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Stabilisation of iridium(III) fluoride complexes with NHCs†‡

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The first neutral, $[IrClF_2(NHC)(COD)]$ and $[IrClF_2(CO)_2(NHC)]$ (NHC = IMes, IPr), and cationic, $[IrF_2py(IMes)(COD)][BF_4]$ and $[IrF_2L(CO)_2(NHC)][BF_4]$ (NHC = IMes, L = PPh₂Et, PPh₂CCPh, py; NHC = IPr, L = py), NHC iridium(III) fluoride complexes, have been synthesised by the xenon difluoride oxidation of iridium(I) substrates. The stereochemistries of these iridium(III) complexes have been confirmed by multinuclear NMR spectroscopy in solution and no examples of fluoride-*trans*-NHC arrangements were observed. Throughout, CO was found to be a better co-ligand for the stabilisation of the iridium(III) fluoride complexes than COD. Attempts to generate neutral trifluoroiridium(III) complexes, $[IrF_3(CO)(NHC)]$, *via* the ligand substitution reaction of $[IrF_3(CO)_3]$ with the free NHCs were unsuccessful.

Introduction

There has been growing interest in the area of organometallic fluoride complexes as a result of the synthetic challenges and potential applications, such as in aryl-F bond formation, of such species. Indeed, the development of more reliable synthetic procedures for the synthesis of late transition metal fluoride coordination and organometallic complexes over the past 10–15 years has led to considerable growth in the total number of examples, in the variation in ligand donor sets and in the appreciation of the criteria for M–F bond stabilisation.[1–8] Throughout most of these studies, phosphine, *N*-donor or σ-aryl ligands have routinely been included in the first coordination sphere to aid product stabilisation and characterisation. In contrast, although the coordination chemistry of *N*-heterocyclic carbenes (NHCs) has been extensively investigated,[9] reports of late transition metal-fluoride-NHC complexes had been restricted to only monofluorides $[AuF(NHC)]$,[10] $[RuFH(CO)_2(NHC)_2]$,[11] $[RuFH(CO)(NHC)(PPh_3)_2]$[12] and $[NiF(Ar^F)(NHC)_2]$,[13,14] until our recent report of the first difluoride complexes $[RuF_2(CO)_2(NHC)_2]$.[15]

We have recently developed two synthetic routes to iridium(III) phosphine and pyridine fluoride complexes, either by ligand substitution reactions at $[IrF_3(CO)_3]$ or oxidation of iridium(I) complexes with xenon difluoride.[8] In view of the recent reports of metal-fluoride-NHC complexes we surmised that iridium(III) *N*-heterocyclic carbene fluoride complexes might be accessible *via* one or both of these routes. Herein, we report the results of these investigations, including the synthesis of a range of neutral and cationic iridium(I) NHC complexes as intermediates in the syntheses of the first examples of iridium(III)-fluoride-NHC complexes.

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Results and discussion

(a) Ligand displacement reactions with $[IrF_3(CO)_3]$

Phosphine ligands undergo facile reactions with $[IrF_3(CO)_3]$,[8] however, in contrast to the air- and moisture-stable ruthenium(II) and osmium(II) fluoride complexes $[MF_2(CO)_2(phosphine)_2]$,[16] the iridium(III) products, $[IrF_3(CO)(phosphine)_2]$, rapidly decompose in solution and in the solid state, even at low temperatures.[8] *N*-heterocyclic carbenes (NHCs), in view of the improved σ-donor and differing steric properties, provide alternative supporting ligands that might confer additional stability on this class of complex. Unfortunately, attempts to react $[IrF_3(CO)_3]$ with either the free NHCs, IMes or IPr, or their imidazolium precursors in the presence of base were unsuccessful, affording complicated mixtures of products, as evidenced by *in situ* NMR spectroscopy, that rapidly decomposed to insoluble black precipitates even at low temperatures, possibly as a consequence of the steric bulk of these ligands. In light of the failure to use ligand metathesis for the synthesis of iridium(III)-fluoride-NHC complexes, we turned our attention to our second, oxidative addition, route (Scheme 1). We,[8] and others,[17] have shown that XeF_2 readily oxidises a variety of neutral and cationic iridium(I) phosphine complexes containing carbonyl, halide and/or COD (1,5-cyclooctadiene) to form iridium(III) difluoride complexes. Since, monosubstituted neutral and cationic complexes of iridium(I), particularly those with COD or CO ligands, are amongst the most extensively investigated metal carbene derivatives,[18] these provided an ideal series for our investigation.
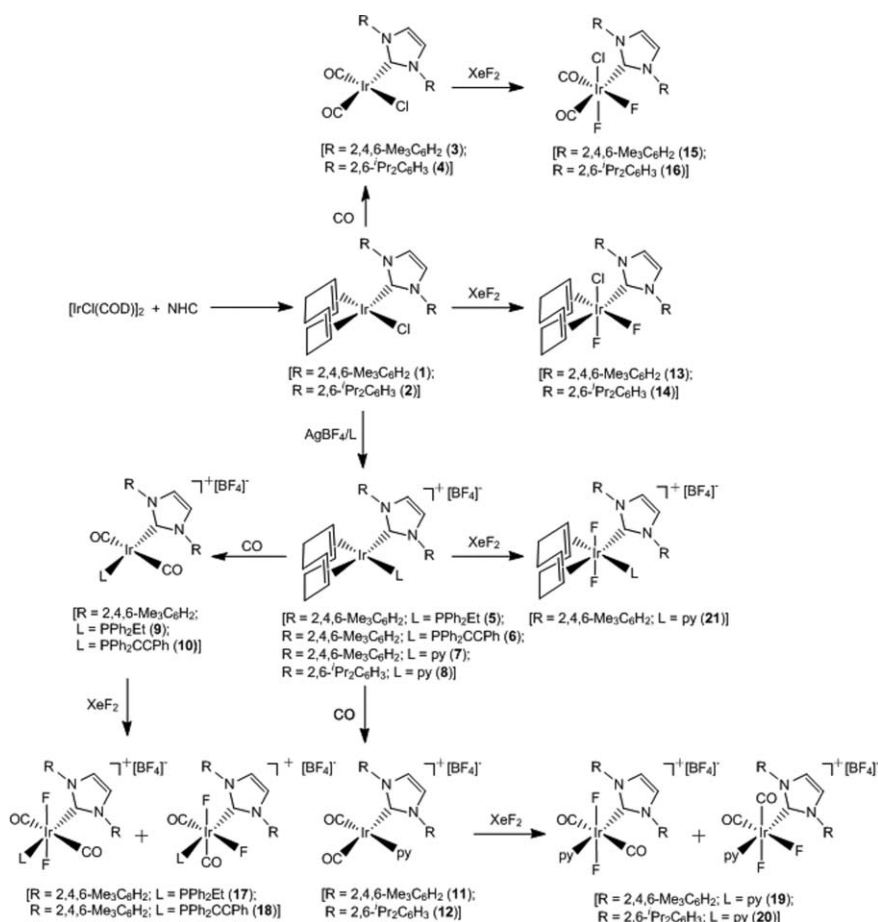
(b) Synthesis of iridium(I) starting materials

Neutral $[IrCl(NHC)(COD)]$ {NHC = IMes = *N*,*N*′-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (1), NHC = IPr = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (2)} and *cis*-$[IrCl(CO)_2(NHC)]$ {NHC = IMes (3), NHC = IPr (4)} were prepared by the literature routes.[18] Chloride abstraction from **1** and introduction of P(ⁿBu)₃ has previously been used to generate a cationic Ir(I) derivative for evaluation as an olefin hydrogenation catalyst.[19] In this work, the steric impact of

[R = 2,4,6-Me₃C₆H₂ (3); R = 2,6-ⁱPr₂C₆H₃ (4)]

[R = 2,4,6-Me₃C₆H₂ (15); R = 2,6-ⁱPr₂C₆H₃ (16)]

[IrCl(COD)]₂ + NHC

[R = 2,4,6-Me₃C₆H₂ (1); R = 2,6-ⁱPr₂C₆H₃ (2)]

[R = 2,4,6-Me₃C₆H₂ (13); R = 2,6-ⁱPr₂C₆H₃ (14)]

