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Bis-Cyclometalation of Fluorinated N-Aryl NHCs

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ABSTRACT: The new imidazolium salts *N*,*N*'-bisfluoroarylimidazolium chloride (fluoroaryl = 4-fluorophenyl (1), 2,4-difluorophenyl (2), 2,4,6-trifluorophenyl (3)) have been prepared by the one-pot condensation of the appropriate aniline with glyoxal and formaldehyde. Reaction of the salts (1, 2) with $[RuF_2(CO)_3]_4$ and $[IrF_3(CO)_3]$ in the presence of KO^tBu generated the bis-cyclometalated carbene carbonyl complexes $[IrCl(CO){\eta^2-1-(C_6H_4-4-F)-3-(C_6H_3-4-F)C_3H_2N_2}_2]$ (4), $[Ru(CO)_2{\eta^2-1-(C_6H_4-4-F)-3-(C_6H_3-4-F)C_3H_2N_2}_2]$ (5), and $[Ru(CO)_2{\eta^2-1-(C_6H_3-2,4-F_2)-3-(C_6H_2-2,4-F_2)-C_3H_2N_2}_2]$ (6), which have been structurally characterized.



INTRODUCTION

The fine-tuning of N-heterocyclic carbene ligands (NHCs), directed toward optimization of the catalytic activity of transition metal complexes in a host of chemical reactions, has led to the construction of a wealth of mono- and bidentate aryl and alkyl carbenes.¹⁻³ In the closely related field of phosphine ligands, the significant steric and electronic impact of fluorine and fluorinated substituents on the ligand and metal complex properties has been extensively studied. Therefore, it is somewhat surprising that the number of reports of fluorinesubstituted NHC ligands is extremely limited, with the first reports only appearing in 2005 (Figure 1). For example, Whittlesey describes transfer of the 1-pentafluorobenzyl-3methylimidazol-2-ylidene ligand from silver to generate fourcoordinate rhodium and iridium carbonyl complexes, where the electronic impact of the C_6F_5 unit is visible in the $\nu(CO)$ data.⁴ Grubbs describes rate acceleration in olefin metathesis arising from a Ru…F intramolecular interaction between one ring of a N,N'-bis(2,6-difluorophenyl)imidazol-2-ylidene and the metal center in the Grubbs II catalyst analogue.^{5,6} This work has been extended with studies of synthesis and catalytic activities of the closely related asymmetric N-2,6-difluorophenyl/N-mesityl,^{7,8} N-2,6-difluorophenyl/N-2,6-diisopropylphenyl,9 N-2,4,6-trifluorophenyl/N-mesityl,9 and N-pentafluorophenyl/N-mesityl9 Grubbs II catalyst analogues.

Part of this lack of investigation appears to stem from the synthetic routes to these derivatives as indicated by Plenio,¹⁰ where the failure to form N,N'-bis(2,6-dimethyl-4-trifluoromethylphenyl)imidazol-2-ylidene was ascribed to the strongly electron-withdrawing influence of the trifluoromethyl unit, although the related N,N'-bis(2,6-dimethyl-4-fluorophenyl)imidazolium salt and related Grubbs II catalyst analogue have subsequently been prepared as part of a wider study of the electronic impact of N-aryl substituents on catalytic activity.¹¹ We have a long-standing interest in the synthesis and chemistry of fluorine-containing ligands^{12–15} and recently reported work on fluoroaryl α -diimine ligands.¹⁶ In addition, we have recently described the first late transition metal NHC

difluoro-ruthenium¹⁷ and -iridium¹⁸ complexes. Here, we outline the synthesis of three new fluoroaryl NHCs and their reactivity toward late transition metal fluoride complexes.

RESULTS AND DISCUSSION

Initial attempts to synthesize new fluorine-containing imidazolium salts centered on the standard one-pot condensation¹⁹ of the desired aniline with glyoxal and *para*-formaldehyde. However, all attempts to react fluorinated anilines (4-FC₆H₄NH₂, 2,4-F₂C₆H₃NH₂, 2,4,6-F₃C₆H₂NH₂) with glyoxal and *para*-formaldehyde failed, with the anilines recovered at the end of the reaction. This is entirely consistent with the reduced nucleophilicity associated with increased fluorine content.²⁰ However, a mild modification of the literature route, essentially prolonged heating of the reaction mixture, facilitated reaction to give the new fluorinated imidazolium chlorides {[1,3-Ar^F₂C₃H₃N₂]⁺CΓ} (1–3) as hygroscopic white solids in high yield (Scheme 1).

