**QUEEN'S
UNIVERSITY
BELFAST**

Orthometallation in iridium N-heterocycle stabilized carbene complexes via carbonhalogen and carbonhydrogen bond activation induced by silver nanoparticles

Marr, A. C., Saunders, G. C., Thomas, H. P., & Wang, Y. (2019). Orthometallation in iridium N-heterocycle stabilized carbene complexes via carbonhalogen and carbonhydrogen bond activation induced by silver nanoparticles. *Inorganica Chimica Acta*, 486, 1-7. <https://doi.org/10.1016/j.ica.2018.10.016>

Published in:
Inorganica Chimica Acta

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
[Link to publication record in Queen's University Belfast Research Portal](#)

Publisher rights

Copyright 2018 Elsevier B. V. All rights reserved.
This manuscript is distributed under a Creative Commons Attribution-NonCommercial-NoDerivs License (<https://creativecommons.org/licenses/by-nc-nd/4.0/>), which permits distribution and reproduction for non-commercial purposes, provided the author and source are cited.

General rights

Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Orthometallation in Iridium *N*-Heterocycle Stabilized Carbene Complexes via Carbon—Halogen and Carbon—Hydrogen Bond Activation induced by Silver Nanoparticles

Andrew C. Marr ^a, Graham C. Saunders ^{b,*}, Hayden P. Thomas ^b and Yue-Ming Wang ^a

^a *School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, United Kingdom*

^b *School of Science, University of Waikato, Private Bag 3105, Hamilton 3240, New Zealand*

Dedicated to Malcolm Green FRS, for his inspiration and guidance.

Abstract

On treatment with silver nanoparticles $[\text{Cp}^*\text{IrCl}_2(\kappa\text{C-MeNC}_3\text{H}_2\text{NCH}_2\text{C}_6\text{H}_4\text{F-2})]$ underwent C—H bond activation to afford the orthometallated product $[\text{Cp}^*\text{IrCl}(\kappa\text{C}^2\text{-MeNC}_3\text{H}_2\text{NCH}_2\text{C}_6\text{H}_3\text{F-6})]$ exclusively. The same product was obtained from $[\text{Cp}^*\text{IrCl}_2(\kappa\text{C-MeNC}_3\text{H}_2\text{NCH}_2\text{C}_6\text{H}_4\text{F}_2\text{-2,6})]$ by C—F bond activation. Treatment of $[\text{Cp}^*\text{IrCl}_2(\kappa\text{C-MeNC}_3\text{H}_2\text{NCH}_2\text{C}_6\text{H}_3\text{F-2-X-6})]$ ($\text{X} = \text{Cl, Br, I}$) with silver nanoparticles induced C—F and C—X bond activation to yield mixtures of the orthometallated products $[\text{Cp}^*\text{IrCl}(\kappa\text{C}^2\text{-MeNC}_3\text{H}_2\text{NCH}_2\text{C}_6\text{H}_3\text{F-6})]$ and $[\text{Cp}^*\text{IrCl}(\kappa\text{C}^2\text{-MeNC}_3\text{H}_2\text{NCH}_2\text{C}_6\text{H}_3\text{X-6})]$. The structures of the products, which are isostructural and co-crystallized, have been determined by single crystal X-ray diffraction.

1. Introduction

There have been a number of reports of $[\text{Cp}^*\text{IrX}_2(\text{NHC})]$ complexes undergoing cyclometallation reactions involving aromatic [1-4], aliphatic [2,5,6] and carborane carbon—hydrogen bond activation [7]. Although an early example, involving $[\text{Cp}^*\text{IrCl}_2(\kappa\text{C-MeNC}_3\text{H}_2\text{NCH}_2\text{C}_6\text{H}_5)]$, was reported to occur spontaneously [1], the reaction is typically induced by base, although acid induced C—H bond activation leading to a putative cyclometallated intermediate has also been reported [8].

Recently we reported the orthometallation of $[\text{Cp}^*\text{IrCl}_2(\kappa\text{C-MeNC}_3\text{H}_2\text{NCH}_2\text{C}_6\text{F}_5)]$ via carbon—fluorine bond activation on treatment with silver particles or nanoparticles [9]. In order to determine whether the combination of $[\text{Cp}^*\text{IrX}_2(\text{NHC})]$ and silver particles could also activate carbon—hydrogen and other carbon—halogen bonds we chose to investigate the 2-fluorophenylmethyl and 2-halo-6-fluorophenylmethyl analogues. Here we report the results of our study.

2. Experimental

2.1 Instrumentation

The ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{19}F NMR spectra were recorded in deuteriochloroform, except where stated otherwise, using Bruker DRX300 or DPX400 spectrometers. ^1H (300.13 or 400.14 MHz) were referenced internally using the residual proto solvent resonance relative to SiMe_4 (δ 0), ^{13}C (75.48 or 100.61 MHz) externally to SiMe_4 (δ 0), and ^{19}F (282.40 MHz) externally to CFCl_3 (δ 0). All chemical shifts are quoted in δ (ppm), using the high frequency positive convention, and coupling constants in Hz. Elemental analyses were carried out by the Campbell Microanalytical Laboratory, The University of Otago. Electrospray mass spectra were recorded on a Bruker Daltonics micrOTOF spectrometer.

2.2 Materials

The imidazolium salts [MeNC₃H₃NCH₂C₆H₃X-2-F-6]Br, X = F, Cl, Br and I [10], and [Cp*IrCl(μ -Cl)]₂ [11] were prepared as previously described. 1-Methylimidazole, silver(I) oxide (Aldrich) and 2-fluorobenzyl bromide (Apollo Scientific) were used as supplied.

2.3 Preparation of 1-(2-fluorophenylmethyl)-3-methylimidazolium bromide

1-Methylimidazole (1.55 g, 18.6 mmol) was added to 2-fluorobenzyl bromide (3.52 g, 18.6 mmol) in dichloromethane (80 cm³). The mixture was left at ambient temperature for 24 h. The solvent was removed by rotary evaporation yielding the product as a pale yellow oil. Yield *ca.* 5 g 100%. [M – Br]⁺: [C₁₁H₁₂FN₂]⁺ requires 191.0985; found 191.1032. δ_H (CDCl₃/(CD₃)₂SO): 9.89 (1H, s, N₂CH), 7.63 (1H, tm J = 7.6 Hz, C₆H), 7.59 (1H, dd, J = 4.7, 1.7 Hz, C₆H), 7.49 (1H, dd, J = 4.2, 1.4 Hz, C₆H), 7.34 (1H, m, HCCH), 7.13 (1H, m, HCCH), 7.05 (1H, tm, J = 9.2 Hz, C₆H), 5.55 (2H, s, CH₂), 3.96 (3H, d, J = 1.2 Hz, CH₃). δ_F (CDCl₃/(CD₃)₂SO): -117.34 (1F, dd, J_{HF} = 8.3, 6.9 Hz).