AgBF₄/L

[R = 2,4,6-Me₃C₆H₂; L = PPh₂Et (9); L = PPh₂CCPh (10)]

[R = 2,4,6-Me₃C₆H₂; L = PPh₂Et (5); R = 2,4,6-Me₃C₆H₂; L = PPh₂CCPh (6); R = 2,4,6-Me₃C₆H₂; L = py (7); R = 2,6-ⁱPr₂C₆H₃; L = py (8)]

[R = 2,4,6-Me₃C₆H₂; L = py (21)]

[R = 2,4,6-Me₃C₆H₂; L = PPh₂Et (17); R = 2,4,6-Me₃C₆H₂; L = PPh₂CCPh (18)]

[R = 2,4,6-Me₃C₆H₂ (11); R = 2,6-ⁱPr₂C₆H₃ (12)]

[R = 2,4,6-Me₃C₆H₂; L = py (19); R = 2,6-ⁱPr₂C₆H₃; L = py (20)]

Scheme 1

the NHC ligands here is significant where only decomposition products were obtained in the reaction of (**1**) with PPh₃ in the presence of AgBF₄, whilst addition of ethyldiphenylphosphine, phenylethynyldiphenylphosphine or pyridine generated the new [Ir(IMes)L(COD)]⁺[BF₄]⁻ [(**5**), (**6**) and (**7**)] respectively in good yields (Scheme 1). In contrast, only the pyridine adduct **8** could be isolated in the analogous elimination reactions with **2** containing the bulkier IPr ligand. We note that both pyridine adducts, as their PF₆⁻ salts, have previously been reported from the displacement of pyridine in [Ir(py)₂(COD)]⁺[PF₆]⁻ with NHCs.[22] Complexes **5–8** have been characterised by multinuclear NMR spectroscopic studies, mass spectrometry, elemental analysis and for **5**, **6** and **8** by X-ray crystallographic studies for crystals grown by careful layering of dichloromethane–hexane solutions.

Views of the complexes are shown in Figs. 1–3 and selected bond lengths and angles are collected in Table 1. For [Ir(IPr)py(COD)]⁺[BF₄]⁻ (**8**), the asymmetric unit contains two unique metal cations, two unique anions and three lattice dichloromethane molecules. The metal-carbene bond lengths for the three complexes are virtually identical and unremarkable.[23] The Ir-COD bond lengths within each complex are not statistically different and the Ir-COD$_{trans\text{-}L}$ distances for the two phosphine adducts are significantly longer than those for the pyridine adducts, in line with their relative donor properties. The only substantive differences within the structures concerns the phenylethynyldiphenylphosphine adduct (**7**) for which the C$_{carbene}$–

Ir–L angle is wider resulting in considerable asymmetry in the Ir–C$_{COD}$ bond lengths and bond angles, presumably as a result of a steric clash arising from the phenylethynyl group.
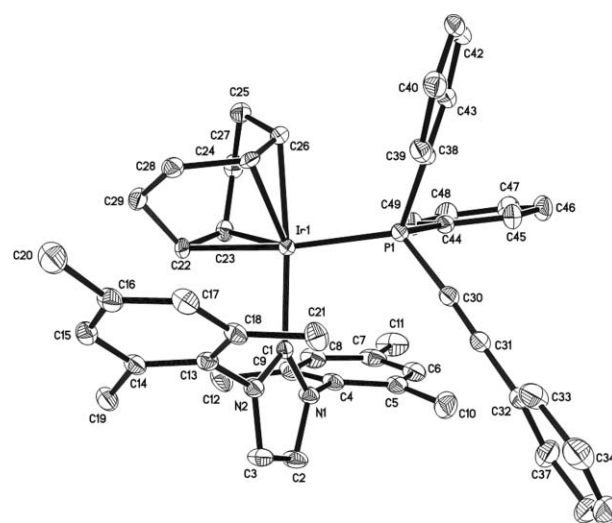
Displacement of COD by CO occurs readily in the quantitative formation of [Ir(NHC)(CO)₂L]⁺[BF₄]⁻ [NHC = IMes, L = PPh₂Et, PPh₂CCPh, py (**9–11**); NHC = IPr, L = py (**12**)] (Scheme 1). All four complexes have two IR active υ(CO) absorptions in their IR spectra but subtle variations in the ¹H NMR data for the *ortho*-Me protons in the IMes ligands suggest differences in their structures, that were confirmed by X-ray crystallographic studies for **9** and **11** for crystals grown either by slow evaporation of a saturated dichloromethane solution of **9** or by slow vapour diffusion of hexane into a saturated dichloromethane solution of **11**. Views of the complexes are shown in Figs. 4 and 5 and selected bond lengths and angles are collected in Table 2. The structural determinations reveal very similar Ir–C$_{carbene}$, Ir–C$_{carbonyl}$ and C–O bond distances, but [Ir(IMes)(CO)₂(PPh₂Et)][BF₄] (**9**) adopts a distorted *trans* stereochemistry whilst [Ir(IMes)(CO)₂(py)][BF₄] (**11**) displays a regular *cis* stereochemistry. For **9**, the two CO molecules are undergoing a distinct out-of-plane deformation, as reflected by the C(1)–Ir(1)–C(2) angle [150.7(4)°], and the C(3)–Ir(1)–P(1) angle [168.95(18)°] is substantially smaller than linear. These distortions create a sterically unencumbered 'pocket' into which the CO molecules are directed. For **11**, the integrity of the square plane is reflected in the C1–Ir–C3 and N3–Ir–C1 angles [91.89(17)° and 176.63(18)°]. The molecular structure reveals that the pyridine ring

Table 1 Selected bond lengths (Å) and angles (°) for (5), (6), (8) and [Ir(IPr)(py)(COD)][PF$_6$]

	(5)	(6)	(8)		[Ir(IPr)(py)(COD)][PF$_6$][25]
Ir(1)–C(carbene)	2.077(5)	2.063(3)	2.076(4)	2.077(4)	2.080(10)
Ir(1)–C(COD$_{trans\text{-carbene}}$)	2.200(5)	2.248(3)	2.194(4)	2.187(4)	2.217(11)
Ir(1)–C(COD$_{trans\text{-carbene}}$)	2.177(5)	2.157(3)	2.178(4)	2.175(4)	2.193(11)
Ir(1)–C(COD$_{trans\text{-L}}$)	2.204(5)	2.213(3)	2.143(5)	2.146(4)	2.216(11)
Ir(1)–C(COD$_{trans\text{-L}}$)	2.197(5)	2.176(3)	2.126(4)	2.117(4)	2.131(10)
Ir(1)–N(3)			2.103(4)	2.106(3)	2.081(9)
Ir(1)–P(1)	2.3575(12)	2.3030(9)			
C–C(COD$_{trans\text{-carbene}}$)	1.402(7)	1.393(5)	1.393(7)	1.402(7)	1.408(15)
C–C(COD$_{trans\text{-L}}$)	1.402(7)	1.406(4)	1.402(7)	1.397(6)	1.383(14)
N(1)–C(carbene)	1.375(5)	1.369(4)	1.357(5)	1.371(5)	—
N(2)–C(carbene)	1.374(5)	1.364(4)	1.377(5)	1.365(5)	—
Av B–F	1.379	1.358	1.358	1.358	—
C(carbene)–Ir(1)– C(COD$_{trans\text{-carbene}}$)	168.74(17)	175.19(11)	162.86(18)	161.08(17)	165.4(4)
C(carbene)–Ir(1)– C(COD$_{trans\text{-carbene}}$)	153.78(18)	141.02(12)	159.84(18)	160.89(18)	157.1(4)
C(COD$_{trans\text{-L}}$)–Ir(1)–L	167.30(15)	171.94(9)	160.26(18)	160.45(15)	159.5(4)
C(COD$_{trans\text{-L}}$)–Ir(1)–L	154.45(15)	136.26(9)	158.80(17)	158.46(16)	159.5(4)
C(carbene)–Ir(1)–L	94.12(13)	98.30(9)	96.12(15)	97.63(14)	95.4(4)
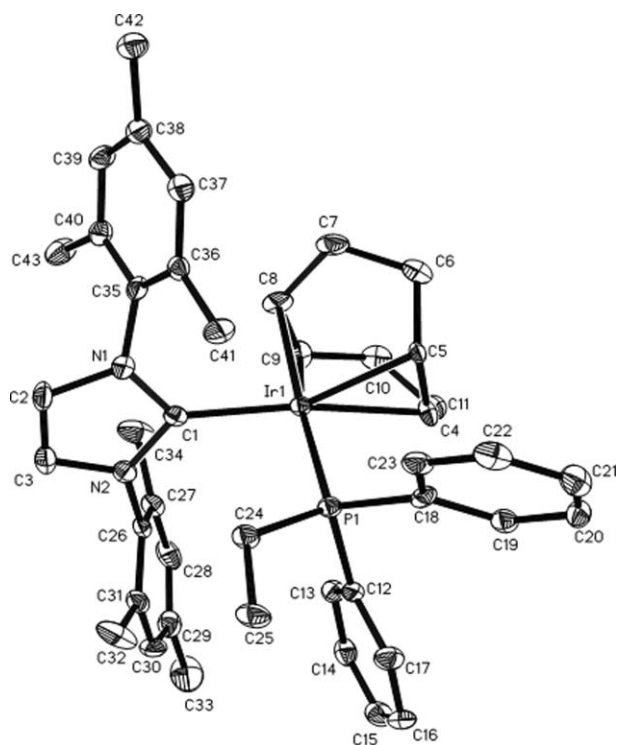
Fig. 1 Molecular structure of the cationic unit in **5** with 30% displacement ellipsoids. H atoms and BF$_4^-$ anion have been omitted for clarity.