Compounds 1–3 were characterized by multinuclear NMR spectroscopies, IR spectroscopy, mass spectrometry, and elemental analysis. As might be anticipated, the fluorine-bearing aromatic carbons appeared substantially deshielded in the ¹³C NMR spectra ($\delta \sim 163$) when compared to their hydrogenbearing congeners ($\delta \sim 125$) and exhibited strong couplings to the halogen (~ 250 Hz), typical of a ¹J_{CF} coupling constant.²¹ The acidic NCHN protons of the salts were clearly visible in the ¹H NMR spectra, typically appearing around δ 10.5–11.0, giving clear evidence of the impact of the fluorine substituents on these species, the related signals for the *N*,*N*'-bis-2,4,6-trimethylphenylimidazolium and *N*,*N*'-bis-2,6-diisopropylphenylimidazolium chlorides appearing at δ 9.22 and 9.63, respectively.¹⁹

An alternative route to imidazolium salts involves the ring closure of aryl α -diimines with one-carbon block units, which

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Figure 1. Some examples of previously reported fluorine-substituted NHC ligands.

Scheme 1



Scheme 2



often provides higher yields than the one-pot condensation protocol.¹⁹ We have recently reported the synthesis of some fluorinated aryl α -diimines ([C₆H_{5-x}F_xNCH]₂; x = 1, 2, 3),¹⁶ but reaction of these fluorinated imines with chloromethyl ethyl ether or dibromomethane did not occur even under forcing conditions, the imines being recovered intact in quantitative yields after the procedure. In addition, attempts to generate free carbenes by the deprotonation of the imidazolium salts (1-3)using KO^tBu in THF, according to the literature procedure,¹⁹ were similarly unsuccessful. Analysis of the reaction mixtures by multinuclear NMR spectroscopy revealed no resonances due to the acidic NCHN protons of the chloride salts, suggesting that deprotonation may have occurred. However, a significant number of fluorine-containing products were present, indicating substantial product decomposition, and no single product could be isolated. Collectively, these results indicate that the electronegative fluorine substituents are influencing the chemistry of these imidazolium salts in comparison to that

observed for the wide range of established *N*-aryl carbene systems. However, we note that in Grubbs's work on the fluorophenylcarbene ruthenium catalysts the free carbene was not isolated, $^{5-9}$ and we continued our investigations in a similar fashion using reactions of the imidazolium salts with metal complexes in the presence of base.

Phosphine ligands undergo facile reactions with $[IrF_3(CO)_3]$;²² however, in contrast to the air- and moisturestable ruthenium(II) and osmium(II) fluoride complexes $[MF_2(CO)_2(\text{phosphine})_2]$,²³ the iridium(III) products, $[IrF_3(CO)(\text{phosphine})_2]$, rapidly decompose in solution and in the solid state, even at low temperatures.²² We reasoned that NHCs, in view of the improved σ -donor and differing steric properties, might provide alternative supporting ligands that confer additional stability on this class of complex. Unfortunately, attempts to react $[IrF_3(CO)_3]$ with either 2 or 3 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. In contrast, on reaction with the electronically less demanding 1 in the presence of $K^+O^tBu^-$ in THF,^{24,25} $[IrF_3(CO)_3]$ afforded a stable, pale yellow, solution, from which a white solid could be obtained (Scheme 2). IR spectroscopy revealed the anticipated single $\nu(CO)$ resonance, while the complicated ¹H NMR spectrum clearly indicated loss of the NCHN resonance of 1 and coordination of the carbene ligand. Unfortunately, ¹⁹F NMR spectroscopy revealed no evidence for any metal-bound fluoride ligands; rather, four distinct aryl-F resonances were observed, two virtually unshifted from those for the starting material and two shifted by ca. 6 ppm downfield. The single reaction product is $[IrCl(CO)\{\eta^2 - 1 - (C_6H_4 - 4 - F) - 3 - (C_6H_3 - 4 - F)C_3H_2N_2\}_2] \quad (4)$ (Scheme 2), involving bis-cyclometalation at the iridium(III) center, with the final coordination sites occupied by carbonyl and chloride ligands, the latter presumably arising from reaction with the chloride ion of the imidazolium salt. It is tempting to presume that the cyclometalation arises from coordination of the carbene to the iridium carbonyl fluoride center followed by 1,2 CH bond activation²⁶ and H-F elimination, but we were unable to spectroscopically identify any intermediates to support this idea. The structure was confirmed in solution by COSY, HMQC, TOCSY, and NOESY NMR studies, allowing assignment of the four inequivalent fluorine resonances and the 14 inequivalent aryl proton environments (Experimental Section; Scheme 2), and the molecular composition was confirmed through mass spectrometry and elemental analysis.

