

Responses to unsaturation in iridium mono(N-heterocyclic carbene) complexes: synthesis and oligomerization of $[L\text{Ir}(\text{H})_2\text{Cl}]$ and $[\text{L}\text{Ir}(\text{H})_2]^+$

Supporting Information

General details of synthetic procedures and instrumentation

Manipulations of air-sensitive reagents were carried out under a nitrogen or argon atmosphere using standard Schlenk line or dry box techniques. Non-deuteriated solvents were dried using a commercially available Braun Solvent Purification System, with the exception of fluorobenzene which was distilled from CaH_2 . C_6D_6 , $\text{C}_6\text{D}_5\text{CD}_3$, and CD_2Cl_2 (all Goss) were degassed and dried over potassium (C_6D_6 , $\text{C}_6\text{D}_5\text{CD}_3$) or molecular sieves (CD_2Cl_2) prior to use. NMR spectra were measured on a Varian Mercury VX-300 or Bruker AVII 500 FT-NMR spectrometer. Residual signals of solvent were used as reference for ^1H and ^{13}C NMR; ^{11}B and ^{19}F NMR spectra were referenced with respect to Et_2OBF_3 and CFCl_3 , respectively. T_1 measurements for **5** and $[\text{Ir}(\text{IPr})(\eta^6-\text{C}_6\text{H}_5\text{Me})(\text{H})_2]^+[\text{BAR}^f_4]^-$ were carried out at temperatures down to 273K, below which precipitation of $[\text{Ir}(\text{IPr})(\text{H})_2(\eta^6\text{-arene})]^+[\text{BAR}^f_4]^-$ became problematic. Elemental microanalyses were carried out at London Metropolitan University. For all crystallographic studies, diffraction data were collected at 150K using an Enraf Nonius Kappa CCD diffractometer;^[s1] structures were solved with SIR92^[s2] and refined using the CRYSTALS software suite,^[s3] as per the information contained in the CIF.

- ³⁰ [s1] Z. Otwinowski and W. Minor, *Methods Enzymol.*, **1997**, *276*, 307.
³¹ [s2] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst.*, **1994**, *27*, 435.
³² [s3] P.W. Betteridge, J.R. Carruthers, R.I. Cooper, C.K. Prout and D.J. Watkin, *J. Appl. Cryst.*, **2003**, *36*, 1487.

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$[\text{Ir}(\text{IPr})(\text{H})_2\text{Cl}]_3$ (2)

To a frozen (-196°C) fluorobenzene solution of **1a** (0.25 g, 0.34 mmol in 20 cm³) in an ampoule equipped with a Young's valve was added hydrogen gas. The reaction mixture was warmed to 20°C (giving a hydrogen pressure of *ca.* 4 atm.), stirred for 12 h, and, after filtration and drying *in vacuo*, the resulting solid was recrystallized from pentane as a yellow powder; single crystals suitable for X-ray diffraction were grown from a concentrated pentane solution at 0°C. Isolated yield 0.12 g, 48 %. ^1H NMR (300 MHz, C_6D_6 , 20°C): $\delta_{\text{H}} -32.93$ (s, 4H, IrH), 1.05 (d, $J = 6.8$ Hz, 36H, CH_3 of 'Pr), 1.28 (d, $J = 6.8$ Hz, 36H, CH_3 of 'Pr), 3.03 (br m, 12H, CH_3 of 'Pr), 6.49 (s, 6H, NCHCHN), 7.03-7.20 (overlapping m, 18H, aromatic CH of dipp). ^{13}C NMR (125 MHz, C_6D_6 , 20°C): δ_{C} 23.5, 27.0, 28.9 (CH and CH_3 of IPr), 122.6 (NCH of IPr), 124.2 (*ortho*-quaternary C of IPr), 129.9 (*meta*-CH of IPr), 146.4 (*para*-CH of IPr), 162.3 (carbene quaternary). Elemental microanalysis: calc. (for **2**, $\text{C}_{81}\text{H}_{114}\text{Cl}_3\text{Ir}_3\text{N}_6$) C 52.43, H 6.20, N 4.53; meas. C 52.46, H 6.00, N 4.47.