Fig. 2 Molecular structure of the cationic unit in **6** with 30% displacement ellipsoids. H atoms and BF$_4^-$ anion have been omitted for clarity.

is aligned parallel with the diametrically opposed mesityl ring. The N(2)–C(3)–Ir(1)–N(3) torsion angle [45.8°] indicates that it does not lie orthogonal to the plane of the imidazolium ring, rather there is a slight twist down the N(3)–Ir(1)–C(1) axis, such that the centroid of the pyridine ring is oriented towards the methyl group of C(23). Similarly, the carbene has undergone a mild twist down the C(3)–Ir(1)–C(2) axis such that the heterocycle bisects the C(2)– Ir(1)–C(1) plane, but does not lie orthogonal to it. This places the two mesityl groups of the carbene in close proximity to the pyridine ring (on one side) and the C(1)–O(1) unit (on the other). It is plausible that the highfield shift of the *ortho*-mesityl protons observed for **11** may be related to this proximity of the C(23)

methyl group to the pyridine ring. A previous study has shown that a coordinated pyridine may significantly shift the proton resonances of proximal groups.[24] Although there is a scarcity of structural data for mixed NHC/phosphine carbonyl complexes in the literature, there is precedent for a *trans* relationship of an NHC and a metal-bound carbonyl in the related complexes *trans*-[RhCl(IMes)(CO)(PPh$_3$)][25] and [IrCl(Ibiox6)(CO)$_2$].[26] Whilst the stereochemistry of **10** and **12** is not unequivocal in the absence of structural characterisations, in light of the similarity of the spectroscopic data for **9** and **10**, and between **11** and **12**, we assign a *trans*-stereochemistry to the phenylethynyldiphenylphosphine adduct **10** and a *cis*-stereochemistry to the IPr-py complex **12**.

(c) Oxidation of [IrCl(NHC)(COD)] and [IrCl(CO)$_2$(NHC)] with XeF$_2$

The neutral iridium(I) NHC-chloride complexes **1–4** can be readily oxidised by XeF$_2$ in solution at low temperatures to afford the first iridium(III) NHC-fluoride complexes, [IrClF$_2$(NHC)(COD)] [NHC = IMes (**13**); IPr (**14**)}] and [IrClF$_2$(CO)$_2$(NHC)]
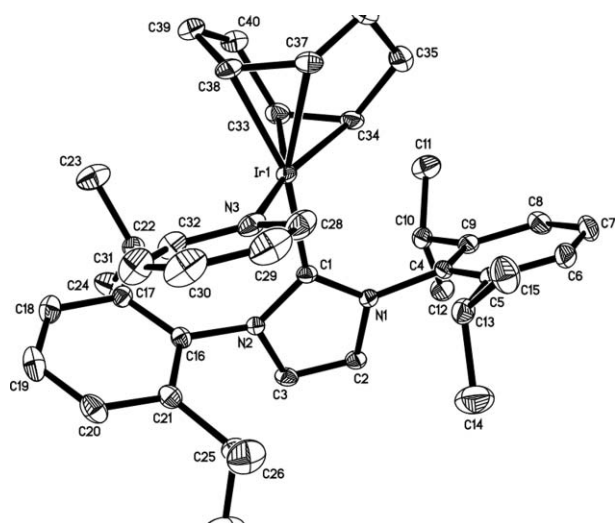
Fig. 3 Molecular structure of one of the unique cationic units of **8** with 30% displacement ellipsoids. H atoms, BF_4^- ions and lattice CH_2Cl_2 have been omitted for clarity.
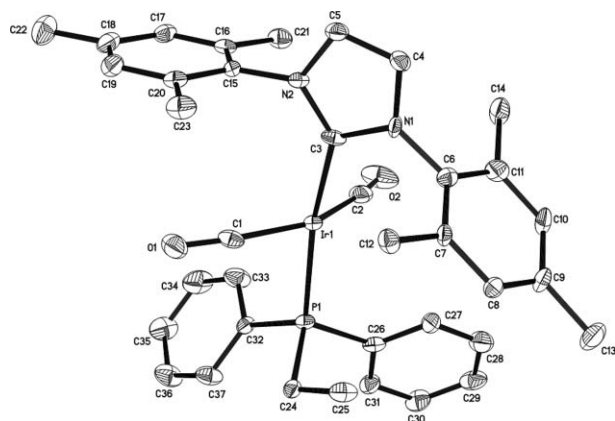

Fig. 4 Molecular structure of the cationic unit in **9** with 30% displacement ellipsoids. H atoms and the BF_4^- anion have been omitted for clarity.
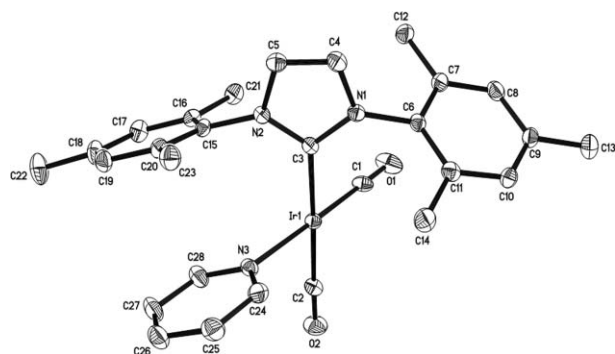

Fig. 5 Molecular structure of the cationic unit in **11** with 30% displacement ellipsoids. H atoms and BF_4^- anion have been omitted for clarity.

[NHC = IMes (**15**); IPr (**16**)] (Scheme 1). Full characterisation was possible for **15** and **16** whilst **13** and **14** were identified by NMR spectroscopy at low temperature and decomposed rapidly at room temperature, supporting our earlier conclusion,[8] that CO is a better ligand than COD for the stabilisation of iridium(III)-fluoride complexes. The ^{19}F NMR spectra (Table 3)

Table 2 Selected bond lengths (Å) and angles (°) for (**9**), (**11**)