2.4 Preparation of (κ C-1-(2-fluorophenylmethyl)-3-methylimidazol-2-ylidene)silver bromide (**1a**)

Silver(I) oxide (0.121 g, 0.5210 mmol) was added to a solution of 1-(2-fluorophenylmethyl)-3-methylimidazolium bromide (0.215 g, 0.794 mmol) in dichloromethane (30 cm³). The mixture was stirred in the absence of light at room temperature for 2 h. The reaction mixture was filtered through celite (2.5 cm), which was subsequently washed with dichloromethane (10 cm³). The solvent was removed from the combined filtrate and washings by rotary evaporation to give yield a yellow-brown oil. The oil was dissolved in chloroform (5 cm³) and filtered through celite (5 cm), which was

subsequently washed with chloroform (5 cm³). The product was obtained as an off-white solid by addition of petroleum ether (b.p. 60-80°C, 30 cm³) to the combined filtrate and washing, and was washed with petroleum ether (b.p. 60-80°C, 30 cm³) and dried in air. Yield: 0.211 g (70%). [2M – AgBr₂]⁺: [C₂₂H₂₂¹⁰⁷AgF₂N₄]⁺ requires 487.0863; found: 487.1346. δ_{H} 7.38 (2H, m, C₆H₄), 7.18 (1H, td, $J = 7.5, 1.2$ Hz, C₆H₄), 7.11 (1H, ddd, $J = 9.8, 8.3, 1.1$ Hz, C₆H₄), 7.05 (1H, dd, $^3J_{\text{HH}} = 1.8$ Hz, $J = 0.9$ Hz, HCCH), 6.98 (1H, t, $^3J_{\text{HH}} = 1.8$ Hz, HCCH), 5.35 (2H, s, CH₂), 3.86 (3H, s, CH₃). δ_{C} 182.0 (AgC), 160.7 (d, $^1J_{\text{CF}} = 248$ Hz, CF), 130.9 (d, $J_{\text{CF}} = 8$ Hz, C₆), 130.7 (d, $J_{\text{CF}} = 3$ Hz, C₆), 125.0 (d, $J_{\text{CF}} = 4$ Hz, C₆), 122.8 (d, $J_{\text{CF}} = 15$ Hz, C₆), 122.4 (NCH), 121.4 (d, $J_{\text{CF}} = 2$ Hz, NCH), 115.8 (d, $J_{\text{CF}} = 21$ Hz, C₆), 49.5 (s, $^3J_{\text{CF}} = 4$ Hz, CH₂), 38.9 (CH₃). δ_{F} -117.57 (1F, m).

2.5 Preparation of (κ C-1-(2,6-difluorophenylmethyl)-3-methylimidazol-2-ylidene)silver bromide (**1b**)

Complex **1b** was obtained as a white solid from

1-(2,6-difluorophenylmethyl)-3-methylimidazolium bromide (0.228 g, 0.789 mmol) and silver(I) oxide (0.103 g, 0.443 mmol) using the procedure in 2.4. Yield: 0.244 g (78%). [2M – AgBr₂]⁺: [C₂₂H₂₀¹⁰⁷AgF₄N₄]⁺ requires 523.0675; found: 523.1214. δ_{H} : 7.36 (1H, m, H_{para}), 7.03 (1H, d, $^3J_{\text{HH}} = 1.8$ Hz, HCCH), 6.97 (1H, d, $^3J_{\text{HH}} = 1.8$ Hz, HCCH), 6.96 (2H, m, H_{meta}), 5.38 (2H, s, CH₂), 3.85 (3H, s, CH₃). δ_{C} : 182.6 (AgC), 161.3 (dd, $^1J_{\text{CF}} = 251$ Hz, $^3J_{\text{CF}} = 7$ Hz, CF), 131.4 (t, $^3J_{\text{CF}} = 11$ Hz, C_{para} or C_{ipso}), 122.5 (CH), 121.0 (CH), 112.0 (m, C_{meta}), 111.7 (t, $^2J_{\text{CF}} = 19$ Hz, C_{para} or C_{ipso}), 43.0 (CH₂), 39.0 (CH₃). δ_{F} : -112.87 (m).

2.6 Preparation of (κ C-1-(2-chloro-6-fluorophenylmethyl)-3-methylimidazol-2-ylidene)silver bromide (**1c**)

Complex **1c** was obtained as an off-white solid from

1-(2-chloro-6-fluorophenylmethyl)-3-methylimidazolium bromide (0.275 g, 0.900 mmol) and silver(I) oxide (0.133 g, 1.15 mmol) using the procedure in 2.4. Yield: 0.331 g (89%). $[2M - AgBr_2]^+$: $[C_{22}H_{20}^{107}Ag^{35}Cl^{37}ClF_2N_4]^+$ requires 557.0180; found: 557.0196. δ_H : 7.37 (1H, td, $J = 8.1, 5.9$ Hz, C_6H_3), 7.31 (1H, m, C_6H_3), 7.11 (1H, m, C_6H_3), 7.02 (1H, d, $^3J_{HH} = 1.8$ Hz, $HCCCH$), 6.97 (1H, d, $^3J_{HH} = 1.8$ Hz, $HCCCH$), 5.48 (2H, d, $^4J_{HF} = 1.8$ Hz, CH_2), 3.86 (3H, s, CH_3). δ_C : 182.7 (AgC), 161.8 (d, $^1J_{CF} = 251$ Hz, CF), 135.9 (d, $J_{CF} = 5$ Hz, C_6), 131.4 (d, $J_{CF} = 10$ Hz, C_6), 126.1 (d, $J_{CF} = 3$ Hz, C_6), 122.3 (CH), 121.2 (d, $J_{CF} = 17$ Hz, C_6), 121.0 (d, $^5J_{CF} = 2$ Hz, NCH), 114.8 (d, $J_{CF} = 22$, NCH), 46.4 (d, $^3J_{CF} = 3$, CH_2), 39.0 (CH_3). δ_F : -110.94 (1F, m).

*2.7 Preparation of (κC -1-(2-bromo-6-fluorophenylmethyl)-3-methylimidazol-2-ylidene)silver I bromide (**1d**)*

Complex **1d** was obtained as a white solid from

1-(2-bromo-6-fluorophenylmethyl)-3-methylimidazolium bromide (0.063 g, 0.273 mmol) and silver(I) oxide (0.155 g, 0.444 mmol) using the procedure in 2.4. Yield: 0.104 g (52%). $[2M - AgBr_2]^+$: $[C_{22}H_{20}^{107}Ag^{79}Br^{81}BrF_2N_4]^+$ requires 644.9170; found: 645.1161. δ_H ($(CD_3)_2SO$): 7.55 (1H, dt, $J = 7.9, 1.0$ Hz, C_6H), 7.45 (1H, d, $^3J_{HH} = 1.8$ Hz, $HCCCH$), 7.40 (1H, td, $J = 8.3, 6.2$ Hz, C_6H), 7.39 (1H, s br, $HCCCH$), 7.32 (1H, m, C_6H), 5.43 (2H, d, $^4J_{HF} = 1.5$ Hz, CH_2), 3.75 (3H, s, CH_3). δ_F ($(CD_3)_2SO$): -109.81 (1F, m). The $^{13}C\{^1H\}$ NMR spectrum could not be obtained because of the low solubility of **1d**.

