

SUPPORTING INFORMATION

Imine-functionalised protic NHC complexes of Ir: Direct formation by C-H activation

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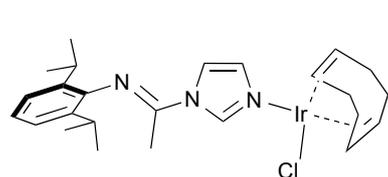
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1 Synthesis and characterization

1.1 General methods

All manipulations involving organometallics were performed under argon in a Braun glove box or using standard Schlenk techniques. Solvents were dried using standard methods and distilled under argon prior use or passed through columns of activated alumina and subsequently purged with argon. NMR spectra of complexes were recorded on Bruker a AVANCE I 300 MHz, AVANCE III 400 MHz or AVANCE I 500 MHz instrument at ambient temperature and referenced using the proton (^1H) or carbon (^{13}C) resonance of the residual solvent. Assignments are based on ^1H , ^1H -COSY, ^1H -NOESY, $^1\text{H}/^{13}\text{C}$ -HSQC, and $^1\text{H}/^{13}\text{C}$ -HMBC experiments. IR spectra were recorded in the region 4000–100 cm^{-1} on a Nicolet 6700 FT-IR spectrometer (ATR mode, diamond crystal). Elemental analyses were performed by the “Service de microanalyses”, Université de Strasbourg.

1.2 Synthesis of 1

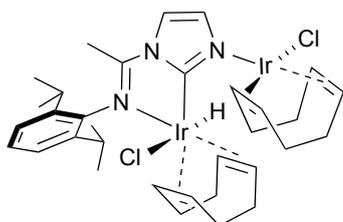


A solution of 1-(2,6-diisopropylphenylimino)ethylimidazole (81 mg, 0.30 mmol) in THF (5 mL) was added to a solution of $[\text{Ir}(\text{cod})(\mu\text{-Cl})_2]$ (100 mg, 0.15 mmol) in

THF (5 mL). The mixture was stirred for 1 h at room temperature and then concentrated under reduced pressure to *ca.* 1 mL. A yellow precipitate was formed after pentane (5 mL) was added to the solution. The precipitate was filtered, washed with pentane (2×3 mL) and dried under vacuum to give a yellow solid (175 mg, 0.29 mmol, 97%). ^1H NMR (500 MHz, CD_2Cl_2): δ 8.88 (s, 1H, NCHN), 7.87 (t, 1H, $^3J = 1.5$ Hz, NCHCHN_(imine)), 7.20–7.10 (m, 4H, NCHCHN_(imine) and aryl-*H*), 4.55–3.96 (br s, 2H, CH_(cod)), 3.96–3.44 (br s, 2H, CH_(cod)), 2.68 (sept, $^3J = 6.9$ Hz, 2H, CH(CH₃)₂), 2.27 (m, 4H, CH_{2(cod)}), 2.20 (s, 3H, CH_{3(imine)}), 1.59 (m, 4H, CH_{2(cod)}), 1.14 (d, $^3J = 6.9$ Hz, 6H, CH(CH₃)₂), 1.11 (d, $^3J = 6.9$ Hz, 6H, CH(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2): δ 148.9 (C=N), 142.1 (*ipso*-C_(dipp)), 138.3 (NCHN), 137.2 (*o*-C_(dipp)), 127.7 (NCHCHN_(imine)), 125.1 (*p*-C_(dipp)), 123.7 (*m*-C_(dipp)), 117.2 (NCHCHN_(imine)), 68.0 (br s, CH_(cod)), 58.6 (br s, CH_(cod)), 31.9 (br s, CH_{2(cod)}), 28.8

(CH(CH₃)₂), 23.4 (CH(CH₃)₂), 23.0 (CH(CH₃)₂), 16.5 (CH_{3(imine)}). IR: ν_{\max} (pure, orbit diamond)/cm⁻¹ 1687 ν (C=N) and 291 ν (Ir-Cl). Anal. calcd for C₂₅H₃₅ClIrN₃ (%): C, 49.61; H, 5.83; N, 6.94. Found: C, 49.38; H, 5.72; N, 7.06.

1.3 Synthesis of 2



The synthesis of complex **2** can be performed by reaction of 1-(2,6-diisopropylphenylimino)ethylimidazole with 1.0 equiv. of [Ir(cod)(μ -Cl)]₂ or by reaction of complex **1** with 0.5 equiv. of [Ir(cod)(μ -Cl)]₂.

a) Addition of 1.0 equiv of [Ir(cod)(μ -Cl)]₂ to 1-(2,6-diisopropylphenylimino)ethylimidazole.