We have recently reported the generation of $[RuF_2(CO)_2(NHC)_2]$ (NHC = IMes, IPr) from the reaction of $[RuF_2(CO)_3]_4$ with the appropriate imidazolium salt in the presence of KO^tBu.¹⁷ Attempts to react 3 in a similar fashion with $[RuF_2(CO)_3]_4$ were unsuccessful. However, both 1 and 2 did react to give single reaction products, with the expected two IR-active $\nu(CO)$ stretching vibrations and with the molecular compositions confirmed through elemental analysis and mass spectrometry. As seen in the iridium(III) reaction, ¹⁹F NMR spectroscopy did not reveal any resonances characteristic of metal-bound fluoride ligands. However, two sets of aryl-F resonances (unshifted and ca. 10 ppm downfield shifted) and extensive 2D NMR studies confirmed that bis-cyclometalation at the ruthenium(II) centers had again occurred to yield $[Ru(CO)_{2}\{\eta^{2}-1-(C_{6}H_{4}-4-F)-3-(C_{6}H_{3}-4-F)C_{3}H_{2}N_{2}\}_{2}]$ (5) and $\left[\operatorname{Ru}(\operatorname{CO})_{2}\left\{\eta^{2}-1-\left(\operatorname{C}_{6}\operatorname{H}_{3}-2,4-\operatorname{F}_{2}\right)-3-\left(\operatorname{C}_{6}\operatorname{H}_{2}-2,4-\operatorname{F}_{2}\right)\operatorname{C}_{3}\operatorname{H}_{2}\operatorname{N}_{2}\right\}_{2}\right] (6),$ respectively (Scheme 2). Here, symmetry renders the two cyclometalated ligands equivalent, leading to two fluorine resonances and seven aryl proton resonances for 5 and four fluorine resonances and five aryl proton resonances for 6.

Confirmation of the assignments for 4, 5, and 6 comes from single crystal X-ray structure determinations for crystals grown by slow diffusion of hexane into saturated dichloromethane solutions. The molecular structures are shown in Figures 2–4. For 5 there are two, virtually identical molecules in the unit cell, but there is no correlation between them in the $P\overline{1}$ space group. For 6 the *ortho*-fluorine atoms on the "free" *N*-aryl rings are disordered (50:50) between two sites. All three complexes adopt distorted octahedral geometries, with *trans*-carbene ligands and *cis*-orthometalated rings, the two cyclometalated rings and the two heterocyclic rings thereby being mutually perpendicular. The metal–NHC distances are very similar (2.043(4) to 2.062(3) Å), consistent with the single-bond character typical for metal–carbene complexes.²⁷ The metal– aryl and metal–carbonyl distances for the two ruthenium(II)



Figure 2. Molecular structure of 4 with 50% displacement ellipsoids and a partial atom label scheme; H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir(1)-C(1), 2.043(4); Ir(1)-C(16), 2.055(4); Ir(1)-C(9), 2.083(4); Ir(1)-C(24), 2.047(4); Ir(1)-C(31), 1.939(4); Ir(1)-Cl(1), 2.4587(11); C(31)-O(1), 1.089(5); C(1)-Ir(1)-C(16), 165.56(14); C(9)-Ir(1)-C(31), 178.30(15); Cl(1)-Ir(1)-C(24), 174.54(10); C(1)-Ir(1)-C(9), 77.86(14); C(16)-Ir(1)-C(24), 78.96(15).