	(**9**)	(**11**)
Ir(1)–C(1)	1.864(8)	1.842(5)
Ir(1)–C(2)	1.895(9)	1.894(5)
Ir(1)–C(3)	2.071(6)	2.076(4)
Ir(1)–N(3)		2.112(4)
Ir(1)–P(1)	2.331(4)	
C(1)–O(1)	1.164(9)	1.132(6)
C(2)–O(2)	1.130(10)	1.135(6)
N(1)–C(3)	1.351(8)	1.361(6)
N(2)–C(3)	1.354(8)	1.357(6)
Av B–F	1.367	1.379
C(1)–Ir(1)–C(2)	150.7(4)	91.0(2)
C(2)–Ir(1)–C(3)	91.5(3)	177.12(19)
C(1)–Ir(1)–N(3)		176.63(18)
C(3)–Ir(1)–P(1)	168.95(18)	

for all four complexes revealed two, mutually-coupled, doublets. The coupling constants are entirely consistent with previously reported $^2J_{FF}$ interactions on iridium(III) {$IrF_3(CO)(PEt_3)_2$ $^2J_{FF}$ = 96 Hz; $IrClF_2(CO)(PEt_3)_2$ $^2J_{FF}$ = 115 Hz; $IrBrF_2(CO)(PEt_3)_2$ $^2J_{FF}$ = 130 Hz}.[17] The lower frequency chemical shifts, at *ca.* δ −390, are in the region diagnostic of F-*trans*-Cl on iridium(III) centres, whilst the variation in chemical shifts for the high frequency doublets for **15** and **16** *vs.* those of **13** and **14** suggests an F-*trans*-CO arrangement for the former complexes,[8,27,28] and an F-*trans*-COD arrangement for the latter (Scheme 1). Although these are the first examples of an iridium(III)-fluoride bound *trans* to an olefin group, this is not an unreasonable assignment in relation to the relative chemical shifts for the most closely related iridium(I) compounds; [IrF(PPh₃)(COD)][4] and [IrF(CO)(PPh₃)₂][29] δ −219.3 and −254 respectively. As expected for such a conformation, the olefinic resonances for the COD ligands are inequivalent, and at *ca.* δ 5.4 are substantially shifted from those for the iridium(I) starting materials.

(d) Oxidation of [IrL(CO)₂(NHC)][BF₄] and [IrL(NHC)(COD)][BF₄] with XeF₂

The iridium(I) carbonyl cations $[Ir(IMes)(CO)_2L]^+[BF_4]^-$ [L = PPh₂Et (**9**), PPh₂CCPh (**10**)] react similarly with XeF₂ in solution to generate, approximately, 1 : 1 mixtures of two isomeric difluoride complexes $[IrF_2(CO)_2(IMes)L]^+[BF_4]^-$ (**17, 18**) (Scheme 1; Table 3) in which the NHC-*trans*-phosphine arrangement of the starting materials are maintained. Related, approximately, 1 : 1 mixtures of isomeric difluoride complexes $[IrF_2(CO)_2(NHC)py]^+[BF_4]^-$ (**19, 20**) (Scheme 1; Table 3) are formed in the oxidation of $[Ir(NHC)(CO)_2py]^+[BF_4]^-$ [NHC = IMes (**11**), IPr (**12**)]. Similar mixtures of isomeric fluorides are formed in the oxidation of $[Ir(CO)_2(phosphine)_2]^+[BF_4]^-$ with XeF₂.[8] Both the absolute and relative values of the ^{19}F NMR resonances and the $^2J_{PF}$ coupling constants are diagnostic of the F-*trans*-F and F-*trans*-CO arrangements on iridium(III); in line with the oxidations of the neutral iridium(I) NHC complexes (*vide supra*) we find no evidence for F-*trans*-NHC arrangements for these products. As indicated earlier, the reduction in stability in moving from CO to COD in this work hampered our studies on the oxidation of the [Ir(NHC)L(COD)]⁺ cations (**5–8**). In all cases, xenon evolution was seen on warming the reaction mixtures to *ca* −80 °C, but this was accompanied by rapid decomposition. Only in

Table 3 ^{19}F NMR data for iridium-NHC-fluoride complexes

	δ (ppm) (J/Hz)			
	F-*trans*-F	F-*trans*-Cl	F-*trans*-CO	F-*trans*-COD
[IrClF$_2$(IMes)(COD)] (**13**)		−382.5 (141^a)		−273.5 (141^a)
[IrClF$_2$(IPr)(COD)] (**14**)		−386.9 (147^a)		−270.3 (147^a)
[IrClF$_2$(IMes)(CO)$_2$] (**15**)		−397.4 (121^a)	−311.3 (121^a)	
[IrClF$_2$(IPr)(CO)$_2$] (**16**)		−400.3 (123^a)	−307.9 (123^a)	
[IrF$_2$(CO)$_2$(IMes)(PEtPh$_2$)]$^+$ (**17**)	−521.8 (20^b)		−328.6 (36^b)	
[IrF$_2$(CO)$_2$(IMes)(PPh$_2$CCPh)]$^+$ (**18**)	−517.3 (25^b)		−335.0 (42^b)	
[IrF$_2$(CO)$_2$(IMes)(py)]$^+$ (**19**)	−455.1		−318.9	
[IrF$_2$(CO)$_2$(IPr)(py)]$^+$ (**20**)	−458.1		−303.4	
[IrF$_2$(IMes)(COD)(py)]$^+$ (**21**)	−425.2			

^{a} $^2J_{FF}$. ^{b} $^2J_{PF}$.

the case of [IrF$_2$(IMes)py(COD)]$^+$[BF$_4$]$^-$ (**21**) could reproducible NMR spectra be obtained, for which the ^{19}F data is diagnostic of an F-*trans*-F stereochemistry (Table 3; Scheme 1).

Each of these iridium(III)-NHC fluoride complexes decompose inconsistently in solution in a few hours, always with loss of the metal-bound fluoride resonances and generation of HF, which precluded all our attempts to grow crystals suitable for structural characterisation. However, crystallographic studies on one of the products, a C–H activated IMes complex, [IrF(η^2-IMes)(CO)$_2$(PPh$_2$Et)]$^+$[BF$_4$]$^-$, formed from decomposition of [IrF$_2$(CO)$_2$(IMes)(PPh$_2$Et)]$^+$[BF$_4$]$^-$ (**17**) in dichloromethane, revealed insight into the decomposition process (Fig. 6). Unfortunately, poor quality data precluded full anisotropic refinement so we do not report here a full structural characterisation. However, the analysis does clearly demonstrate a single Ir(III)–F bond, the loss of one fluoride ligand and a cyclometalated IMes ligand.[30]
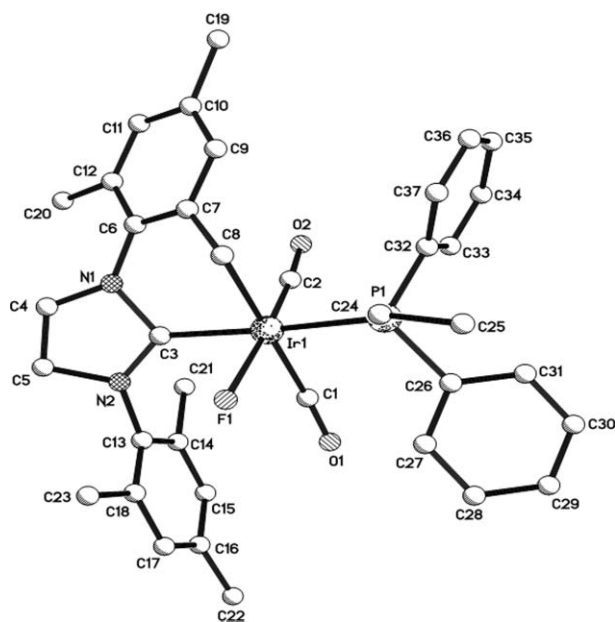

Fig. 6 Molecular structure of the cationic unit in the cyclometallated IMes complex [IrF(IMes)(CO)$_2$(PPh$_2$Et)]$^+$[BF$_4$]$^-$. H atoms and BF$_4^-$ anion have been omitted for clarity.

Conclusions

A series of neutral and cationic iridium(I) NHC complexes have been prepared and characterised. Oxidation of these complexes with xenon difluoride in solution generates difluoroiridium(III) complexes stabilised by NHC ligands. The stereochemistries have been confirmed by multinuclear NMR spectroscopy in solution, but in no cases were fluoride-*trans*-NHC arrangements adopted. Throughout CO was found to be a better co-ligand for these derivatives than COD. In contrast, ligand substitution reactions of NHCs with [IrF$_3$(CO)$_3$] did not afford iridium-NHC-fluoride complexes.

