2.25 (6H, m, CH_3). δ_F (CD_2Cl_2) −151.5 (s, $[BF_4]^-$), −304.0 (t, $^2J_{PF}$ 38, IrF_2 {F-*trans*-CO}), −510.6 (br s, IrF_2 {F-*trans*-F}). δ_P (CD_2Cl_2) −19.9 (t, $^2J_{PF}$ 38, IrP_2), −33.0 (br s, IrP_2).

Bis(phenylethynyldiphenylphosphine)(dicarbonyl)iridiumdifluoride tetrafluoroborate (**20**) as a buff powder. Found: C, 53.2; H, 3.1. Calc. for $C_{42}H_{30}BF_6IrO_2P_2$: C, 53.3; H 3.2%. *m/z* (FAB) 793 ([M-2F-CO-BF$_4$]$^+$). ν_{max}/cm^{-1} 3054w, 2164 s (CC), 2000br (CO), 1435 s, 1042 s (s, $[BF_4]^-$), 752 s, 686s. δ_H (CD_2Cl_2) 7.70-7.20 (m, 30H, Ph). δ_F (CD_2Cl_2) −149.8 (s, $[BF_4]^-$), −331.2 (t, $^2J_{PF}$ 32, IrF_2 {F-*trans*-CO}); −514.1 (br s, IrF_2 {F-*trans*-F}); δ_P (CD_2Cl_2) 5.2 (t, $^2J_{PF}$ 32, IrP_2{F-*trans*-CO}), −25.3 (br s, IrP_2 {F-*trans*-F}).

Glyoxal-bis-(2,4,6-trimethylphenylimine)(dicarbonyl)iridiumdifluoride tetrafluoroborate (**21**) as a dark brown powder. Found: C, 39.6; H, 3.5; N, 4.1. Calc. for $C_{22}H_{24}BF_6IrN_2O_2$: C, 39.7; H 3.6; N, 4.2%. *m/z* (FAB) 560 ([M-HF-BF$_4$]$^+$), 541 ([M-2F-BF$_4$]$^+$). ν_{max}/cm^{-1} 2924w, 2084 s (CO), 2028 s (CO), 1602br, 1474br, 1046vs ($[BF_4]^-$), 856s. δ_H (CD_2Cl_2) 9.02 (s, 2H, NCH), 6.95 (s, 4H, *meta*-CH), 2.29 (s, 6H, *para*-CH_3), 2.25 (s, 12H, *ortho*-CH_3). δ_F (CD_2Cl_2) −149.2 (s, $[BF_4]^-$), −460.0 (s, IrF_2).

Glyoxal-bis-(2,6-diisopropylphenylimine)(dicarbonyl)iridiumdifluoride tetrafluoroborate (**22**) as a dark brown powder. Found: C, 43.0; H, 4.3; N, 3.5. Calc. for $C_{28}H_{36}BF_6IrN_2O_2{\cdot}0.5DCM$: C, 43.2; H 4.7; N, 3.5%. *m/z* (+ FAB) 643 ([M-HF-BF$_4$]$^+$), 625 ([M-2F-BF$_4$]$^+$); ν_{max}/cm^{-1} 2969w, 2090 s (CO), 2034 s (CO), 1457br, 1365br, 1046vs ($[BF_4]^-$), 797 s, 752s. δ_H ($CDCl_3$) 9.14 (s, 2H, NCH), 7.34 (m, 6H, ArH), 3.05 (sep, 4H, $^3J_{HH}$ 6.4, CH_3CH), 1.19 (d, 12H, $^3J_{HH}$ 6.4, CH_3CH), 1.14 (d, 12H, $^3J_{HH}$ 6.4, CH_3CH). δ_F ($CDCl_3$) –149.6 (s, $[BF_4]^-$), –456.5 (s, IrF_2).

Crystal data

(**9**) $C_{43}H_{42}FIrOP_2$, $M = 847.91$, monoclinic, $a = 10.4725(15)$ Å, $b = 11.1807(16)$ Å, $c = 15.201(2)$ Å, $\beta = 92.106(3)°$, $U = 1778.7(4)$ Å^3, $T = 150(2)$ K, space group $P_{21/n}$, graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, $Z = 2$, $D_c = 1.583$ g cm^{-3}, $F(000) = 848$, dimensions $0.18 \times 0.12 \times 0.08$ mm^3, μ(Mo-Kα) = 3.882 mm^{-1}, empirical absorption correction based on ψ scans, maximum and minimum transmission factors of 0.733 and 0.498, respectively, Bruker APEX 2000 CCD diffractometer structure, ω scans, data collection range $2.26 < \theta < 26.00°$, $-12 \le h \le 12$, $-12 \le k \le 13$, $-18 \le l \le 18$; 12187 reflections were measured, and 3499 were unique ($R_{int} = 0.0579$).

(**15**) $C_{18}H_{22}BF_6IrN_2$, $M = 583.39$, tetragonal, $a = 17.4108(15)$ Å, $b = 17.4108(15)$ Å, $c = 25.463(3)$ Å, $U = 7718.8(13)$ Å^3, $T = 150(2)$ K, space group I 41/a c d, graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, $Z = 16$, $D_c = 2.008$ Mg m^{-3}, $F(000) = 4480$, dimensions $0.37 \times 0.04 \times 0.03$ mm^3, μ(Mo-Kα) = 6.981 mm^{-1}, semi-empirical absorption correction, maximum and minimum transmission factors of 0.811 and 0.413, respectively, Bruker APEX 2000 CCD diffractometer structure, ω scans, data collection range $2.30 < \theta < 26.00°$, $-21 \le h \le 21$, $-21 \le k \le 21$, $-31 \le l \le 30$; 23152 reflections were measured, 1904 were unique ($R_{int} = 0.1342$)

Structure solution and refinement

The structures were solved by direct methods. The structure refinement on F^2 employed SHELXTL VERSION 6.10 (SHELXTL, an integrated system for solving, refining and displaying crystal structures).[30] Hydrogen atoms were included in calculated positions (C–H = 0.96 Å) riding on the bonded atom with isotropic displacement parameters set to 1.2 U_{eq}(C). All non-H atoms were refined with anisotropic displacement parameters.

(**9**) Final $R_1 = 0.0470$ and w$R_2 = 0.0827$ ($R_1 = 0.0715$ and w$R_2 = 0.0892$, respectively, for all data) for 229 variables. The final residual Fourier map showed peaks of 1.197 and –0.739 e Å^{-3}.

(**15**) Final $R_1 = 0.0553$ and w$R_2 = 0.1223$ ($R_1 = 0.0879$ and w$R_2 = 0.1353$, respectively, for all data) for 125 variables. The final residual Fourier map showed peaks of 1.887 and –2.214 e Å^{-3}.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC reference numbers 720281 and 720282. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We thank EPSRC for financial support and Dr Joseph Wright for assistance with the structural studies.

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