*2.8 Preparation of (κC -1-(2-iodo-6-fluorophenylmethyl)-3-methylimidazol-2-ylidene)silver bromide (**1e**)*

Complex **1e** was obtained as a white solid from

1-(2-iodo-6-fluorophenylmethyl)-3-methylimidazolium bromide (0.063 g, 0.273 mmol) and

silver(I) oxide (0.155 g, 0.444 mmol) using the procedure in 2.4. Yield: 0.100 g (60%). [2M – AgBr₂]⁺: [C₂₂H₂₀¹⁰⁷AgI₂F₂N₄]⁺ requires 738.8796; found: 739.1174. δ_{H} ((CD₃)₂SO): 7.78 (1H, dm, J = 7.8 Hz, C₆H), 7.45 (1H, d, J_{HH} = 1.8 Hz, HCCH), 7.33 (2H, m, C₆H and HCCH), 7.22 (1H, td, J = 7.9, 6.0 Hz, C₆H), 5.41 (2H, d, $^4J_{\text{HF}}$ = 1.8 Hz, CH₂), 3.76 (3H, s, CH₃). δ_{F} ((CD₃)₂SO): -108.27 (1F, m). The ¹³C{¹H} NMR spectrum could not be obtained because of the low solubility of **1e**.

2.9 Preparation of

(η^5 -pentamethylcyclopentadienyl)iridium(κ C-1-(2-fluorophenylmethyl)-3-methylimidazol-2-ylidene) dichloride (**2a**)

Complex **1a** (0.131g, 0.346 mmol) was dissolved in dichloromethane (5 cm³) and filtered through celite into a solution of [Cp*IrCl(μ -Cl)]₂ (0.138 g, 0.174 mmol) in dichloromethane (30 cm³), giving a yellow solution and white precipitate. The reaction mixture was left for 3 hours in the absence of light. The solution was filtered through celite, which was subsequently washed with dichloromethane (2 x 10 cm³). The solvent was removed from the combined filtrate and washings by rotary evaporation giving an orange oil, which was dissolved in dichloromethane (2 cm³) and filtered through silica. Removal of the solvent by evaporation gave an orange solid which was recrystallized from chloroform and petroleum ether (b.p. 60-80°C). Yield: 0.174 g (85%). Anal. Calc. for C₂₁H₂₆Cl₂FIrN₂.¹/₈(CHCl₃): C, 42.0; H, 4.4; N, 4.6. Found: C, 41.8; H, 4.6; N, 5.2%. [M – Cl]⁺: [C₂₁H₂₆³⁵ClF¹⁹³IrN₂]⁺ requires 553.1471; found: 553.1342. δ_{H} 7.64 (1H, td., J = 7.7, 1.7 Hz, C₆H₄), 7.33 (1H, m, C₆H₄), 7.14 (1H, td, J = 7.4, 1.2, Hz, C₆H₄), 7.09 (1H, ddd., J = 9.5, 8.2, 1.2 Hz, C₆H₄), 6.90 (1H, d, $^3J_{\text{HH}}$ = 2.0 Hz, HCCH), 6.69 (1H, t, $^3J_{\text{HH}}$ = 2.0 Hz, HCCH), 6.08 (1H, d, $^2J_{\text{HH}}$ = 14.5 Hz, NCHH), 5.30 (1H, d, $^2J_{\text{HH}}$ = 14.5 Hz, NCHH), 4.02 (3H, s, NCH₃), 1.67 (15H, s, CH₃). δ_{C} : 160.8 (d, $^1J_{\text{CF}}$ = 246 Hz, CF), 156.6 (IrCN₂), 132.0 (d, J_{CF} = 3 Hz, C₆), 130.1 (d, J_{CF} = 8 Hz,

C₆), 124.8 (d, $J_{\text{CF}} = 3$ Hz, C₆), 123.5 (C₆), 123.3 (NCH), 121.4 (NCH), 115.1 (d, $J_{\text{CF}} = 22$ Hz, C₆), 88.9 (C₅), 47.6 (s, $^3J_{\text{CF}} = 4$ Hz, CH₂), 38.7 (NCH₃), 9.2 (CH₃). δ_{F} : -112.65 (1F, m).

2.10 Preparation of

(η^5 -pentamethylcyclopentadienyl)iridium(κ C-1-(2,6-difluorophenylmethyl)-3-methylimidazol-2-ylidene) dichloride (**2b**)

Complex **1b** (0.099g, 0.249 mmol) and [Cp*IrCl(μ -Cl)]₂ (0.100 g, 0.125 mmol) were treated as in 2.9. Yield: 0.119 g, (79%). Anal. Calc. for C₂₁H₂₅Cl₂F₂IrN₂· $\frac{1}{4}$ (CHCl₃): C, 40.1; H, 4.0; N, 4.4. Found: C, 40.2; H, 4.4; N, 4.9%. [M – Cl]⁺ : [C₂₁H₂₅³⁵ClF₂¹⁹³IrN₂]⁺ requires 571.1376 ; found: 571.1263. δ_{H} 7.40 (1H, m, H_{para}), 6.98 (2H, m, H_{meta}), 6.88 (1H, d, $^3J_{\text{HH}} = 2.2$ Hz, HCCH), 6.49 (1H, d, $^3J_{\text{HH}} = 2.2$ Hz, HCCH), 5.98 (1H, d, $^2J_{\text{HH}} = 15.3$ Hz, NCHH), 5.40 (1H, d, $^2J_{\text{HH}} = 15.3$ Hz, NCHH), 4.01 (3H, s, NCH₃), 1.71 (15H, s, CH₃). δ_{C} 161.9 (dd, $^1J_{\text{CF}} = 251$ Hz, $^3J_{\text{CF}} = 7$ Hz, CF), 156.8 (IrCN₂), 132.5 (t, $J_{\text{CF}} = 11$ Hz, C₆), 122.7 (NCH), 120.2 (NCH), 111.9 (dm, $J_{\text{CF}} = 25$ Hz, C₆), 89.0 (C₅), 43.5 (t, $^3J_{\text{CF}} = 4$, NCH₂), 38.8 (NCH₃), 9.1 (CH₃). The resonance of C_{ipso} could not be observed; it is presumed that it is obscured by a coincidental resonance. δ_{F} -119.57 (2F, dd, $J = 6.9, 6.9$ Hz).

2.11 Preparation of

(η^5 -pentamethylcyclopentadienyl)iridium(κ C-1-(2-chloro-6-fluorophenylmethyl)-3-methylimidazol-2-ylidene) dichloride (**2c**)

Complex **1c** (0.101g, 0.244 mmol) and [Cp*IrCl(μ -Cl)]₂ (0.096 g, 0.121 mmol) were treated as in 2.9. Yield: 0.133 g (88%). Anal. Calc. for C₂₁H₂₅Cl₃FIrN₂: C, 40.5; H, 4.0; N, 4.5. Found: C, 40.0; H, 4.3; N, 4.7%. [M – Cl]⁺ : [C₂₁H₂₅³⁵Cl₂¹⁹³FIrN₂]⁺ requires 587.1081; found: 587.0999. δ_{H} 7.37 (1H, dt, $J = 8.0, 5.9$ Hz, C₆H₃), 7.33 (1H, m, C₆H₃), 7.07 (1H, m, C₆H₃), 6.84 (1H, d, $^3J_{\text{HH}} = 2.0$ Hz, HCCH), 6.39 (1H, d, $^3J_{\text{HH}} = 2.0$ Hz, HCCH), 6.30 (1H, d, $^2J_{\text{HH}} =$