$\text{Ir}_3(\text{IMes})_2(\text{IMes}')\text{Cl}_3\text{H}_5$ (3)

To a frozen (-196°C) fluorobenzene solution of **1b** (0.30 g, 0.47 mmol in 20 cm³) in an ampoule equipped with a Young's valve was added hydrogen gas. The reaction mixture was warmed to 20°C (giving a hydrogen pressure of *ca.* 4 atm.), and then heated at 50°C for 24 h; after filtration and drying *in vacuo*, the resulting solid was recrystallized from pentane as a yellow powder; single crystals suitable for X-ray diffraction were grown from a concentrated hexane solution at 0°C. Isolated yield 0.13 g (43 %). ^1H NMR (300 MHz, C_6D_6 , 20°C): $\delta_{\text{H}} -32.52$, -30.28, -28.62, -27.00, -22.96 (s, each 1H, IrH), 1.93 (s, 6H, *ortho*- CH_3 of IMes), 2.20 (s, 3H, *ortho*- CH_3 of IMes'), 2.20 (overlapping s, 24H, *ortho*- CH_3 of IMes), 2.04 (s, 3H, *para*- CH_3 of IMes'), 2.12 (s, 3H, *para*- CH_3 of IMes'), 2.04 (s, 3H, *para*- CH_3 of IMes).

5 2.16 (s, 6H, *para*- CH_3 of IMes), 2.25 (s, 6H, *para*- CH_3 of IMes), 5.71 (s, 2H, NCH of IMes), 6.06 (s, 2H, NCH of IMes), 6.12 (s, 2H, NCH of IMes'), 6.48 (s, 2H, NCH of IMes'), 6.52 (s, 4H, *meta*-CH of IMes), 6.83 (s, 4H, *meta*-CH of IMes), 6.92 (s, 2H, *meta*-CH of IMes'), 7.07 (s, 1H, *meta*-CH of IMes'), 7.26 (s, 1H, *meta*-CH of IMes'). Attempts to obtain 10 reproducible ^{13}C NMR data for **3** were frustrated by its reactivity towards deuteriated solvents (C_6D_6 , $\text{C}_6\text{D}_5\text{CD}_3$, CD_2Cl_2) over the timescale of spectral acquisition. Elemental microanalysis: calc. (for **3**, $\text{C}_{63}\text{H}_{76}\text{Cl}_3\text{Ir}_3\text{N}_6$) C 47.26, H 4.79, N 5.15; meas. C 47.51, H 4.50, N 5.25.

$[\text{Ir}(\text{IPr}'')(\text{cod})]^+[\text{BAR}^f_4]^-$ (4)