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[31] or in a nitrogen purged dry box. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use.[32] ^{1}H, ^{19}F and ^{31}P NMR spectroscopic studies 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$_4$ (^{1}H), external CFCl$_3$ (^{19}F) and to external H$_3$PO$_4$ (^{31}P) using the high frequency positive convention. Abbreviations for NMR spectral multiplicities are as follows: s = singlet, d = doublet, m = multiplet. Elemental analyses were performed by the Elemental Analysis Service at the London Metropolitan University. 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.

[IrCl(NHC)(COD)] and *cis*-[IrCl(CO)$_2$(NHC)] (NHC = IMes, NHC)[18–21] were prepared by the literature routes.

(Ethyldiphenylphosphine)(1,3-bis{2,4,6-trimethylphenyl}imidazol-2-ylidene)(cyclo-octa-1,5-diene)iridium tetrafluoroborate (5). A Schlenk tube was charged in the dry box with (1,3-bis{2,4,6-trimethylphenyl}imidazol-2-ylidene)(cyclo-octa-1,5-diene)iridium chloride[19] (0.250 g, 0.390 mmol) and AgBF$_4$ (84 mg, 0.429 mmol). THF (10 cm^3) was transferred onto the solids *via* cannular, and the resulting suspension stirred in the dark for 2 h.

The precipitated silver salts were filtered off, and a solution of PPh$_2$Et (83 mg, 0.390 mmol) in THF (10 cm^3) added dropwise to the stirred mother liquor. The resulting orange solution was stirred for an additional two hours, and the solvent removed *in vacuo*. The orange powder was recrystallized from DCM–hexane, giving the product [Ir(COD)(IMes)(PPh$_2$Et)]$^+$[BF$_4$]$^-$ (**5**) as an air-sensitive orange powder (0.25 g; 71%). Anal. Calc. for C$_{43}$H$_{51}$BF$_4$IrN$_2$P: C, 56.98, H, 5.68, N, 3.09. Found: C, 56.94, H, 5.73, N, 3.01. ν_{max}/cm^{-1} 2927br, 1482br, 1381br, 1299(s, 1249 s, 1030br ([BF$_4$]$^-$), 746 s, 696s. ^{1}H NMR (CDCl$_3$): 7.40–6.90 (m, 16H, Ar*H* and NC*H*C*H*N), 4.21 (br s, 2H, COD-C*H*), 2.91 (br s, 2H, COD-C*H*), 2.38 (s, 6H, *ortho*-C*H$_3$*), 2.29 (s, 6H, *ortho*-C*H$_3$*), 2.00 (s, 6H, *para*-C*H$_3$*), 1.94 (q, 2H, $^3J_{HH}$ = $^2J_{PH}$ 6.5 Hz, PC*H$_2$*), 1.70–1.40 (m, 8H, COD-C*H$_2$*), 0.72 (dt, 3H, $^3J_{PH}$ 13.0, $^3J_{HH}$ 6.5 Hz, PCH$_2$C*H$_3$*). ^{19}F{^{1}H} NMR (CDCl$_3$): −153.4 (s, [BF$_4$]$^-$). ^{31}P{^{1}H} NMR (CDCl$_3$): 11.3 (s, Ir*P*Ph$_2$Et). *m/z* (FAB) 819 ([M-BF$_4$]$^+$), 711 ([M-COD-BF$_4$]$^+$), 605 ([M-PPh$_2$Et-BF$_4$]$^+$).

(Phenylethynyldiphenylphosphine)(1,3-bis{2,4,6-trimethylphenyl}imidazol-2-ylidene)(cyclo-octa-1,5-diene)iridium tetrafluoroborate (6). The title compound, an air-sensitive orange solid, was isolated in a similar manner to that described for **5** (0.28 g, 73%). Anal. Calc. for C$_{49}$H$_{51}$BF$_4$IrN$_2$P: C, 60.16, H, 5.26, N, 2.86. Found: C, 60.02, H, 5.25, N, 2.86. ν_{max}/cm^{-1} 2917br, 2175 s (CC$_{acetylene}$), 1608br, 1483w, 1437w, 1035 s ([BF$_4$]$^-$), 757 s, 690 s (Solid State). ^{1}H NMR (CDCl$_3$): 7.45–7.00 (m, 19H, Ar*H*), 6.62 (s, 2H, NC*H*C*H*N), 4.75 (br s, 2H, COD-C*H*), 3.17 (br s, 2H, COD-C*H*), 2.42 (s, 12H, *ortho*-C*H$_3$*), 2.33 (s, 6H, *para*-C*H$_3$*), 1.70–1.40 (m, 8H, COD-C*H$_2$*). ^{19}F{^{1}H} NMR (CDCl$_3$): −154.2 (s, [BF$_4$]$^-$). ^{31}P{^{1}H} NMR (CDCl$_3$): −6.6 (s, Ir*P*Ph$_2$CCPh). *m/z* (FAB) 891 ([M-BF$_4$]$^+$, 783 ([M-COD-BF$_4$]$^+$), 605 ([M-PPh$_2$CCPh-BF$_4$]$^+$).

(Pyridine)(1,3-bis{2,4,6-trimethylphenyl}imidazol-2-ylidene)-(cyclo-octa-1,5-diene)iridium tetrafluoroborate (7). The title compound, an air-sensitive yellow solid, was isolated in a similar manner to that described for **5** (0.21 g, 70%). Anal. Calc. for C$_{34}$H$_{41}$BF$_4$IrN$_3$: C, 52.95, H, 5.36, N, 5.45. Found: C, 52.80, H, 5.39, N, 5.39. ν_{max}/cm^{-1} 2919w, 1485w, 1443 s, 1032vs ([BF$_4$]$^-$), 758 s, 699s. ^{1}H NMR (CDCl$_3$): 7.67 (m, 2H, Ar*H*), 7.64 (m, 1H, Ar*H*), 7.11 (m, 2H, Ar*H*), 6.95 (br s, 6H, Ar*H* and NC*H*C*H*N), 3.56 (m, 2H, COD-C*H*), 3.13 (m, 2H, COD-C*H*), 2.34 (s, 6H, *para*-C*H$_3$*), 2.04 (s, 12H, *ortho*-C*H$_3$*), 2.00–1.50 (m, 8H, COD-C*H$_2$*). ^{19}F{^{1}H} NMR (CDCl$_3$): −153.1 (s, [BF$_4$]$^-$). *m/z* (FAB) 684 ([M-BF$_4$]$^+$), 605 ([M-Py-BF$_4$]$^+$).

(Pyridine)(1,3-bis{2,6-diisopropylphenyl}imidazol-2-ylidene)-(cyclo-octa-1,5-diene)iridium tetrafluoroborate (8). The title compound, an air-sensitive yellow solid, was isolated in a similar manner to that described for **5** (0.19 g, 57%). Anal. Calc. for C$_{40}$H$_{53}$BF$_4$IrN$_3$·0.5CH$_2$Cl$_2$: C, 54.17, H, 6.07, N, 4.68. Found: C, 54.01, H, 6.30, N, 4.33. ν_{max}/cm^{-1} 2964 s, 1444 s, 1032 s ([BF$_4$]$^-$), 752s. ^{1}H NMR (CDCl$_3$): 7.66 (m, 4H, Ar*H*), 7.60 (m, 2H, Ar*H*), 7.41 (m, 5H, Ar*H*), 3.65 (m, 2H, COD-C*H*), 3.08 (m, 2H, COD-C*H*), 2.02 (m, 2H, CH$_3$C*H*), 1.91 (m, 2H, CH$_3$C*H*), 1.40–1.00 (m, 32H, C*H$_3$*CH and COD-C*H$_2$*). ^{19}F{^{1}H} NMR (CDCl$_3$): −152.9 (s, [BF$_4$]$^-$). *m/z* (FAB) 768 ([M]$^+$), 689 ([M-Py]$^+$).