15.1 Hz, NCHH), 5.34 (1H, d, $^2J_{\text{HH}} = 15.1$ Hz, NCHH), 4.01 (3H, s, NCH₃), 1.71 (15H, s, CH₃). δ_{C} 162.2 (d, $^1J_{\text{CF}} = 252$ Hz, CF), 156.3 (IrCN₂), 137.1 (d, $J_{\text{CF}} = 6$ Hz, C₆), 131.0 (d, $J_{\text{CF}} = 10$ Hz, C₆), 126.0 (d, $J_{\text{CF}} = 3$ Hz, C₆), 122.5 (NCH), 121.7 (d, $J_{\text{CF}} = 18$ Hz, C₆) 120.1 (NCH), 114.6 (d, $J_{\text{CF}} = 23$ Hz, C₆), 88.9 (C₅), 44.2 (d, $^3J_{\text{CF}} = 3$ Hz, NCH₂), 38.9 (NCH₃), 9.2 (CH₃). δ_{F} -110.01 (1F, m).

2.12 Preparation of

(η^5 -pentamethylcyclopentadienyl)iridium(κ C-1-(2-bromo-6-fluorophenylmethyl)-3-methylimidazol-2-ylidene) dichloride (**2d**)

Complex **1d** (0.069g, 0.150 mmol) and [Cp*IrCl(μ -Cl)]₂ (0.060 g, 0.075 mmol) were treated as in 2.9. Yield: 0.080 g (80%). $[\text{M} - \text{Cl}]^+ : [\text{C}_{21}\text{H}_{25}^{79}\text{Br}^{35}\text{Cl}^{193}\text{FIrN}_2]^+$ requires 631.0576; found: 631.0476. δ_{H} 7.51 (1H, dt, $J = 8.2, 1.0$ Hz, C₆H₃), 7.30 (1H, dt, $J = 8.3, 6.1$ Hz, C₆H₃), 7.10 (1H, ddd, $J = 9.5, 8.4, 1.1$ Hz, C₆H₃), 6.84 (1H, d, $^3J_{\text{HH}} = 2.1$ Hz, HCCH), 6.39 (1H, d, $^3J_{\text{HH}} = 2.0$ Hz, HCCH), 6.31 (1H, d, $^2J_{\text{HH}} = 14.5$ Hz, NCHH), 5.37 (1H, d, $^2J_{\text{HH}} = 14.5$ Hz, NCHH), 4.01 (3H, s, NCH₃), 1.71 (15H, s, CH₃). δ_{C} 162.1 (d, $^1J_{\text{CF}} = 253$ Hz, CF), 156.3 (IrCN₂), 131.4 (d, $J_{\text{CF}} = 10$ Hz, C₆), 129.3 (d, $J_{\text{CF}} = 3$ Hz, C₆), 127.2 (d, $J_{\text{CF}} = 4$ Hz, C₆), 123.5 (d, $J_{\text{CF}} = 18$ Hz, C₆), 122.4 (NCH), 120.2 (NCH), 115.2 (d, $J_{\text{CF}} = 23$ Hz, C₆), 88.9 (C₅), 49.7 (NCH₂), 38.9 (NCH₃), 9.2 (CH₃). δ_{F} -108.71 (1F, m).

2.13 Preparation of

(η^5 -pentamethylcyclopentadienyl)iridium(κ C-1-(2-iodo-6-fluorophenylmethyl)-3-methylimidazol-2-ylidene) dichloride (**2e**)

Complex **1e** (0.056g, 0.110 mmol) and [Cp*IrCl(μ -Cl)]₂ (0.044 g, 0.055 mmol) were treated as in 2.9. Yield: 0.067 g (85%). $[\text{M} - \text{Cl}]^+ : [\text{C}_{21}\text{H}_{25}^{35}\text{ClFI}^{193}\text{IrN}_2]^+$ requires 679.0437; found:

679.0330. δ_{H} 7.86 (1H, m, C₆H₃), 7.12 (2H, m, C₆H₃), 6.85 (1H, d, $J_{\text{HH}} = 2.1$ Hz, HCCH), 6.38 (1H, d, $J_{\text{HH}} = 2.1$ Hz, HCCH), 6.18 (1H, br s, NCHH), 5.47 (1H, br s, NCHH), 4.01 (3H, s, NCH₃), 1.72 (15H, s, CH₃). δ_{C} 161.1 (d, $^1J_{\text{CF}} = 253$ Hz, CF), 156.3 (IrCN₂), 136.1 (C₆), 132.0 (d, $J_{\text{CF}} = 9$ Hz, C₆), 126.7 (d, $J_{\text{CF}} = 17$ Hz, C₆), 122.5 (NCH), 120.2 (NCH), 116.2 (d, $J_{\text{CF}} = 23$ Hz, C₆), 103.2 (d, $J_{\text{CF}} = 3$ Hz, C₆), 88.9 (C₅), 54.7 (NCH₂), 38.9 (NCH₃), 9.2 (CH₃). δ_{F} -108.27 (1F, br s).

2.14 Treatment of

(η^5 -pentamethylcyclopentadienyl)iridium(κ C-1-(2-fluorophenylmethyl)-3-methylimidazol-2-ylidene) dichloride and
(η^5 -pentamethylcyclopentadienyl)iridium(κ C-1-(2-halo-6-fluorophenylmethyl)-3-methylimidazol-2-ylidene) dichloride with silver particles.

A deuteriochloroform solution (*ca.* 0.8 cm³) of **2a** – **2e** (*ca.* 15 mg) in an NMR tube was treated with silver nanoparticles (*ca.* 25 mg) formed from silver nitrate and triethylamine in methanol or ethanol [12]. The tube was shaken and left overnight, after which time the NMR spectra showed the reaction had reached completion. The solution was diluted with dichloromethane (5 cm³) and *ca.* 0.2 g of anhydrous magnesium sulphate was added. The solution was then filtered through a glass pipette containing a plug of cotton wool and celite (5 cm). The celite was washed with dichloromethane (5 cm³). Evaporation of the solvent from the combined filtrate and washing yielded the product as a yellow oil. Recrystallization by slow diffusion of pentane into a dichloromethane solution gave yellow needles.