A mixture of **1a** (0.13 g, 0.18 mmol), $\text{Na}[\text{BAR}^f_4]$ (0.16 g, 0.18 mmol) and fluorobenzene (50 mL) was stirred for 48 h, during which time a colour change from yellow to orange was observed. Filtration, concentration *in vacuo* and layering with pentane led to the formation of large, red-orange crystals suitable for single crystal X-ray diffraction studies. Isolated yield 0.21 g, 73 %. ^1H NMR (300 MHz, CD_2Cl_2 , 20°C): δ_{H} 1.10 (d, $J = 6.7$ Hz, 3H, CH_3 of 'Pr), 1.12 (d, $J = 6.7$ Hz, 3H, CH_3 of 'Pr), 1.15 (d, $J = 6.7$ Hz, 3H, CH_3 of 'Pr), 1.27 (d, $J = 6.7$ Hz, 3H, CH_3 of 'Pr), 1.43 (d, $J = 7.0$ Hz, 3H, CH_3 of 'Pr), 1.49 (d, $J = 6.7$ Hz, 3H, CH_3 of 'Pr), 1.12-1.40 (overlapping m, 3H, CH of cod), 1.64-1.78 (overlapping m, 2H, CH of cod), 1.88 (s, 3H, CH_3 of $\text{H}_2\text{C}=\text{CMe}$), 1.89-2.16 (overlapping m, 2H, CH of cod), 1.94 (m, 1H, CH of 'Pr), 2.28 (m, 1H, CH of cod), 3.04 (sep, $J = 6.7$ Hz, 1H, CH of 'Pr), 3.19 (m, 1H, CH of cod), 3.27 (sep, $J = 6.7$ Hz, 1H, CH of 'Pr), 3.52 (br s, 1H, CH of $\text{H}_2\text{C}=\text{CMe}$), 3.77 (m, 1H, CH of cod), 4.21 (br s, 1H, CH of $\text{H}_2\text{C}=\text{CMe}$), 4.39 (m, 1H, CH of cod), 5.28, (m, 1H, CH of cod), 7.20 (d, $J = 1.5$ Hz, 1H, NCHCHN), 7.34 (d, $J = 1.5$ Hz, 1H, NCHCHN), 7.41-7.66 (overlapping m, 6H, aryl CH of IPr''), 7.57 (s, 4H, *para*-CH of $[\text{BAR}^f_4]$), 7.72 (s, 8H, *ortho*-CH of $[\text{BAR}^f_4]$). ^{13}C { ^1H } NMR (125 MHz, CD_2Cl_2 , 20°C): (i) signals due to cation: δ_{C} 22.7, 23.3, 23.4, 24.5 (2 signals), 25.0, 26.3, 26.9, 27.8, 28.1, 29.2, 29.3, 34.5, 37.3, (CH and CH_3 of IPr'': CH_2 of cod), 69.7, 76.7 (2 signals), 90.8, 91.3 (CH_2 of $\text{H}_2\text{C}=\text{CMe}$) and CH of cod), 115.4, 115.7, 123.2, 124.2, 125.4, 128.4, 130.8, 131.3, 134.6, 135.3, 137.1, 141.4, 145.3, 146.5 (carbene backbone CH; aromatic CH and aromatic quaternary C of IPr''), 170.9 (carbene 10 quaternary of IPr''); (ii) signals due to $[\text{BAR}^f_4]$ anion: δ_{C} 118.0 (m, *para*-CH), 125.2 (q, $J = 272.1$ Hz, CF₃), 129.4 (q, $J = 31.0$ Hz, *meta*-C), 135.4 (s, *ortho*-CH), 162.3 (q, $J = 50.2$ Hz, *ipso*-C). ^{11}B NMR (96 MHz, CD_2Cl_2 , 20°C): $\delta_{\text{B}} -6.7$ ($[\text{BAR}^f_4]$). ^{19}F NMR (CD_2Cl_2 282 MHz, 20°C): δ_{F} -62.1. CI-MS(+): $m/z = 687.5$ (15 %) [M]⁺; accurate mass: calc. 685.3257, 105 meas. 685.3261. CI-MS(-): $m/z = 862.9$ (100 %) $[\text{BAR}^f_4]$ ⁻; accurate mass: calc. 862.0689, meas. 862.0691. Elemental microanalysis: calc. (for **4**, $\text{C}_{67}\text{H}_{58}\text{BF}_2\text{IrN}_2$) C 51.91, H 3.77, N 1.81; meas. C 51.88, H 3.75, N 1.77.