(Ethyldiphenylphosphine)(1,3-bis{2,4,6-trimethylphenyl}imidazol-2-ylidene)(dicarbonyl)iridium tetrafluoroborate (9). Carbon monoxide was bubbled through a stirred solution of **5** (400 mg,

0.440 mmol) in DCM (5 cm^3) at room temperature, after which the solution was poured into diethylether (20 cm^3). The precipitate was collected and recrystallized from DCM–hexane to afford the product [Ir(IMes)(CO)$_2$(PPh$_2$Et)]$^+$[BF$_4$]$^-$ (**9**) as an air-sensitive orange powder (0.36 g, 96%). Anal. Calc. for C$_{37}$H$_{39}$BF$_4$IrN$_2$O$_2$P·0.5CHCl$_3$: C, 49.28, H, 4.36, N, 3.07. Found: C, 50.05, H, 4.34, N, 3.09. ν_{max}/cm^{-1} 2924w, 2069 s (CO), 1977 s (CO), 1608w, 1486 s, 1437 s, 1049vs ([BF$_4$]$^-$), 695s. ^{1}H NMR (CDCl$_3$): 7.50–7.10 (m, 16H, Ar*H* and NC*H*C*H*N), 2.50 (q, 2H, $^2J_{PH}$ = $^3J_{HH}$ 7.9 Hz, PC*H$_2$*), 2.33 (s, 6H, *para*-C*H$_3$*), 2.10 (s, 12H, *ortho*-C*H$_3$*), 0.95 (dt, 3H, $^3J_{PH}$ 12.8, $^3J_{HH}$ 7.9 Hz, PCH$_2$C*H$_3$*). ^{19}F{^{1}H} NMR (CDCl$_3$): −153.9 (s, [B*F$_4$*]$^-$). ^{31}P{^{1}H} NMR (CDCl$_3$): 10.6 (s, Ir*P*Ph$_2$Et). *m/z* (FAB) 767 ([M-BF$_4$]$^+$), 739 ([M-CO-BF$_4$]$^+$).

(Phenylethynyldiphenylphosphine)(1,3-bis{2,4,6-trimethylphenyl}imidazol-2-ylidene)(dicarbonyl)iridium tetrafluoroborate (10). The title compound, an air-sensitive orange solid, was isolated in a similar manner to that described for **9** (0.40 g, 98%). Anal. Calc. for C$_{43}$H$_{39}$BF$_4$IrN$_2$O$_2$P: C, 55.75, H, 4.25, N, 3.03. Found: C, 55.81, H, 4.18, N, 2.97. ν_{max}/cm^{-1} 2918w, 2168 s (CC), 2078 s (CO), 1989 s (CO), 1483 s, 1438 s, 1046 s ([BF$_4$]$^-$), 850 s, 752 s, 688s. ^{1}H NMR (CDCl$_3$): 7.61–7.00 (m, 19H, Ar*H*), 7.10 (s, 2H, NC*H*C*H*N), 2.34 (s, 6H, *para*-C*H$_3$*), 2.15 (s, 12H, *ortho*-C*H$_3$*). ^{19}F{^{1}H} NMR (CDCl$_3$): −154.0 (s, [B*F$_4$*]$^-$). ^{31}P{^{1}H} NMR (CDCl$_3$): −12.9 (s, Ir*P*Ph$_2$CCPh). *m/z* (FAB) 839 ([M-BF$_4$]$^+$), 811 ([M-CO-BF$_4$]$^+$), 783 ([M-2CO-BF$_4$]$^+$).

(Pyridine)(1,3-bis{2,4,6-trimethylphenyl}imidazol-2-ylidene)-(dicarbonyl)iridium tetrafluoroborate (11). The title compound, an air-sensitive yellow powder, was isolated in a similar manner to that described for **9** (0.29 g, 92%). Anal. Calc. for C$_{28}$H$_{29}$BF$_4$IrN$_3$O$_2$: C, 46.77, H, 4.07, N, 5.85. Found: C, 46.81, H, 4.18, N, 5.97. ν_{max}/cm^{-1} 2073 s (CO), 2006 s (CO), 1485w, 1446w, 1030 s ([BF$_4$]$^-$), 758 s, 697s. ^{1}H NMR (CDCl$_3$): 7.96 (t, 1H, $^3J_{HH}$ = 7.6 Hz, Py*H*), 7.71 (d, 2H, $^3J_{HH}$ = 7.2 Hz, Py*H*), 7.42 (t, 2H, $^3J_{HH}$ = 6.8 Hz, Py*H*), 7.19 (s, 2H, NC*H*C*H*N), 6.93 (s, 4H, Ar*H*), 2.33 (s, 6H, *para*-C*H$_3$*), 1.98 (s, 12H, *ortho*-C*H$_3$*). ^{19}F{^{1}H} NMR (CDCl$_3$): −153.3 (s, [B*F$_4$*]$^-$). *m/z* (FAB) 632 ([M-BF$_4$]$^+$), 576 ([M-2CO-BF$_4$]$^+$).

(Pyridine)(1,3-bis{2,6-diisopropylphenyl}imidazol-2-ylidene)-(dicarbonyl)iridium tetrafluoroborate (12). The title compound, an air-sensitive yellow powder, was isolated in a similar manner to that described for **9** (0.35 g, 99%). All attempts to obtain satisfactory elemental analysis data for **12** were unsuccessful due to the air sensitivity. ν_{max}/cm^{-1} 2970w, 2068 s (CO), 2000 s (CO), 1451 s, 1032 s ([BF$_4$]$^-$), 758 s, 695s. ^{1}H NMR (CDCl$_3$): 7.99 (m, 1H, Ar*H* 7.63 (t, 2H, $^3J_{HH}$ = 7.9 Hz, Ar*H* 7.52 (m, 4H, Ar*H* 7.36 (4H, d, $^3J_{HH}$ = 7.9 Hz, Ar*H* 2.72 (sep, 4H, $^3J_{HH}$ = 6.7 Hz, CH$_3$C*H*), 1.23 (d, 12H, $^3J_{HH}$ = 7.0 Hz, C*H$_3$*CH), 1.17 (d, 12H, $^3J_{HH}$ = 6.7 Hz, C*H$_3$*CH). ^{19}F{^{1}H} NMR (CDCl$_3$): −153.1 (s, [BF$_4$]$^-$). *m/z* (FAB) 716 ([M-BF$_4$]$^+$), 637 ([M-py-BF$_4$]$^+$).

(1,3-Bis{2,4,6-trimethylphenyl}imidazol-2-ylidene)(cyclo-octa-1,5-diene)chlorodifluoroiridium(III) (13). Complex **1** (41 mg, 0.064 mmol) was loaded into a pre-seasoned 4 mm O.D. (outside diameter) FEP (perfluoroethylene/propylene copolymer) tube connected to a T-union. XeF$_2$ (14 mg, 0.083 mmol was loaded into a 4 mm O.D. FEP tube connected to the perpendicular elbow of the union, ensuring that mixing of the two solids could not

occur. The reactor was re-connected to the line, and the connectors passivated. Freshly distilled dichloromethane (*ca.* 1 cm³) was condensed into both FEP tubes at -196 °C, and the solutions cautiously warmed to ensure complete dissolution of the solids. The solution of **1** was cooled to −196 °C, and the XeF₂ solution added in a single aliquot. The solution was cautiously warmed to −80 °C with agitation. Once reaction was deemed complete, the FEP tube was heat sealed for NMR studies at −60 °C. ¹H NMR (CDCl₃): 7.19 (s, 2H, NC*H*C*H*N), 6.89 (s, 4H, Ar*H*), 5.95 (br s, 1H, COD-C*H*), 5.60 (br s, 1H, COD-C*H*), 5.10 (br s, 2H, COD-C*H*), 2.50–1.85 (m, 26H, C*H₃* and COD-C*H₂*). ¹⁹F{¹H} NMR (CDCl₃): −273.5 (d, $^2J_{FF}$ = 141 Hz, Ir*F* {F-*trans*-olefin}), -382.5 (d, $^2J_{FF}$ = 141 Hz, Ir*F* {F-*trans*-Cl}).