3b was obtained as a partial pentane solvate. Anal. Calc. for C₂₁H₂₅ClFIrN₂· $\frac{1}{4}$ C₅H₁₂: C, 46.9; H, 4.95; N, 4.9. Found: C, 46.6; H, 4.7 N, 4.9%. $[\text{M} - \text{Cl}]^+$: $[\text{C}_{21}\text{H}_{25}\text{F}^{193}\text{IrN}_2]^+$ requires 517.1704; found: 517.1650. δ_{H} 7.40 (1H, dd, $J_{\text{HH}} = 7.6, 1.1$ Hz, C₆H₃), 7.01 (1H, d, $^3J_{\text{HH}} = 2.0$ Hz, HCCH), 6.96 (1H, m, C₆H₃), 6.93 (1H, t, $^3J_{\text{HH}} = 2.0$ Hz, HCCH), 6.55 (1H, ddd, $J_{\text{FF}} = 10.4$

Hz, $J_{\text{HH}} = 8.2, 1.1$ Hz, C_6H_3), 5.28 (1H, d, $^2J_{\text{HH}} = 14.4$ Hz, CHH), 4.55 (1H, d, $^2J_{\text{HH}} = 14.4$ Hz, CHH), 3.94 (3H, s, NCH_3), 1.69 (15H, s, CH_3). δ_{C} 157.4 (d, $^1J_{\text{CF}} = 246$ Hz, CF), 157.1 (IrCN_2), 148.1 ($\text{IrC}(\text{C}_6)$), 136.8 (d, $J_{\text{CF}} = 3$ Hz, C_6), 124.8 (d, $J_{\text{CF}} = 9$ Hz, C_6), 121.4 (NCH), 120.7 (NCH), 108.2 (d, $J_{\text{CF}} = 22$ Hz, C_6), 90.4 (C_5), 48.5 (d, $^3J_{\text{CF}} = 6$ Hz, NCH_2), 36.9 (NCH₃), 9.4 (CH_3). δ_{F} -123.00 (1F, dd, $J_{\text{HF}} = 10.4, 6.1$ Hz).

3c (obtained as a mixture with **3b** from **2c**) $[\text{M} - \text{Cl}]^+$: $[\text{C}_{21}\text{H}_{25}^{35}\text{Cl}^{193}\text{IrN}_2]^+$ requires 533.1408; found: 533.1542. δ_{H} 7.54 (1H, dd, $J_{\text{HH}} = 6.4, 2.4$ Hz, C_6H_3), 7.01 (1H, d, $^3J_{\text{HH}} = 2.0$ Hz, HCCH), 6.96 (2H, m, C_6H_3), 6.92 (1H, d, $^3J_{\text{HH}} = 2.0$ Hz, HCCH), 5.49 (1H, d, $^2J_{\text{HH}} = 14.5$ Hz, NCHH), 4.59 (1H, d, $^2J_{\text{HH}} = 14.5$ Hz, NCHH), 3.92 (3H, s, NCH_3), 1.68 (15H, s, CH_3). δ_{C} 157.4 (IrCN_2), 147.8 ($\text{IrC}(\text{C}_6)$), 140.3 (C_6), 135.3 (C_6), 128.9 (C_6), 128.5 (C_6), 122.9 (C_6), 121.4 (NCH), 120.8 (NCH), 90.4 (C_5), 52.7 (NCH_2), 36.9 (NCH₃), 9.4 (CH_3).

3d (obtained as a mixture with **3b** from **2d**) $[\text{M} - \text{Cl}]^+$: $[\text{C}_{21}\text{H}_{25}^{79}\text{Br}^{193}\text{IrN}_2]^+$ requires 577.0903; found: 577.1098. δ_{H} 7.58 (1H, dd, $J_{\text{HH}} = 7.5, 1.1$ Hz, C_6H_3), 7.06 (1H, dd, $J_{\text{HH}} = 7.8, 1.2$ Hz, C_6H_3), 7.01 - 6.92 (2H, HCCH), 6.82 (1H, t, $J_{\text{HH}} = 7.6$ Hz, C_6H_3), 5.48 (1H, d, $^2J_{\text{HH}} = 14.6$ Hz, NCHH), 4.62 (1H, d, $^2J_{\text{HH}} = 14.5$ Hz, NCHH), 3.92 (3H, s, NCH_3), 1.68 (15H, s, CH_3). δ_{C} 157.7 (IrCN_2), 148.2 ($\text{IrC}(\text{C}_6)$), 141.0 (C_6), 129.0 (C_6), 126.2 (C_6), 121.4 (NCH), 120.8 (NCH), 119.9 (C_6), 90.4 (C_5), 55.7 (NCH_2), 36.9 (NCH₃), 9.4 (CH_3). The resonance of one phenyl carbon atom could not be observed; it is presumed that it is obscured by a coincidental resonance.

3e (obtained as a mixture with **3b** from **2e**) $[\text{M} - \text{Cl}]^+$: $[\text{C}_{21}\text{H}_{25}\text{I}^{193}\text{IrN}_2]^+$ requires 625.0765; found: 625.0673. δ_{H} 7.61 (1H, dd, $J_{\text{HH}} = 7.5, 1.2$ Hz, C_6H_3), 7.35 (1H, dd, $J_{\text{HH}} = 7.8, 1.2$ Hz, C_6H_3), 7.02 (1H, d, $^3J_{\text{HH}} = 2.0$ Hz, HCCH), 6.93 (1H, d, $^3J_{\text{HH}} = 2.0$ Hz, HCCH), 6.65 (1H, t, $J_{\text{HH}} = 7.8$ Hz, C_6H_3), 5.36 (1H, d, $^2J_{\text{HH}} = 14.6$ Hz, NCHH), 4.69 (1H, d, $^2J_{\text{HH}} = 14.6$ Hz, NCHH), 3.93 (3H, s, NCH_3), 1.68 (15H, s, CH_3). δ_{C} 158.4 (IrCN_2), 147.8 ($\text{IrC}(\text{C}_6)$), 142.0

(C₆), 139.9 (C₆), 133.2 (C₆), 129.6 (C₆), 121.4 (NCH), 120.8 (NCH), 96.7 (C₆), 90.4 (C₅), 61.3 (NCH₂), 36.8 (NCH₃), 9.4 (CH₃).

2.15 X-ray crystallography

Crystals of **2a**, **2c** and **2d** were obtained by diffusion of pentane into a chloroform solution of the relevant complex. Crystals of **3b**, **3b/3c**, **3b/3d** and **3b/3e** were obtained by diffusion of pentane into the liquid decanted from the NMR tube reactions. Diffraction data were collected on an Agilent SuperNova, single source at offset, Atlas diffractometer with graphite-monochromated Cu—K α radiation. The structures were solved using Olex2 [13] with olex2.solve [14] structure solution programme using Charge Flipping and refined with the olex2.refine [14] refinement package using Gauss-Newton minimization. The non-hydrogen atoms, except for the partial fluorine atom of **3c**, were refined with anisotropic thermal parameters. Hydrogen atom positions were added in idealized positions and a riding model with fixed thermal parameters ($U_{ij} = 1.2U_{eq}$ for the atom to which they are bonded (1.5 for CH₃)) was used for subsequent refinements. The function minimized was $\Sigma[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2 |F_o|^2 + (g1P)^2 + (g2P)^2]$ where $P = [\max(|F_o|^2 + 2|F_c|^2)]/3$. In addition to the 8 molecules, the unit cell of **3b** contained ca. 153 electrons, consistent with ca. 3.2 molecules of pentane, occupying a void of 682 Å³. Attempts to model these data were unsuccessful. Consequently the data were treated with the Solvent Mask routine [14].