$[\text{Ir}(\text{IPr})(\eta^6\text{-C}_6\text{H}_5\text{F})(\text{H})_2]^+[\text{BAR}^f_4]^-$ (5)

110 To a solution of **4** (0.288g, 0.18 mmol) in fluorobenzene (20 cm³) at 20°C in an ampoule equipped with a Young's valve was added hydrogen gas (4 atm.). The reaction mixture was stirred for 3 h at 20°C, and the resulting colourless solution filtered, and concentrated *in vacuo*. Colourless crystals suitable for diffraction were obtained by layering this fluorobenzene 115 solution with pentane. Isolated yield 0.23 g, 82 %. ^1H NMR (300 MHz, CD_2Cl_2 , 20°C): $\delta_{\text{H}} -15.57$ (d, $J = 3.0$ Hz, $T_1 = 1.52$ s, 2H, IrH), 1.15 (d, $J = 6.0$ Hz, 12H, CH_3 of IPr), 1.32 (d, $J = 6.0$ Hz, 12H, CH_3 of IPr), 2.37 (sep, $J = 6.0$ Hz, 4H, CH of IPr), 5.66, (m, 1H, *para*-CH of $\text{C}_6\text{H}_5\text{F}$), 5.78 (m, 2H, *meta*-CH of $\text{C}_6\text{H}_5\text{F}$), 5.94 (m, 2H, *ortho*-CH of $\text{C}_6\text{H}_5\text{F}$), 7.22 (s, 2H, NCH of IPr), 7.42 (d, $J = 6.6$ Hz, 4H, *meta*-CH of IPr), 7.57 (s, 4H, *para*-CH of $[\text{BAR}^f_4]$), 7.64 (t, $J = 6.6$ Hz, 2H, *para*-CH of IPr), 7.73 (s, 8H, *ortho*-CH of $[\text{BAR}^f_4]$). ^{13}C NMR (75 MHz, CD_2Cl_2 , 20°C): (i) signals due to cation: δ_{C} 22.2, 25.1 (CH_3 of IPr), 29.2 (CH of IPr), 81.0, 91.4, 99.2, 120.9 ($\text{C}_6\text{H}_5\text{F}$), 123.7 (NCH of IPr), 134.4 (*ortho*-quaternary C of IPr), 135.2 (*meta*-CH of IPr), 145.8 (*para*-CH of IPr), carbene quaternary carbon of IPr and N-bound aryl quaternary signals not observed; (ii) signals due to $[\text{BAR}^f_4]$ anion: δ_{C} 117.9 (*para*-CH), 124.5 (1:3:3:1 q, $J = 272.5$ Hz, CF₃), 128.8 (1:3:3:1 q, $J = 31.1$ Hz, *meta*-quaternary C), 137.7 (*ortho*-CH), 161.7 (1:1:1:1 q, $J = 49.5$ Hz, *ipso*-quaternary C). ^{11}B NMR (130 MHz, CD_2Cl_2 , 20°C): $\delta_{\text{B}} -6.6$. ^{19}F NMR (CD_2Cl_2 , 282 MHz): $\delta_{\text{F}} -62.8$ ($[\text{BAR}^f_4]$), -115.9 ($\text{C}_6\text{H}_5\text{F}$). Crystallographic data for **5** ($\text{C}_{65}\text{H}_{55}\text{BF}_2\text{IrN}_2$): $M_r = 1542.15$, orthorhombic, Pbca , $a = 18.7562(1)$, $b = 25.4332(1)$, $c = 53.9834(3)$ Å, $V = 25751.7(2)$ Å³, $Z = 16$, $D_x = 1.591$ Mg m⁻³, $T = 150(2)$ K. 135985 reflections collected, 28197 independent [$R(\text{int}) = 0.0637$], $R_1 = 135 = 0.0659$, $wR_2 = 0.1526$ for observed unique reflections [$I > 2\sigma(I)$]; $R_1 =$

0.1052, $wR_2 = 0.1733$ for all unique reflections. Max. and min. residual electron densities: 3.61 and -3.50 e Å⁻³. CCDC 802161.