Figure 3. Molecular structure of one of the unique molecules of 5 with a partial atom label scheme and 50% displacement ellipsoids; H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)-C(1), 1.907(5); Ru(1)-C(2), 1.914(5); Ru(1)-C(3), 2.043(4); Ru(1)-C(18), 2.050(5); Ru(1)-C(6), 2.117(5); Ru(1)-C(21), 2.122(4); C(1)-O(1), 1.149(5); C(2)-O(2), 1.143(5); C(3)-Ru(1)-C(18), 161.80(18); C(1)-Ru(1)-C(6), 168.07(18); C(2)-Ru(1)-C(21), 174.65(19); C(3)-Ru(1)-C(6), 77.40(18); C(18)-Ru(1)-C(21), 78.35(17).



Figure 4. Molecular structure of **6** with 50% displacement ellipsoids and a partial atom label scheme; H atoms are omitted for clarity. The fluorine atoms F8/F8' and F4/F4' represent the 50:50 disorder between *ortho*-sites in two of the aryl rings. Selected bond lengths (Å) and angles (deg): Ru(1)–C(1), 1.924(3); Ru(1)–C(2), 1.903(3); Ru(1)–C(3), 2.063(3); Ru(1)–C(18), 2.052(3); Ru(1)–C(7), 2.122(3); Ru(1)–C(22), 2.118(3); C(1)–O(1), 1.132(3); C(2)– O(2), 1.146(3); C(3)–Ru(1)–C(18), 161.90(10); C(1)–Ru(1)– C(22), 174.66(10); C(2)–Ru(1)–C(7), 172.14(10); C(3)–Ru(1)– C(7), 77.35(10); C(18)–Ru(1)–C(22), 77.20(10).

complexes 5 and 6 are also statistically invariant. For 4, the metal-aryl bond lengths are asymmetric, in line with the different *trans*-influence of the chloride and carbonyl ligands, and are shorter than those for the ruthenium complexes as a consequence of the higher formal oxidation state for iridium. The $C_{aryl}-M-C_{carbene}$ angles within the metallocycles are very similar and comparable to that seen for other orthometalated arylcarbene metal complexes.²⁸⁻³² The $C_{carbene}-M-C_{carbene}$ angles display marked distortions from linearity, being more pronounced for the ruthenium complexes than the iridium complex, presumably due to the steric constraints of metallocycle formation.

CONCLUSIONS

Prolonged heating and reaction times allows the formation of fluoroaryl-imidazolium salts from a one-pot condensation of glyoxal, formaldehyde, and the respective fluorinated aniline. Various experimental observations, including the inability to isolate the related free NHCs, indicate that the fluorine substituents do influence the chemistry of these systems. Attempts to react the N,N'-bis(2,4,6-trifluorophenylimidazo-lium) salt with ruthenium and iridium carbonyl fluoride reagents failed. However, coordination of the related 4-fluorophenyl- and 2,4-difluorophenylcarbenes, with concomitant aryl C–H bond activation, to both iridium and ruthenium afforded new bis-cyclometalated metal carbene derivatives.

EXPERIMENTAL SECTION

All reactions, unless otherwise stated, were carried out under an atmosphere of dry, oxygen-free nitrogen, using standard Schlenk line or metal vacuum line techniques or in a nitrogen-purged drybox. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use.³³ $[IrF_3(CO)_3]^{22}$ and $[RuF_2(CO)_3]_4^{34}$ were prepared by the literature routes. The reagents 4-fluoroaniline, 2,4difluoroaniline, and 2,4,6-trifluoroaniline were purchased from Fluorochem and were distilled before use; para-formaldehyde and glyoxal were purchased from Aldrich Chemical Co. and used without further purification. All other chemicals were obtained commercially and used without further purification. ¹H, ¹³C, and ¹⁹F NMR spectroscopies were carried out on a Bruker DRX400 spectrometer at 400.13, 100.16, and 376.46 MHz, respectively, and were referenced to external SiMe₄ (¹H, ¹³C) and to external CFCl₃ (¹⁹F). Elemental analyses were performed at the Science Technical Support Unit, 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.