CCDC 1839757 (**2a**) 1839758 (**2c**), 1839759 (**2d**), 1839760 (**3b**), 1839761 (**3b/3c**), 1839762 (**3b/3d**) and 1839763 (**3b/3e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and discussion

The iridium complexes $[\text{Cp}^*\text{IrCl}_2(\kappa\text{C-MeNC}_3\text{H}_2\text{NCH}_2\text{C}_6\text{H}_3\text{X-2-F-6})]$ (**2a** X = H, **2b** X = F, **2c** X = Cl, **2d** X = Br, **2e** X = I) were obtained in high yields by the treatment of $[\text{Cp}^*\text{IrCl}(\mu\text{-Cl})]_2$ with the silver NHC complexes $[\text{AgBr}(\kappa\text{C-MeNC}_3\text{H}_2\text{NCH}_2\text{C}_6\text{H}_3\text{X-2-F-6})]$ (**1a** X = H, **1b** X = F, **1c** X = Cl, **1d** X = Br, **1e** X = I), which were formed by treating the imidazolium salts $[\text{MeNC}_3\text{H}_3\text{NCH}_2\text{C}_6\text{H}_3\text{X-2-F-6}]\text{Br}$ [10] with silver(I) oxide. The complexes were characterized by NMR spectroscopy and high resolution mass spectrometry. Complexes **2a**, **2b** and **2c** were also characterized by elemental analysis. The structures of complexes **2a**, **2c** and **2d** (Figures 1 - 3) were determined by single crystal X-ray diffraction studies.

Fig. 1. Structure of

(η^5 -pentamethylcyclopentadienyl)iridium($\kappa\text{C-1-(2-fluorophenylmethyl)-3-methylimidazol-2-ylidene}$) dichloride (**2a**). Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

Fig. 2. Structure of

(η^5 -pentamethylcyclopentadienyl)iridium(κ C-1-(2-chloro-6-fluorophenylmethyl)-3-methylimidazol-2-ylidene) dichloride (**2c**). Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

Fig. 3. Structure of

(η^5 -pentamethylcyclopentadienyl)iridium(κ C-1-(2-bromo-6-fluorophenylmethyl)-3-methylimidazol-2-ylidene) dichloride (**2d**). Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

In order to investigate the reactions between complexes **2a** – **2e** and silver nanoparticles [12] by *in situ* NMR spectroscopy, experiments were performed in deuteriochloroform in NMR tubes, and the final products were also analysed by mass spectrometry and single-crystal X-ray diffraction. Treatment of a solution of **2a** with silver particles over 12 hours gave the C—H bond activated product, **3b**, exclusively. Treatment of **2b** with silver particles also gave **3b**, but by C—F bond activation. The structure of **3b** was determined by single crystal X-ray diffraction (Figure 4). The crystal structure contained additional electron density, which can be ascribed to the presence of *ca.* 0.4 molecules of

pentane per molecule of **3b**. This could not be modelled, presumably because its position and conformation in channels parallel to the *c* axis, which account for *ca.* 15 % of the volume (Figure 5), are severely disordered. The presence of pentane is consistent with the elemental analysis and is also observed in the ^1H NMR spectrum.

Scheme. Reaction of

(η^5 -pentamethylcyclopentadienyl)iridium(κ C-1-(2-fluorophenylmethyl)-3-methylimidazol-2-ylidene) dichloride complexes with silver particles.

Fig. 4. Structure of

(η^5 -pentamethylcyclopentadienyl)iridium(κ^2 C-1-(2-fluorophenylmethyl)-3-methylimidazol-2-ylidene) chloride (**3b**). Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

Fig. 5. Crystal structure of $(\eta^5\text{-pentamethylcyclopentadienyl})\text{iridium}(\kappa^2\text{C-1-(2-fluorophenylmethyl)-3-methylimidazol-2-ylidene})\text{chloride}$ (**3b**) showing the channels parallel to the *c* axis.

On treatment with silver particles complexes **2c**, **2d** and **2e** underwent C—X and C—F bond activation to yield mixtures of **3b** and **3c**, **3b** and **3d**, and **3b** and **3e** in *ca.* 1:4, 1:1 and 3:2 ratio respectively as evidenced by NMR spectroscopy. Mass spectrometry indicated that there was no exchange of the carbon bound halogen atom of **3d** and **3e** for chlorine, an atom of which is lost as chloride from the metal centre, and it is therefore surmised that exchange of atoms at this site does not occur in any of the reactions or for any of the halogens. Crystals were obtained from the reactions and the structures of the products, which co-crystallized, were elucidated by single-crystal X-ray diffraction studies. The co-crystals are isomorphous with those of **3b** and the compounds **3b** - **3e** are isostructural. The structure of the co-crystal

of **3b** and **3d** is shown in Figure 6. (The structures of **3b** and **3c**, and **3b** and **3e** are contained in the supplementary material.) The crystal structures of the co-crystals were modelled with **3b:3c**, **3b:3d** and **3b:3e** ratios of 44:56, 43:57 and 64:36 respectively, without the inclusion of solvent, although residual electron density suggested the presence of a small amount (< 0.1 molecule per molecule of product). The bond distances and angles around iridium (Table 2) are similar to those of $[\text{Cp}^*\text{IrCl}(\kappa\text{C}^2\text{-MeNC}_3\text{H}_2\text{NCH}_2\text{C}_6\text{F}_4)]$ [9].

Fig. 6. Structure of the product from the co-crystal of $(\eta^5\text{-pentamethylcyclopentadienyl})\text{iridium}(\kappa\text{C}^2\text{-1-(2-fluorophenylmethyl)-3-methylimidazol-2-ylidene})$ chloride (**3b**) and $(\eta^5\text{-pentamethylcyclopentadienyl})\text{iridium}(\kappa\text{C}^2\text{-1-(2-bromophenylmethyl)-3-methylimidazol-2-ylidene})$ chloride (**3d**). Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

Since C—H and C—F bonds possess opposite polarity, and base induces orthometallation involving C—H, but not C—F, bond activation [1-4,15], it is suggested that the exclusive preference for C—H bond activation over C—F bond activation in the reaction of **2a** is a consequence of different mechanisms for the reaction, rather than a consequence of the relative strengths of the C—H and C—F bonds ($\text{C}_6\text{H}_5\text{—H}$ 466 kJ mol⁻¹, $\text{C}_6\text{H}_5\text{—F}$ 526 kJ mol⁻¹ [16]). The exclusive generation of **3b** indicates that the reaction involving C—H bond activation is significantly more rapid than that involving C—F bond activation. The increasing ratios of C—X to C—F bond activation for **2c**, **2d** and **2e** correlates with the decreasing C—X bond strength ($\text{C}_6\text{H}_5\text{—Cl}$ 400 kJ mol⁻¹, $\text{C}_6\text{H}_5\text{—Br}$ 337 kJ mol⁻¹, $\text{C}_6\text{H}_5\text{—I}$ 274 kJ mol⁻¹ [16]). However, the greater strength of the C—F bond compared to the C—Cl bond indicates that bond strength alone cannot account for the preference for which bond is activated.

3. Conclusion

Orthometallation occurs exclusively by carbon–hydrogen bond activation when (η^5 -pentamethylcyclopentadienyl)iridium($\kappa\text{C-1-(2-fluorophenylmethyl)-3-methylimidazol-2-ylidene}$) dichloride (**2a**) is treated with silver particles. The same product is formed from (η^5 -pentamethylcyclopentadienyl)iridium($\kappa\text{C-1-(2,6-fluorophenylmethyl)-3-methylimidazol-2-ylidene}$) dichloride by carbon–fluorine bond activation. When (η^5 -pentamethylcyclopentadienyl)iridium($\kappa\text{C-1-(2-halo-6-fluorophenylmethyl)-3-methylimidazol-2-ylidene}$) dichlorides (**2c - 2e**) are treated with silver particles, orthometallation by carbon–halogen bond activation occurs giving a mixture of two products. The identities of the four products have been confirmed by single-crystal X-ray diffraction.