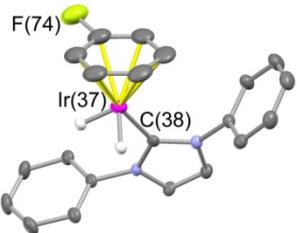


Figure S1: Structure of one of the cationic components of **5** in the asymmetric unit; hydrogen atoms (except metal-bound hydrogens), carbene 'Pr groups, [BAr^f₄]⁻ counter-ions and minor disorder component omitted for clarity. Thermal ellipsoids set at the 40% probability level.

[{Ir(IPr)(H)(μ-H)₂}²⁺[BAr^f₄]₂] (6)

A colorless solution of **5** (0.15 g, 0.1 mmol) in CH₂Cl₂ (20 cm³) was heated to 80°C for a period of 7 d. The resulting orange solution was filtered, dried *in vacuo* and orange crystals suitable for diffraction obtained from fluorobenzene/pentane layering at 20°C. Isolated yield 0.05 g, 31 %. ¹H NMR (300 MHz, CD₂Cl₂, 20°C): δ_H -15.73 (s, 4H, IrH), 1.12 (d, *J* = 6.6 Hz, 24H, CH₃ of IPr), 1.21 (d, *J* = 6.8 Hz, 24H, CH₃ of IPr), 2.27 (m, 8H, CH of IPr), 7.34 (d, *J* = 6.6 Hz, 8H, *meta*-CH of IPr), 7.48 (s, 8H, *para*-CH of [BAr^f₄]⁻), 7.58 (t, *J* = 6.0 Hz, 4H, *para*-CH of IPr), 7.63 (s, 16H, *ortho*-CH of [BAr^f₄]⁻), 8.26 (s, 4H, NCH of IPr). ¹³C NMR (76 MHz, CD₂Cl₂, 20°C): (i) signals due to cation: δ_C 23.5, 24.3 (CH₃ of IPr), 29.3 (CH of IPr), 122.3 (NCH of IPr), 132.8 (*ortho*-quaternary C of IPr), 136.3 (*meta*-CH of IPr), 144.8 (*para*-CH of IPr), carbene quaternary C of IPr and N-bound aryl quaternary signals not observed; (ii) signals due to [BAr^f₄]⁻ anion: 117.4 (*para*-CH), 124.5 (q, *J* = 273 Hz, CF₃), 128.9 (q, *J* = 30 Hz, *meta*-quaternary C), 134.7 (*ortho*-CH), 161.7 (q, *J* = 50 Hz, *ipso*-quaternary C), ¹¹B NMR (96 MHz, CD₂Cl₂, 20°C): δ_B -6.6. ¹⁹F NMR (282 MHz, CD₂Cl₂, 20°C): δ_F -62.8.