(1,3-Bis{2,6-diisopropylphenyl}imidazol-2-ylidene)(cyclo-octa-1,5-diene)chlorodifluoroiridium(III) (14). The title compound was generated in a similar manner to that described for **13**. NMR spectra were recorded at −60 °C. ¹H NMR (CDCl₃): 7.34 (t, 2H, $^3J_{HH}$ = 7.7 Hz, *para*-C*H*), 7.18 (d, 4H, $^3J_{HH}$ = 7.6 Hz, *meta*-C*H*), 5.89 (br s, 1H, COD-C*H*), 5.48 (br s, 1H, COD-C*H*), 4.95 (br s, 2H, COD-C*H*), 3.05 (sep, 2H, $^3J_{HH}$ = 7.1 Hz, CH₃C*H*), 2.87 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, CH₃C*H*), 2.23–1.50 (m, 8H, COD-C*H₂*), 1.03 (d, 12H, $^3J_{HH}$ = 6.7 Hz, C*H₃*CH), 1.00 (d, 12H, $^3J_{HH}$ = 7.1 Hz, C*H₃*CH).¹⁹F{¹H} NMR (CDCl₃): −270.3 (d, $^2J_{FF}$ = 147 Hz, Ir*F* {F-*trans*-olefin}), −386.9 (d, $^2J_{FF}$ = 147 Hz, Ir*F* {F-*trans*-Cl}).

(1,3-Bis{2,4,6-trimethylphenyl}imidazol-2-ylidene)(dicarbonyl)-chlorodifluoroiridium(III) (15). The title compound was prepared in a similar manner to that described for **13**. Once reaction was deemed complete, the FEP tube was either heat sealed for NMR studies, or the solvent removed *in vacuo*, affording [IrF₂Cl(IMes)(CO)₂] **(15)** as an air-sensitive pale yellow powder. NMR spectra were recorded at −60 °C. Anal. Calc. for C₂₃H₂₄ClF₂IrN₂O₂: C, 44.10, H, 3.86, N, 4.47. Found: C, 44.11, H, 3.74, N, 4.41. v_{max}/cm⁻¹ 2050 (CO), 1969 (CO), 1485 s 850 s, 705s. ¹H NMR (CDCl₃): 7.20 (s, 2H, NC*H*C*H*N), 6.95 (s, 4H, Ar*H*), 2.28 (s, 6H, *para*-C*H₃*), 2.14 (s, 12H, *ortho*-C*H₃*). ¹⁹F{¹H} NMR (CDCl₃): −311.3 (d, $^2J_{FF}$ = 121 Hz, Ir*F* {F-*trans*-CO}), −397.4 (d, $^2J_{FF}$ = 121 Hz, Ir*F* {F-*trans*-Cl}).

(1,3-Bis{2,6-diisopropylphenyl}imidazol-2-ylidene)(dicarbonyl)-chlorodifluoroiridium(III) (16). The title compound, an air-sensitive pale yellow powder, was isolated in a similar manner to that described for **13**. NMR spectra were recorded at −60 °C. Anal. Calc. for C₂₉H₃₆ClF₂IrN₂O₂: C, 49.02, H, 5.11, N, 3.94. Found: C, 48.96, H, 5.00, N, 3.91. v_{max}/cm⁻¹ 2964 s, 2146 s (CO), 2056 s (CO), 1460 s, 800 s, 755 s, 708s. ¹H NMR (CDCl₃): 7.46 (t, 2H, $^3J_{HH}$ = 7.6 Hz, *para*-C*H*), 7.25 (d, 4H, $^3J_{HH}$ = 7.6 Hz, *meta*-C*H*), 7.03 (s, 2H, NC*H*C*H*N), 2.75 (m, 4H, CH₃C*H*), 1.27 (d, 12H, $^3J_{HH}$ = 6.8 Hz, C*H₃*CH), 1.05 (d, 12H, $^3J_{HH}$ = 6.8 Hz, C*H₃*CH). ¹⁹F{¹H} NMR (CDCl₃): −307.9 (d, $^2J_{FF}$ = 122 Hz, Ir*F* {F-*trans*-CO}), −400.3 (d, $^2J_{FF}$ = 123 Hz, Ir*F* {F-*trans*-Cl}).

Difluoro(ethyldiphenylphosphine)(1,3-bis{2,4,6-trimethylphenyl}imidazol-2-ylidene)(dicarbonyl)iridium tetrafluoroborate (17). The title compound, an air-sensitive pale yellow powder, was isolated in a similar manner to that described for **13**. Repeated attempts to obtain satisfactory elemental analysis data for **17** were unsuccessful due to the air sensitivity. NMR spectra were recorded at −60 °C. v_{max}/cm⁻¹ 2924w, 2090 s (CO), 2067 s (CO), 1986br (CO), 1483 s, 1435 s, 1051 s ([BF₄]⁻), 741 s, 690s. ¹H NMR (CDCl₃):

7.61–7.03 (m, 16H, Ar*H* and NC*H*C*H*N), 2.65 (m, 2H, PC*H₂*), 2.43–1.95 (m, 18H, C*H₃*), 1.10–0.92 (m, 3H, PCH₂C*H₃*). ¹⁹F{¹H} NMR (CDCl₃): −152.2 (s, [B*F₄*]⁻) −328.6 (d, $^2J_{PF}$ = 36 Hz, Ir*F₂*, F-*trans*-CO isomer), −521.8 (d, $^2J_{PF}$ = 20 Hz, Ir*F₂*, F-*trans*-F isomer). ³¹P{¹H} NMR (CDCl₃): −2.9 (t, $^2J_{PF}$ = 36 Hz, Ir*P₂*, F-*trans*-CO isomer), −22.1 (t, $^2J_{PF}$ = 20 Hz, Ir*P₂*, F-*trans*-F isomer). *m/z* (FAB) 805 ([M-BF₄]⁺), 785 ([M-HF-BF₄]⁺), 777 ([M-CO-BF₄]⁺), 767 ([M-2F-BF₄]⁺), 758 ([M-CO-HF-BF₄]⁺).

Difluoro(phenylethynyldiphenylphosphine)(1,3-bis{2,4,6-trimethylphenyl}imidazol-2-ylidene)(dicarbonyl)iridium tetrafluoroborate (18). The title compound, an air-sensitive pale yellow powder, was isolated in a similar manner to that described for **13**. NMR spectra were recorded at −60 °C. Anal. Calc. for C₄₃H₃₉BF₆IrN₂O₂P: C, 53.56, H, 4.08, N, 2.91. Found: C, 53.49, H, 4.13, N, 2.93. v_{max}/cm⁻¹ 2168 s (CC), 2084 s (CO), 1994 s (CO), 1479 s, 1438 s, 1052 s ([BF₄]⁻) 853 s, 752 s, 685s. ¹H NMR (CDCl₃): 7.75–7.20 (m, 19H, Ar*H*), 7.18 (s, 2H, NC*H*C*H*N), 2.38–1.89 (m, 18H, C*H₃*). ¹⁹F{¹H} NMR (CDCl₃): −152.7 (s, [B*F₄*]⁻), −335.0 (d, $^2J_{FP}$ = 42 Hz, Ir*F₂* {F-*trans*-CO}); −517.3 (d, $^2J_{FP}$ = 25 Hz, Ir*F₂* {F-*trans*-F}). ³¹P{¹H} NMR (CD₂Cl₂): −42.9 (t, $^2J_{PF}$ = 25 Hz, Ir*P₂* {F-*trans*-F}), −36.3 (t, $^2J_{PF}$ = 42 Hz, Ir*P₂* {F-*trans*-CO}). *m/z* (FAB) 877 ([M-BF₄]⁺), 857 ([M-HF-BF₄]⁺), 839 ([M-2F-BF₄]⁺), 829 ([M-HF-CO-BF₄]⁺).

Difluoro(pyridine)(1,3-bis{2,4,6-trimethylphenyl}imidazol-2-ylidene)(dicarbonyl)iridium tetrafluoroborate (19). The title compound, an air-sensitive pale yellow powder, was isolated in a similar manner to that described for **13**. NMR spectra were recorded at −60 °C. Anal. Calc. for C₂₈H₂₉BF₆IrN₃O₂: C, 44.02, H, 3.86, N, 5.55. Found: C, 44.07, H, 3.91, N, 5.43. v_{max}/cm⁻¹ 2924w, 2062 s (CO), 1483 s, 1454 s, 1030 s ([BF₄]⁻), 761 s, 697s. ¹H NMR (CDCl₃): 8.10–7.25 (m, 9H, Ar*H*), 7.20 (s, 2H, NC*H*C*H*N), 2.36–1.97 (m, 18H, C*H₃*). ¹⁹F{¹H} NMR (CDCl₃) −151.9 (s, [B*F₄*]⁻), −318.9 (s, Ir*F₂* {F-*trans*-CO}), −455.1 (s, Ir*F₂* {F-*trans*-F}). *m/z* (FAB) 650 ([M-HF-BF₄]⁺), 632 ([M-2F-BF₄]⁺), 622 ([M-HF-CO-BF₄]⁺).