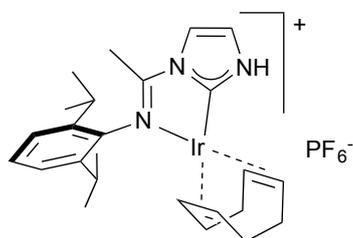
To a solution of 1-(2,6-diisopropylphenylimino)ethylimidazole (40 mg, 0.15 mmol) in THF (4 mL) was added [Ir(cod)(μ -Cl)]₂ (100 mg, 0.15 mmol) under magnetic stirring in a glove box. The mixture was stirred for 3 h at room temperature and then concentrated under reduced pressure to *ca.* 0.5 mL. Yellow-green crystals suitable for X-ray analysis were obtained after 2-3 days and a crystalline product was isolated (120 mg, 0.13mmol, 86%).

b) Addition of 0.5 equiv. of [Ir(cod)(μ -Cl)]₂ to complex **1**.

To a solution of complex **1** (90 mg, 0.15 mmol) in THF (4 mL) was added [Ir(cod)(μ -Cl)]₂ (50 mg, 0.075 mmol) under magnetic stirring in a glove box. The same product was obtained as in a) with an identical work-up. ¹H NMR (400 MHz, THF-d₈): δ 7.43 (d, ³J = 2.1 Hz, 1H, NCHCHN_(imine)), 7.29–6.26 (m, 3H, aryl-H), 7.15 (d, ³J = 2.1 Hz, 1H, NCHCHN_(imine)), 6.28 (m, 1H, CH_(cod)), 6.10 (m, 1H, CH_(cod)), 4.25 (m, 1H, CH_(cod)), 4.15-4.04 (m, 3H, CH_(cod)), 4.02 (sept, ³J = 6.7 Hz, 1H, CH(CH₃)₂), 3.89 (m, 1H, CH_(cod)), 3.24 (m, 1H, CH_(cod)), 3.19 (sept, ³J = 6.7 Hz, 1H, CH(CH₃)₂), 2.98–2.87 (m, 1H, CH_{2(cod)}), 2.81–2.71 (m, 2H, CH_{2(cod)}), 2.50–2.37 (m, 1H, CH_{2(cod)}), 2.42 (s, 3H, CH_{3(imine)}), 2.33-2.04 (m, 8H, CH_{2(cod)}), 2.00–1.90 (m, 1H, CH_{2(cod)}), 1.90–1.79 (m, 1H, CH_{2(cod)}), 1.60–1.45 (m, 2H, CH_{2(cod)}), 1.42 (d, ³J = 6.7 Hz, 3H, CH(CH₃)₂), 1.28 (d, ³J = 6.7 Hz, 3H, CH(CH₃)₂), 1.11 (d, ³J = 6.7 Hz, 3H, CH(CH₃)₂), 1.00 (d, ³J = 6.7 Hz, 3H, CH(CH₃)₂), -14.74 (d, ⁴J = 1.8Hz, 1H, Ir-H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, THF- d_8): δ 166.6 (C=N), 158.7 (NCN_(imine)), 144.4 (*o*-C_(dipp)), 143.2 (*o*-C_(dipp)), 139.9 (*ipso*-C_(dipp)), 130.7 (NCHCHN_(imine)), 129.3 (*p*-C_(dipp)), 125.7 (*m*-C_(dipp)), 125.2 (*m*-C_(dipp)), 117.0 (NCHCHN_(imine)), 96.0, 94.3, 78.4, 76.9, 68.4, 66.6, 60.8 and 57.1 (CH_(cod)), 37.4, 33.7, 32.8, 32.5, 31.1, 29.8, 29.2 and 28.2 (CH_{2(cod)}), 28.4 and 28.1 (CH(CH₃)₂), 25.7, 25.5, 25.1 and 23.6 (CH(CH₃)₂), 16.1 (CH_{3(imine)}). IR (CsI, Nujol mull): $\nu(\text{Ir-H}) = 2200 \text{ cm}^{-1}$, $\nu(\text{C=N}) = 1621 \text{ cm}^{-1}$, $\nu(\text{Ir-Cl}) = 290 \text{ cm}^{-1}$. Anal. Calcd for C₃₃H₄₇Cl₂Ir₂N₃ (941.09): C, 42.12; H, 5.03; N, 4.47. Found: C, 41.98, H, 5.03; N, 4.32.