[{Ir(IPr)(η⁶-C₆H₅Me)(H)₂}²⁺[BAr^f₄]⁻

To a solution of **2** (0.29 g, 0.18 mmol) in toluene (20 cm³) at 20°C in an ampoule equipped with a Young's valve was added hydrogen gas (4 atm.). The reaction mixture was stirred for 3 h at 20°C, and the resulting colourless solution filtered, and concentrated *in vacuo*. Colourless crystals suitable for diffraction were obtained by layering this toluene solution with pentane. Isolated yield 0.28 g, 90 %. ¹H NMR (300 MHz, C₆D₅CD₃, 20°C): δ_H -16.33 (s, *T*₁ = 1.08 s, 2H, IrH), 0.85 (d, *J* = 6.6 Hz, 12H, CH₃ of IPr), 1.05 (d, *J* = 6.6 Hz, 12H, CH₃ of IPr), 1.26 (sept, *J* = 6.6 Hz, 4H, CH of IPr), 1.48 (s, 3H, CH₃ of toluene), 4.64 (d, *J* = 6.6 Hz, 2H, *ortho*-CH of toluene), 4.83 (t, *J* = 6.6 Hz, 2H, *meta*-CH of toluene), 4.88 (t, *J* = 6.6 Hz, 1H, *para*-CH of toluene), 6.28 (s, 2H, NCH of IPr), 6.97 (d, *J* = 6.8 Hz, *meta*-CH of IPr), 7.19 (t, *J* = 6.6 Hz, 2H, *para*-CH of IPr), 7.66 (s, 4H, *para*-CH of [BAr^f₄]⁻), 8.28 (s, 8H, *ortho*-CH of *para*-CH of [BAr^f₄]⁻). ¹³C NMR (300 MHz, C₆D₆, 126 MHz): (i) signals due to cation: δ_C 22.4 (CH₃ of toluene), 25.3, 29.5 (CH₃ of IPr), 34.7 (CH of IPr), 92.3 (*ortho*-CH of toluene), 95.5 (*meta*-CH of toluene), 98.9 (*para*-CH of toluene), 122.5 (NCH of IPr), 131.9 (*ortho*-quaternary C of IPr), 136.8 (*meta*-CH of IPr), 145.8 (*para*-CH of IPr) carbene quaternary carbon of IPr and N-bound aryl quaternary signals not observed; (ii) signals due to [BAr^f₄]⁻ anion: δ_C 118.4 (*para*-CH), 125.6 (1:3:3:1 q, *J* = 272.9 Hz, CF₃), 130.3 (1:3:3:1 q, *J* = 31.5 Hz, *meta*-quaternary C), 135.9 (*ortho*-CH), 162.6 (1:1:1:1 q, *J* = 53.7 Hz, *ipso*-quaternary C). ¹¹B NMR (96 MHz, C₆D₅CD₃, 20°C): δ_B -6.1. ¹⁹F NMR (282 MHz, C₆D₅CD₃, 20°C): δ_F -61.6. Anal. Calcd for C₆₆H₅₇N₂IrBF₂₄: C, 51.57; H, 3.74 N, 1.82. Found: C, 51.36; H, 3.58; N, 1.93. Crystallographic data for [{Ir(IPr)(η⁶-C₆H₅Me)(H)₂}²⁺[BAr^f₄]⁻] (C₆₆H₅₈BF₂₄IrN₂): M_r = 1538.18, triclinic, P-1, *a* = 12.3412(1), *b* = 16.5275(1), *c* = 17.7468(1) Å, α = 113.861(1), β = 97.829(1), γ = 92.592(1), *V* = 3259.4(1) Å³, *Z* = 2, *D_x* = 1.567 Mg m⁻³, *T* = 150(2) K, λ = 0.71073 Å. 50614 reflections collected, 14817 independent [R(int) = 0.000], which were used in all calculations. R₁ = 0.0387, wR₂ = 0.0964 for observed unique reflections [*I* > 2σ(*I*)] and R₁ = 0.0418, wR₂ = 0.0989 for all unique reflections. Max. and min. residual electron densities 2.94 and -1.48 e Å⁻³. CSD ref.: 802163.

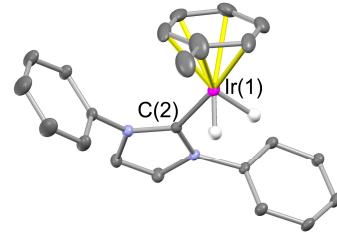


Figure S2: Structure of the cationic component of [Ir(IPr)(η⁶-C₆H₅Me)(H)₂}²⁺[BAr^f₄]⁻; hydrogen atoms (except metal-bound hydrogens), carbene 'Pr groups, [BAr^f₄]⁻ counter-ion and minor disorder component omitted for clarity. Thermal ellipsoids set at the 40% probability level.