References

- [1] R. Corberán, M. Sanaú, E. Peris, Highly Stable Cp*—Ir(III) Complexes with *N*-Heterocyclic Carbene Ligands as C—H Activation Catalysts for the Deuteration of Organic Molecules, *J. Am. Chem. Soc.* 128 (2006) 3974-3979.
- [2] R. Corberán, M. Sanaú, E. Peris, Aliphatic and Aromatic Intramolecular C—H Activation on Cp*Ir(NHC) Complexes, *Organometallics* 25 (2006) 4002-4008.
- [3] R. Corberán, V. Lillo, J.A. Mata, E. Fernandez, E. Peris, Enantioselective Preparation of a Chiral-at-Metal Cp*Ir(NHC) Complex and Its Application in the Catalytic Diboration of Olefins, *Organometallics* 26 (2007) 4350-4353.
- [4] A. Pontes da Costa, M. Sanaú, E. Peris, B. Royo, Easy preparation of Cp*-functionalized N-heterocyclic carbenes and their coordination to rhodium and iridium, *Dalton Trans.* (2009) 6960-6966.
- [5] Y. Tanabe, F. Hanasaka, K. Fujita, R. Yamaguchi, Scope and Mechanistic Studies of Intramolecular Aliphatic C—H Bond Activation of N-Heterocyclic Carbene Iridium Complexes, *Organometallics* 26 (2007) 4618-4626.
- [6] M. Benítez, E. Mas-Marzá, J.A. Mata, E. Peris, Intramolecular Oxidation of the Alcohol Functionalities in Hydroxyalkyl-N-Heterocyclic Carbene Complexes of Iridium and Rhodium, *Chem. Eur. J.* 17 (2011) 10453-10461.
- [7] J. Holmes, C.M. Pask, C.E. Willans, Chelating N-heterocyclic carbene—carboranes offer flexible ligand coordination to Ir^{III}, Rh^{III} and Ru^{II}: effect of ligand cyclometallation in catalytic transfer hydrogenation, *Dalton Trans.* 45 (2016) 15818-15827.

- [8] M. Prinz, M. Grosche, E. Herdtweck, W.A. Herrmann, Unsymmetrically Substituted Iridium(III)–Carbene Complexes by a CH-Activation Process, *Organometallics* 19 (2000) 1692-1694.
- [9] H.P. Thomas, Y.-M. Wang, F. Lorenzini, S.J. Coles, P.N. Horton, A.C. Marr, G.C. Saunders, Cyclometallation via Carbon-Fluorine Bond Activation induced by Silver Particles, *Organometallics* 36 (2017) 960-963.
- [10] F. Lorenzini, A.C. Marr, G.C. Saunders, H.P. Thomas, The structures of 1-(2-halo-6-fluorophenylmethyl)-1-methylimidazolium bromide salts, *J. Fluor. Chem.* 210 (2018) 102-111.
- [11] C. White, A. Yates, P.M. Maitlis, (η^5 -Pentamethylcyclopentadienyl)Rhodium and – Iridium Compounds, *Inorg. Synth.* 29 (1992) 228-234.
- [12] J.-T. Wu, S. L.-C. Hsu, Preparation of triethylamine stabilized silver nanoparticles for low-temperature sintering, *J. Nanopart. Res.* 13 (2011) 3877–3883.
- [13] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *OLEX2*: a complete structure solution, refinement and analysis program, *J. Appl. Cryst.* 42 (2009) 339-341.
- [14] L.J. Bourhis, O.V. Dolomanov, R.J. Gildea, J.A.K. Howard, H. Puschmann, The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment - Olex2 dissected, *Acta Crystallogr. A* 71 (2015) 59-75.
- [15] S.J. McGrandle, G.C. Saunders, Group 9 complexes of an N-heterocycle carbene bearing a pentafluorobenzyl substituent: Attempted dehydrofluorinative coupling of cyclopentadienyl and N-heterocycle carbene ligands, *J. Fluorine Chem.* 126 (2005) 451-455.
- [16] D.F. McMillen, D.M. Golden, Hydrocarbon bond dissociation energies, *Ann. Rev. Phys. Chem.* 33 (1982) 493-532.

Table 1

Crystallographic data for (η^5 -pentamethylcyclopentadienyl)iridium(κ C-1-(2-fluorophenylmethyl)-3-methylimidazol-2-ylidene) dichloride, **2a**, (η^5 -pentamethylcyclopentadienyl)iridium(κ C-1-(2-chloro-6-fluorophenylmethyl)-3-methylimidazol-2-ylidene) dichloride, **2c**, (η^5 -pentamethylcyclopentadienyl)iridium(κ C-1-(2-bromo-6-fluorophenylmethyl)-3-methylimidazol-2-ylidene) dichloride, **2d**, (η^5 -pentamethylcyclopentadienyl)iridium(κ C²-1-(2-fluorophenylmethyl)-3-methylimidazol-2-ylidene) chloride, **3b**, and co-crystals with (η^5 -pentamethylcyclopentadienyl)iridium(κ C²-1-(2-chlorophenylmethyl)-3-methylimidazol-2-ylidene) chloride, **3c**, with (η^5 -pentamethylcyclopentadienyl)iridium(κ C²-1-(2-bromophenylmethyl)-3-methylimidazol-2-ylidene) chloride, **3d**, and with (η^5 -pentamethylcyclopentadienyl)iridium(κ C²-1-(2-iodophenylmethyl)-3-methylimidazol-2-ylidene) chloride, **3e**.^a

	2a	2c	2d	3b	3b/3c	3b/3d	3b/3e
Formula	C ₂₂ H ₂₆ Cl ₂ FIrN ₂	C ₂₁ H ₂₅ Cl ₃ FIrN ₂	C ₂₁ H ₂₅ BrCl ₂ FIrN ₂	C ₂₁ H ₂₅ ClFIrN ₂	C ₂₁ H ₂₅ Cl _{1.56} F _{0.44} IrN ₂	C ₂₁ H ₂₅ Br _{0.57} ClF _{0.43} IrN ₂	C ₂₁ H ₂₅ ClF _{0.64} I _{0.36} IrN ₂
Formula weight	588.57	623.02	667.47	552.11	561.33	587.13	590.96
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	<i>Pbca</i>	<i>Pna</i> 2 ₁	<i>Pna</i> 2 ₁	<i>Iba</i> 2	<i>Iba</i> 2	<i>Iba</i> 2	<i>Iba</i> 2