Difluoro(pyridine)(1,3-bis{2,6-diisopropylphenyl}imidazol-2-ylidene)(dicarbonyl)iridium tetrafluoroborate (20). The title compound, an air-sensitive pale yellow powder, was isolated in a similar manner to that described for **13**. NMR spectra were recorded at −60 °C. Anal. Calc. for C₃₄H₄₁BF₆IrN₃O₂: C, 48.54, H, 4.92, N, 5.00. Found: C, 48.41, H, 4.79, N, 4.97. v_{max}/cm⁻¹ 2969 s, 2056 s (CO), 1978 s (CO), 1452 s, 1051 s ([BF₄]⁻), 758 s, 697s. ¹H NMR (CDCl₃): 8.12 (m, 2H, Ar*H*), 7.91 (m, 2H, Ar*H*), 7.50–7.03 (m, 7H, Ar*H*), 7.19 (s, 2H, NC*H*C*H*N), 2.48 (m, 2H, CH₃C*H*), 2.29 (m, 2H, CH₃C*H*), 1.32–1.09 (m, 24H, C*H₃*CH). ¹⁹F{¹H} NMR (CDCl₃) −151.3 (s, [B*F₄*]⁻), −303.4 (s, Ir*F₂* {F-*trans*-CO}), −458.1 (s, Ir*F₂* {F-*trans*-F}).

Difluoro(pyridine)(1,3-bis{2,4,6-trimethylphenyl}imidazol-2-ylidene)(cyclo-octa-1,5-diene)iridium tetrafluoroborate (21). The title compound was isolated in a similar manner to that described for **13**. NMR spectra were recorded at −60 °C. v_{max}/cm⁻¹ 2919w, 1483 s, 14492, 1029vs ([BF₄]⁻), 761 s, 699s. ¹H NMR (CDCl₃): 8.50 (m, 2H, Ar*H*), 8.02 (m, 2H, Ar*H*), 7.44 (m, 1H, Ar*H*), 6.88 (m, 6H, Ar*H* and NC*H*C*H*N), 5.88 (br s, 2H, COD-C*H*), 4.94 (br s, 2H, COD-C*H*), 2.40–1.80 (m, 26H, C*H₃* and COD-C*H₂*). ¹⁹F{¹H} NMR (CDCl₃) −152.3 (s, [B*F₄*]⁻), −425.2 (s, Ir*F₂*). *m/z* (FAB) 722 ([M]⁺).

Table 4 Crystallographic and data processing parameters^a for (**5**), (**6**), (**8**), (**9**) and (**11**)

Complex	(**5**)	(**6**)	(**8**)	(**9**)	(**11**)
Formula	$C_{43}H_{47}BF_4IrN_2P$	$C_{49}H_{51}BF_4IrN_2P$	$C_{83}H_{104}B_2Cl_6F_8Ir_2N_6$	$C_{37.5}H_{39.5}BCl_{1.5}F_4IrN_2O_2P$	$C_{28}H_{29}BF_4IrN_3O_2$
M	901.81	977.90	1956.44	913.37	718.55
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P2_12_12_1$	P1	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
a/Å	11.9712(16)	10.3704(17)	11.0104(17)	8.472(13)	10.8033(18)
b/Å	15.996(2)	13.371(2)	19.823(3)	15.20(2)	15.976(3)
c/Å	19.958(3)	15.841(3)	21.835(3)	16.07(2)	16.117(3)
α (°)	90	87.867(3)	66.828(2)	81.60(2)	90
β (°)	90	75.097(2)	78.610(2)	76.57(2)	90
γ (°)	90	89.756(3)	78.803(2)	76.53(2)	90
U/Å^3	3821.7(9)	2121.1(6)	4258.9(11)	1948(5)	2781.7(8)
Z	4	2	2	2	4
D_c/g cm^{-3}	1.567	1.531	1.526	1.557	1.716
μ(Mo-Kα)/mm^{-1}	3.589	3.240	3.373	3.624	4.857
$F(000)$	1808	984	1964	906	1408
Crystal size/mm	$0.08 \times 0.15 \times 0.17$	$0.30 \times 0.24 \times 0.11$	$0.29 \times 0.19 \times 0.18$	$0.36 \times 0.27 \times 0.13$	$0.37 \times 0.11 \times 0.09$
Theta range (°)	1.63 to 27.00	1.52 to 26.00	1.78 to 27.00	1.31 to 27.00	1.79 to 27.00
Index Ranges	$-15 \le h \le 15$	$-12 \le h \le 12$	$-13 \le h \le 14$	$-10 \le h \le 10$	$-13 \le h \le 13$
	$-20 \le k \le 20$	$-16 \le k \le 16$	$-25 \le k \le 25$	$-19 \le k \le 18$	$-20 \le k \le 20$
	$-25 \le l \le 25$	$-19 \le l \le 19$	$-27 \le l \le 27$	$-19 \le l \le 20$	$-20 \le l \le 19$
Reflections collected	32446	16617	35820	16473	23340
Independent reflections	8344	8227	18210	8374	6030
R_{int}	0.0489	0.0244	0.0261	0.0713	0.0433
Max. and min. transmission	0.7115 and 0.8621	0.928 and 0.651	0.861 and 0.620	0.928 and 0.467	0.862 and 0.503
Restraints/parameters	0/476	0/528	0/989	0/440	0/385
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0310$	$R_1 = 0.0270,$	$R_1 = 0.0355,$	$R_1 = 0.0455$	$R_1 = 0.0258$
	$wR_2 = 0.0536$	$wR_2 = 0.0643$	$wR_2 = 0.0932$	$wR_2 = 0.1235$	$wR_2 = 0.0528$
All data	$R_1 = 0.0370$	$R_1 = 0.0296,$	$R_1 = 0.0447,$	$R_1 = 0.0504$	$R_1 = 0.0295$
	$wR_2 = 0.0551$	$wR_2 = 0.0654$	$wR_2 = 0.0970$	$wR_2 = 0.1406$	$wR_2 = 0.0535$
Goodness of fit of F^2 (all data)	0.913	1.008	1.028	1.175	0.976
Largest diff. peak and hole/e Å^{-3}	1.208 and -0.568	1.369 and -0.937	2.467 and -0.945	2.844 and -2.785	1.846 and -1.027

^{a} Data in common: graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å; $R_1 = \sum\|F_o\| - |F_c\|/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2]$, $P = [\max(F_o^2,0) + 2(F_c^2)]/3$, where a is a constant adjusted by the program; goodness of fit $= [\sum(F_o^2 - F_c^2)2/(n - p)]^{1/2}$ where n is the number of reflections and p the number of parameters.

Crystallography

Single crystals of **5**, **6** and **8** were grown by careful layering of DCM–hexane solutions evaporation, crystals of **9** by slow evaporation of a saturated chloroform solution and crystals of **11** by slow vapour diffusion of a hexane into a saturated DCM solution. Data for each of the crystals were collected on a Bruker APEX 2000 CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Details of data collection, refinement and crystal data are listed in Table 4. Data for the cyclometallated IMes complex, [IrF(IMes)(CO)$_2$(PPh$_2$Et)]$^+$[BF$_4$]$^-$, were collected similarly, but were not stable to full anisotropic refinement. The data were corrected for Lorentz and polarization effects and empirical corrections applied. The structures were solved by direct methods. The structure refinement on F^2 employed SHELXTL VERSION 6.10.[33] Hydrogen atoms were included in calculated positions (C–H = 0.93–0.98 Å) riding on the bonded atom with isotropic displacement parameters set to 1.5 U_{eq}(C) for methyl H atoms and 1.2 U_{eq}(C) for all other H atoms. All non-H atoms were refined with anisotropic displacement parameters. Disordered solvent was omitted using the SQUEEZE option in Platon[34] for [**9** (0.5 CHCl$_3$)].

Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary information CCDC numbers 723140–723144.‡ 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).

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