[{Ir(IMes)(cod)}₂(μ-Cl)²⁺[BAr^f₄]⁻

A mixture of **1b** (0.12 g, 0.18 mmol), Na[BAr^f₄] (0.16 g, 0.18 mmol) and fluorobenzene (50 cm³) was stirred for 48 h, during which time a colour change from yellow to orange was observed. Filtration, concentration *in vacuo* and layering with pentane led to the formation of large red crystals suitable for diffraction studies. Isolated yield 0.14 g, 76 %. ¹H NMR (300 MHz, C₆D₅CD₃, 20°C): δ_H 0.91, 1.12, 1.45, 1.51 (m, each 4H, CH₂ of cod), 1.88, 1.94 (s, each 12H, *ortho*-CH₃ of IMes), 2.16 (s, 12H, para-CH₃ of IMes), 3.25 (br m, 4H, CH of cod), 6.10 (s, 4H, NCH of IMes), 6.74 (s, 8H, aromatic CH of Mes), 7.70 (s, 4H, *para*-CH of [BAr^f₄]⁻), 8.35 (s, 8H, *ortho*-CH of [BAr^f₄]⁻). ¹³C NMR (75 MHz, C₆D₆, 20°C): (i) signals due to cation: δ_C 17.4, 18.6 (CH₂ of cod), 20.5 (*ortho*-CH₃ of IMes), 20.9 (*para*-CH₃ of IMes), 123.7 (NCH of IMes), 129.3, 129.7 (*ortho*-quaternary C of IMes), 134.3, 135.5 (*meta*-CH of IMes), 139.2 (para-quaternary C of IMes), 176.9 (carbene quaternary C of IMes), N-bound aryl quaternary signal not observed; (ii) signals due to [BAr^f₄]⁻ anion: 117.6 (*para*-CH), 124.9 (1:3:3:1 q, *J* = 272.3 Hz, CF₃), 129.5 (1:3:3:1 q, *J* = 28.2 Hz, *meta*-quaternary C), 135.2 (*ortho*-CH), 162.3 (1:1:1:1 q, *J* = 50.2 Hz, *ipso*-quaternary C). ¹¹B NMR (96 MHz, C₆D₅CD₃, 20°C): δ_B -6.0. ¹⁹F NMR (282 MHz, C₆D₅CD₃, 20°C): δ_F -61.6. Elemental microanalysis: calc. (for [{Ir(IMes)(cod)}₂(μ-Cl)²⁺[BAr^f₄]⁻] C₉₀H₈₄BClF₂₄Ir₂N₄): C, 51.27; H, 4.02 N, 2.66. meas. C, 51.19; H, 3.92; N, 2.51. Crystallographic data for [{Ir(IMes)(cod)}₂(μ-Cl)²⁺[BAr^f₄]⁻] (C₉₀H₈₄BClF₂₄Ir₂N₄): M_r = 2108.34, triclinic, P 1̄, *a* = 15.333(3), *b* = 15.589(3), *c* = 19.855(4) Å, α = 94.97(3), β = 110.90(3), γ = 94.15(3), *V* = 4389.4(18) Å³, *Z* = 2, *D_x* = 1.595 Mg m⁻³, *T* = 150(2) K, λ = 0.71073 Å. 71291 reflections collected, 19838 independent [R(int) = 0.030], which were used in all calculations. R₁ = 0.0498, wR₂ = 0.1035 for observed unique reflections [*I* > 2σ(*I*)] and R₁ = 0.0837, wR₂ = 0.1206 for all unique reflections. Max. and min. residual electron densities 3.06 and -3.36 e Å⁻³. CSD ref.: 802164.

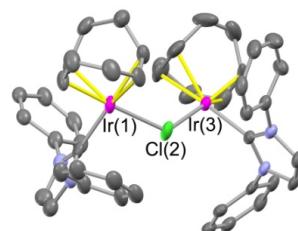


Figure S3: Structure of the cationic component of [{Ir(IMes)(cod)}₂(μ-Cl)²⁺[BAr^f₄]⁻; hydrogen atoms, carbene Me groups, [BAr^f₄]⁻ counter-ion and minor disorder component omitted for clarity. Thermal ellipsoids set at the 40% probability level.