a , Å	8.65896(14)	17.8456(4)	21.4894(5)	26.8949(6)	27.0311(5)	19.5638(3)	26.7156(6)
b , Å	18.7242(3)	12.5932(2)	9.5002(2)	19.5780(4)	19.4538(4)	26.8744(5)	19.9311(5)
c , Å	25.2239(4)	9.50997(17)	10.7341(2)	8.48341(19)	8.47896(15)	8.49006(19)	8.4836(2)
V , Å ³	4089.61(12)	2137.21(7)	2191.41(8)	4466.92(17)	4458.72(15)	4463.77(15)	4517.29(19)
Z	8	4	4	8	8	8	8
D_c (g cm ⁻³)	1.912	1.936	2.0230	1.642	1.672	1.747	1.738
Crystal size (mm ³)	0.204 × 0.058 × 0.037	0.155 × 0.043 × 0.040	0.106 × 0.042 × 0.030	0.790 × 0.117 × 0.069	0.200 × 0.077 × 0.046	0.165 × 0.084 × 0.026	0.219 × 0.096 × 0.057
μ (mm ⁻¹)	15.186	15.697	16.232	12.785	13.386	13.959	16.482
θ range (°)	3.48 — 73.90	4.30 — 73.92	4.11 — 74.00	6.57 — 73.75	6.55 — 73.80	4.52 — 73.91	4.44 — 73.72
Total reflections	11,857	10,700	6,491	11,337	6,809	11,566	13,285
Unique reflections (R_{int})	4,001 (0.0233)	4,135 (0.0373)	3,182 (0.0359)	4,022 (0.0324)	3,621 (0.0221)	4,043 (0.0231)	4,360 (0.0305)
Observed reflections	3,445	3,710	2,930	3,743	3,248	3,808	4,096

$[I > 2\sigma(I)]$							
Parameters	250	259	259	241	245	250	250
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0253,$ $wR_2 = 0.685$	$R_1 = 0.0323,$ $wR_2 = 0.0885$	$R_1 = 0.0311,$ $wR_2 = 0.0720$	$R_1 = 0.0240,$ $wR_2 = 0.0604$	$R_1 = 0.0335,$ $wR_2 = 0.0841$	$R_1 = 0.0229,$ $wR_2 = 0.0590$	$R_1 = 0.0349,$ $wR_2 = 0.0946$
R indices (all data)	$R_1 = 0.0331,$ $wR_2 = 0.738$	$R_1 = 0.0387,$ $wR_2 = 0.0928$	$R_1 = 0.0357,$ $wR_2 = 0.0766$	$R_1 = 0.0263,$ $wR_2 = 0.0624$	$R_1 = 0.0397,$ $wR_2 = 0.0890$	$R_1 = 0.0256,$ $wR_2 = 0.0607$	$R_1 = 0.0386,$ $wR_2 = 0.0975$
Weighting scheme	$w = 1/[\sigma^2(F_o)^2 + \{0.0440 (F_o^2 + 2F_c^2)/3\}^2 + 8.0600 (F_o^2 + 2F_c^2)/3]$	$w = 1/[\sigma^2(F_o)^2 + \{0.0600 (F_o^2 + 2F_c^2)/3\}^2 + 3.3550 (F_o^2 + 2F_c^2)/3]$	$w = 1/[\sigma^2(F_o)^2 + \{0.0300 (F_o^2 + 2F_c^2)/3\}^2 + 5.2490 (F_o^2 + 2F_c^2)/3]$	$w = 1/[\sigma^2(F_o)^2 + \{0.0360 (F_o^2 + 2F_c^2)/3\}^2]$	$w = 1/[\sigma^2(F_o)^2 + \{0.0350 (F_o^2 + 2F_c^2)/3\}^2 + 88.7070 (F_o^2 + 2F_c^2)/3]$	$w = 1/[\sigma^2(F_o)^2 + \{0.0400 (F_o^2 + 2F_c^2)/3\}^2 + 4.4700 (F_o^2 + 2F_c^2)/3]$	$w = 1/[\sigma^2(F_o)^2 + \{0.0580 (F_o^2 + 2F_c^2)/3\}^2 + 37.4550 (F_o^2 + 2F_c^2)/3]$
Max., min. $\Delta\rho$ (eÅ ⁻³)	1.117, -1.553	0.878, -1.948	1.936, -0.986	0.866, -0.792	1.157, -0.975	0.555, -0.750	2.389, -1.128
Goodness of fit on F^2	1.017	1.027	1.039	1.026	1.051	1.035	1.030
Flack	—	0.004(17)	0.014(15)	-0.005(15)	-0.01(2)	0.015(14)	0.006(16)

parameter							

^a Estimated standard deviations are given in parentheses.

Table 2 Selected distances (Å) and angles (°) for for (η^5 -pentamethylcyclopentadienyl)iridium(κ C-1-(2-fluorophenylmethyl)-3-methylimidazol-2-ylidene) dichloride, **2a**, (η^5 -pentamethylcyclopentadienyl)iridium(κ C-1-(2-chloro-6-fluorophenylmethyl)-3-methylimidazol-2-ylidene) dichloride, **2c**, (η^5 -pentamethylcyclopentadienyl)iridium(κ C-1-(2-bromo-6-fluorophenylmethyl)-3-methylimidazol-2-ylidene) dichloride, **2d**, (η^5 -pentamethylcyclopentadienyl)iridium(κ C²-1-(2-fluorophenylmethyl)-3-methylimidazol-2-ylidene) chloride, **3b**, and co-crystals with (η^5 -pentamethylcyclopentadienyl)iridium(κ C²-1-(2-chlorophenylmethyl)-3-methylimidazol-2-ylidene) chloride, **3c**, with (η^5 -pentamethylcyclopentadienyl)iridium(κ C²-1-(2-bromophenylmethyl)-3-methylimidazol-2-ylidene) chloride, **3d**, and with (η^5 -pentamethylcyclopentadienyl)iridium(κ C²-1-(2-iodophenylmethyl)-3-methylimidazol-2-ylidene) chloride, **3e**.^a

	2a	2c	2d	3b	3b/3c	3b/3d	3b/3e
Cp*—Ir	1.806(4)	1.807(7)	1.823(7)	1.860(5)	1.863(9)	1.856(4)	1.858(8)
Ir—Cl(1)	2.4440(9)	2.445(1)	2.418(2)	2.4173(9)	2.422(2)	2.4251(8)	2.4176(13)
Ir—Cl(2)	2.4366(9)	2.442(1)	2.435(1)	—	—	—	—
Ir—C(11)	2.041(4)	2.054(5)	2.026(9)	2.029(5)	2.000(9)	2.006(4)	1.986(7)
Ir—C(17)	—	—	—	2.072(5)	2.076(9)	2.077(4)	2.080(7)
C—F	1.372(5)	1.376(9)	1.34(1)	1.380(7)	1.47(2)	1.44(1)	1.52(2)
C—X (X)	—	1.681(7) (Cl)	1.876(9) (Br)	—	1.78(1) (Cl)	1.896(5) (Br)	2.086(9) (I)

Cp*—Ir—Cl(1)	122.1(1)	122.9(2)	125.6(2)	122.9(1)	122.5(2)	122.6(1)	122.3(2)
Cp*—Ir—Cl(2)	125.1(1)	124.1(2)	123.5(2)	—	—	—	—
Cp*—Ir—C(11)	126.1(2)	129.6(2)	127.71(2)	128.3(2)	129.3(3)	128.8(2)	128.9(3)
Cp*—Ir—C(17)	—	—	—	128.2(2)	128.0(3)	128.4(2)	128.7(3)

^a Estimated standard deviations are given in parentheses.