1,3-Bis(4-fluorophenyl)imidazolium Chloride (1). A solution of 4-fluoroaniline (15.000 g, 135 mmol) in toluene (15 mL) was added dropwise to a stirred suspension of para-formaldehyde (2.054 g, 68 mmol) in toluene (50 mL). After addition was complete, the suspension was heated to 100 °C for 1 h, dissolving all the solids. The resulting solution was allowed to cool to 40 °C, whereupon a solution of glyoxal (9.890 g of a 40% aqueous solution, 68 mmol) in toluene (10 mL) was slowly added. The solution was stirred for an additional 5 min at this temperature, before HCl (22.6 mL of a 3 M HCl solution, 68 mmol) was added dropwise. The solution was then reheated to 100 °C and maintained at this temperature for 8 h. After cooling to room temperature, all volatiles were removed in vacuo, giving a dark precipitate. Repeated recrystallization from DMSO/ diethyl ether gave 1 as a hygroscopic white powder (13.530 g, 68%). Mp: 267–268 °C. Anal. Calcd for C₁₅H₁₁ClF₂N₂: C, 61.53, H 3.79, N, 9.57. Found: C, 61.58, H, 3.70, N, 9.37. IR: ν_{max}/cm⁻¹ 3028br, 1556s, 1508s, 1459w, 1232s, 837br. ¹H NMR (DMSO): 10.97 (s, 1H, NCHN), 8.83 (br s, 2H, NCHCHN), 8.29 (m, 2H, 3-CH), 7.63 (t, ${}^{3}J_{\rm HH}$ = 8.7 Hz, 2-CH). ${}^{13}C{}^{1}H$ NMR (DMSO): 162.5 (d, ${}^{1}J_{\rm CF}$ = 248 Hz, 4-C), 135.3 (s, NCHN), 131.4 (d, ${}^{4}J_{CF} = 3$ Hz, 1-C), 124.8 (d, ${}^{3}J_{CF} = 9$ Hz, 2-C), 122.4 (s, NCHCHN), 117.2 (d, ${}^{2}J_{CF} = 24$ Hz, 3-C). ¹⁹F{¹H} NMR (DMSO): -111.0 (s, 4-CF). MS m/z (FAB): 257 ([M - Cl]⁺, 72%). Acc. Mass: C₁₅H₁₁F₂N₂ ([M - Cl]⁺), requires 257.08903, found 257.08905.

1,3-Bis(2,4-difluorophenyl)imidazolium Chloride (2). This was prepared as a hygroscopic white powder in a similar manner (13.405 g, 60%). Mp: 293–295 °C. Anal. Calcd for $C_{15}H_9ClF_4N_2$: C, 54.79, H 2.76, N, 8.52. Found: C, 54.62, H, 2.84, N, 8.63. IR: ν_{max}/cm^{-1} 2995w, 1554s, 1498s, 1274w, 1155s, 1068s, 974s, 803s, 652s. ¹H NMR (DMSO): 10.43 (s, 1H, NCHN), 8.50 (br s, 2H, NCHCHN), 8.18 (m, 2H, ArH), 7.82 (m, 2H, ArH), 7.49 (m, 2H, ArH). ¹⁹F{¹H} NMR (DMSO): -105.5 (d, 2F, ⁴J_{FF} = 8.8 Hz, 4-CF), -118.5 (d, 2F, ⁴J_{FF} = 8.8 Hz, 2-CF). MS m/z (FAB): 293 ([M - Cl]⁺, 100%). Acc. Mass: $C_{15}H_9F_4N_2$ ([M - Cl]⁺, requires 293.07013, found 293.07019.

1,3-Bis(2,4,6-trifluorophenyl) imidazolium Chloride (3). This was prepared as a hygroscopic white powder in a similar manner (14.892 g, 60%). Mp: 325–328 °C (dec). Anal. Calcd for $C_{15}H_7ClF_6N_2$: C, 49.38, H 1.94, N, 7.68. Found: C, 49.48, H, 1.87, N, 7.59. IR: ν_{max}/cm^{-1} 3060br, 1616s, 1562s, 1495s, 1457s, 1258w, 1190w, 1133s, 996s, 897br. ¹H NMR (DMSO): 10.38 (s, 1H, NCHN), 8.51 (br s, 2H, NCHCHN), 7.78 (br s, 4H, 3-CH). ¹⁹F{¹H} NMR (DMSO): -101.8 (br s, 2F, 4-CF), -117.1 (br s, 4F, 2-CF). MS m/z (FAB): 329 ([M - Cl]⁺, 100%). Acc. Mass: $C_{15}H_7F_6N_2$ ([M - Cl]⁺), requires 329.05134, found 329.05131 Bis(η^2 -1,3-bis(4-fluorophenyl)imidazol-2-ylidene)-

Bis(η^2 -1,3-bis(4-fluorophenyl)imidazol-2-ylidene)carbonyliridium Chloride (4). 1,3-Bis(4-fluorophenyl)imidazolium chloride (0.680 g, 2.32 mmol) (1), potassium *tert*-butoxide (0.260 g, 2.32 mmol), and *fac*-[IrF₃(CO)₃] (0.091 g, 0.27 mmol) were stirred in dry tetrahydrofuran (50 mL) under nitrogen for 16 h. After removal of all volatiles *in vacuo*, the dark solid was recrystallized from

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Table 1. Crystal Data and Structure Refinement for Compounds 4-6

6
C IL ENO D

5

Article

formula	C ₃₇ H ₃₀ ClF ₄ IrN ₄ O ₃	$C_{32}H_{18}F_4N_2O_2Ru$	$C_{32}H_{14}F_8N_2O_2Ru$
М	882.30	667.57	739.54
temperature (K)	150(2)	150(2)	150(2)
cryst syst	triclinic	triclinic	triclinic
space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
a (Å)	10.851(2)	11.167(2)	9.800(2)
b (Å)	11.657(2)	13.402(2)	10.001(3)
c (Å)	14.243(3)	19.173(3)	14.635(4)
α (deg)	86.119(3)	80.490(3)	102.091(4)
β (deg)	71.898(3)	79.394(3)	96.820(4)
γ (deg)	79.698(3)	89.312(3)	92.092(4)
U (Å ³)	1684.5(6)	2781.0(9)	1389.8(6)
Ζ	2	4	2
$D_{\rm c} ({\rm g \ cm^{-3}})$	1.739	1.594	1.767
μ (Mo K α) (mm ⁻¹)	4.108	0.628	0.658
F(000)	868	1336	732
cryst size (mm ³)	$0.21 \times 0.16 \times 0.15$	$0.11\times0.10\times0.04$	$0.35\times0.14\times0.06$
theta range (deg)	1.78 to 27.00	1.10 to 26.00	1.43 to 26.00
index ranges	$-13 \le h \le 13$	$-13 \le h \le 13$	$-12 \le h \le 12$
	$-14 \le k \le 14$	$-16 \le k \le 16$	$-12 \le k \le 12$
	$-18 \le l \le 17$	$-23 \le l \le 22$	$-18 \le l \le 18$
reflns collected	14 195	21 646	10 813
indep reflns	7200	10 783	5384
R _{int}	0.0271	0.0490	0.0222
max. and min transmn	0.862 and 0.647	0.929 and 0.752	0.862 and 0.728
restraints/params	0/455	0/775	0/442
final R indices $(I > 2\sigma(I))$	$R_1 = 0.0283$	$R_1 = 0.0495$	$R_1 = 0.0327$
	$wR_2 = 0.0642$	$wR_2 = 0.0815$	$wR_2 = 0.0785$
all data	$R_1 = 0.0327$	$R_1 = 0.0905$	$R_1 = 0.0381$
	$wR_2 = 0.0654$	$wR_2 = 0.0911$	$wR_2 = 0.0907$
goodness of fit of F^2 (all data)	1.009	0.886	1.042
largest diff peak and hole (e $Å^{-3}$)	1.749 and -1.063	1.074 and -0.854	0.879 and -0.463

dichloromethane/hexane to give the product as a white powder (0.052 g, 25%). Anal. Calcd for C₃₁H₁₈ClF₄IrN₄O: C, 48.58; H, 2.37; N, 7.31. Found: C, 49.01; H, 1.78; N, 7.49. MS m/z (FAB): 766 ([M]⁺), 738 $([M - CO]^+)$, 731 $([M - Cl]^+)$, 703 $([M - CO - Cl]^+)$. IR: ν_{max} cm⁻¹ 3070w, 2022s, 1513s, 1469s, 1222s, 1189s, 948s, 836s, 800s, 694s. ¹H{¹⁹F} NMR (CD₂Cl₂): 7.85 (2H, m, H-26,30), 7.74 (1H, d, ${}^{3}J_{\rm HH}$ = 1.98 Hz, H-2), 7.64 (1H, d, ${}^{3}J_{\rm HH}$ = 1.98 Hz, H-17), 7.59 (2H, d, ${}^{3}J_{\rm HH}$ = 9.04 Hz, H-11,15), 7.40 (1H, d, ${}^{3}J_{\rm HH}$ = 2.00 Hz, H-3), 7.35 (1H, d, ${}^{3}J_{HH}$ = 1.99 Hz, H-18), 7.30 (2H, d, ${}^{3}J_{HH}$ = 8.97 Hz, H-27,29), 7.21 (4H, m, H-5,12,14,20), 6.70 (1H, m, H-21), 6.69 (1H, m, H-6), 6.24 (1H, d, ${}^{4}J_{HH}$ = 2.73 Hz, H-23), 6.14 (1H, d, ${}^{4}J_{HH}$ = 2.73 Hz, H-8). ¹H NMR (CD₂Cl₂): 7.85 (2H, m, H-26,30), 7.74 (1H, d, ${}^{3}J_{HH} = 1.98$ Hz, H-2), 7.64 (1H, d, ${}^{3}J_{HH}$ = 1.98 Hz, H-17), 7.59 (2H, d, ${}^{3}J_{HH}$ = 9.04 Hz, H-11,15), 7.40 (1H, d, ${}^{3}J_{HH}$ = 2.00 Hz, H-3), 7.35 (1H, d, ${}^{3}J_{HH}$ = 1.99 Hz, H-18), 7.30 (2H, m, H-27,29), 7.21 (4H, m, H-5,12,14,20), 6.70 (1H, m, H-21), 6.69 (1H, m, H-6), 6.24 (1H, dd, ${}^{3}J_{HF} = 8.98$ Hz, ${}^{4}J_{\rm HH}$ 2.73 Hz, H-23), 6.14 (1H, dd, ${}^{3}J_{\rm HF}$ = 8.87 Hz, ${}^{4}J_{\rm HH}$ = 2.73 Hz, H-8). ${}^{19}F{}^{1}H}$ NMR (CD₂Cl₂): -111.8 (1F, s, F-28), -113.0 (1F, s, F-28), -1 13), -117.2 (1F, s, F-22), -117.3 (1F, s, F-7).

Bis(η^2 -1,3-bis{4-fluorophenyl}imidazol-2-ylidene)-(dicarbonyl)ruthenium (5). (Tricarbonyl)ruthenium difluoride tetramer (0.250 g, 0.28 mmol), (1,3-bis(4-fluorophenyl)imidazolium chloride (1) (0.680 g, 2.32 mmol), and potassium *tert*-butoxide (0.260 g, 2.32 mmol) were loaded in a drybox into a preseasoned, with elemental fluorine (1 atm; 30 min), Kel-F pot (200 mL). THF (50 mL) was transferred into the reaction vessel, and the mixture stirred at room temperature for 10 h. All volatiles were removed *in vacuo*, and the crude reaction product was washed with methanol to afford **5** as moisture-sensitive colorless needles (0.200 g, 27%). Anal. Calcd for C₃₂H₁₈F₄N₄O₂Ru: C, 57.55; H, 2.70; N, 8.40. Found: C, 57.65; H, 2.72; N, 8.49. IR: ν_{max}/cm^{-1} 1988s (CO), 1933s (CO), 1508s, 1463s, 1220s, 1180s, 839s, 792s, 685s. MS *m/z* (FAB): 612 ([M – 2CO]⁺). ¹H{¹⁹F} NMR (CDCl₃): 7.69 (br s, 2H, H-2), 7.64 (d, 4H, ³J_{HH} = 8.7 Hz, H-12,14), 7.37 (br s, 2H, H-3), 7.28 (d, 4H, ³J_{HH} = 8.9 Hz, H-11,15), 7.14 (d, 2H, ³J_{HH} = 8.5 Hz, H-5), 6.60 (dd, 2H, ³J_{HH} = 8.8 Hz, ⁴J_{HH} = 2.2 Hz, H-6), 6.23 (d, 2H, ⁴J_{HH} = 2.2 Hz, H-8). ¹⁹F{¹H} NMR (CDCl₃): -112.9 (s, F-13), -119.5 (s, F-7). ¹³C{¹H} NMR (CDCl₃): 164.9 (br s, C-1), 162.7 (d, ¹J_{CF} = 249 Hz, C-13), 160.0 (d, ¹J_{CF} = 246 Hz, C-7), 142.7 (br s, C-9), 137.0 (br s, C-10), 128.8 (d, ²J_{CF} = 10 Hz, C-12,14), 124.0 (d, ²J_{CF} = 16 Hz, C-8), 122.7 (s, C-2), 116.4 (d, ³J_{CF} = 24 Hz, C-11,15), 115.7 (s, C-3), 111.7 (d, ³J_{CF} = 8 Hz, C-5), 108.6 (d, ²J_{CF} = 24 Hz, C-6).

Bis(η²-1,3-bis{2,4-difluorophenyl}imidazol-2-ylidene)-(dicarbonyl)ruthenium (6). This was prepared in a similar manner, using (tricarbonyl)ruthenium difluoride tetramer (0.250 g, 0.28 mmol), 1,3-bis(2,4-difluorophenyl)imidazolium chloride (2) (0.763 g, 2.32 mmol), and potassium *tert*-butoxide (0.260 g, 2.32 mmol). Washing the crude reaction product with methanol afforded **6** as moisture-sensitive colorless plates (0.830 g, 20%). Anal. Calcd for $C_{32}H_{14}F_8N_4O_2Ru: C, 51.95; H, 1.91; N, 7.58.$ Found: C, 52.03; H, 1.84; N, 7.54. IR: ν_{max} /cm⁻¹ 2011s (CO), 1952s (CO), 1611s, 1580s, 1513s, 1454s, 1334s, 1256s, 1144s, 1083s, 789s, 697s, 663s. MS: *m/z* (FAB) 684 ([M – 2CO]⁺). ¹H{¹⁹F} NMR (CDCl₃): 7.96 (br s, 2H, H-2), 7.47 (m, 2H, H-6), 7.16 (br s, 2H, H-3), 6.99 (m, 4H, H-14,15), 6.30 (m, 2H, H-12), 6.23 (d, 2H, ⁴J_{HH} = 1.9 Hz, H-8). ¹⁹F{¹H} NMR (CDCl₃): –106.2 (s, 2F, F-13), –116.2 (s, 4F, F-7,15), –126.2 (s, 2F, F-5).

X-ray Crystallography. Crystals of 4, 5, and 6 were grown by slow diffusion of hexane into saturated DCM solutions. Data were collected on a Bruker APEX 2000 CCD diffractometer using graphite-

monochromated Mo K α radiation, $\lambda = 0.71073$ Å. Data collection and refinement details are detailed in Table 1. 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 (SHELXTL, an integrated system for solving, refining, and displaying crystal structures).³⁵ Hydrogen atoms were included in calculated positions (C–H = 0.96 Å) riding on the bonded atom with isotropic displacement parameters set to $1.2U_{eq}$ (C). All non-H atoms were refined with anisotropic displacement parameters. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 847423–847425. 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 email: deposit@ccdc.cam.ac.uk).

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