1.4 Synthesis of $3^+[\text{PF}_6]^-$

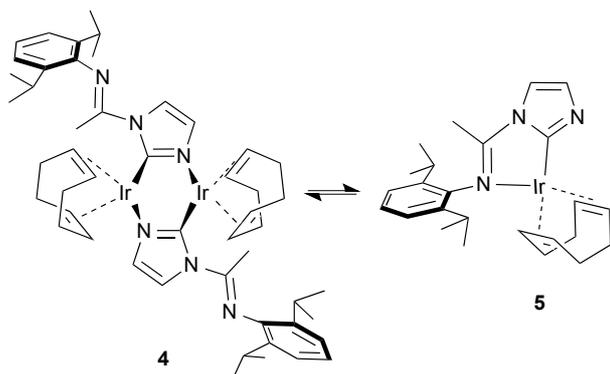


The synthesis of complex $3^+[\text{PF}_6]^-$ can be performed by reaction of either complex **1** or complex **2** with 1.0 equiv. of TlPF₆.

a) Reaction of complex **1** with TlPF₆. To a solution of **1** (121 mg, 0.20 mmol) in CH₂Cl₂ or CH₃CN (5 mL), was added TlPF₆ (70 mg, 0.20 mmol). The reaction mixture was stirred for 12 h at room temperature. After filtration through Celite, the filtrate was concentrated under reduced pressure to *ca.* 2 mL and then was stratified with Et₂O to yield dark green crystals, which were collected by filtration and dried in vacuo (122 mg, 0.17 mmol, 85%). ^1H NMR (500 MHz, CD₂Cl₂): δ 10.36 (br s, 1H, NH), 7.38–7.29 (m, 4H, NHCHCHN_(imine) and aryl-H), 7.25 (t, $^3J = 2.0$ Hz, 1H, NHCHCHN_(imine)), 4.35 (m, 2H, CH_(cod)), 4.17 (m, 2H, CH_(cod)), 3.02 (sept, $^3J = 6.8$ Hz, 2H, CH(CH₃)₂), 2.36 (s, 3H, CH_{3(imine)}), 2.27–1.96 (m, 8H, CH_{2(cod)}), 1.34 (d, $^3J = 6.8$ Hz, 6H, CH(CH₃)₂), 1.13 (d, $^3J = 6.8$ Hz, 6H, CH(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD₂Cl₂): δ 173.6 (NHCN_(imine)), 168.0 (C=N), 141.3 (*o*-C_(dipp)), 138.2 (*ipso*-C_(dipp)), 129.1 (*p*-C_(dipp)), 124.8 (*m*-C_(dipp)), 122.2 (NHCHCHN_(imine)), 116.6 (NHCHCHN_(imine)), 95.9 (CH_(cod)), 65.4 (CH_(cod)), 33.2 (CH_{2(cod)}), 30.3 (CH_{2(cod)}), 28.9 (CH(CH₃)₂), 25.1 (CH(CH₃)₂), 23.4 (CH(CH₃)₂), 16.2 (CH_{3(imine)}). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD₂Cl₂): δ -144.3 (sept, $^1J_{\text{P,F}} = 712$ Hz, PF₆⁻). $^{19}\text{F}\{^1\text{H}\}$ NMR (282.4 MHz, CD₂Cl₂): δ -73.3 (d, $^1J_{\text{F,P}} = 712$ Hz, PF₆⁻). IR: ν_{max} (pure, orbit diamond)/cm⁻¹ 3359 $\nu(\text{N-H})$, 1613 $\nu(\text{C=N})$ and 832 $\nu(\text{P-F})$. Anal. calcd for C₂₅H₃₅F₆IrN₃P (%): C, 42.01; H, 4.94; N, 5.88. Found: C, 41.73; H, 4.83; N, 5.84.

b) Reaction of complex **2** with TlPF₆. Complex **2** (5.4 mg, 0.0057 mmol), TlPF₆ (2.0 mg, 0.0057 mmol) and CD₂Cl₂ (0.5 mL) were added into a Young NMR tube in a glove box. After 12 h, the colour of this solution turned to dark green. **3**⁺[PF₆]⁻ and [Ir(cod)(μ-Cl)]₂ were obtained in quantitative NMR yields.

1.5 Synthesis of **4** and **5**

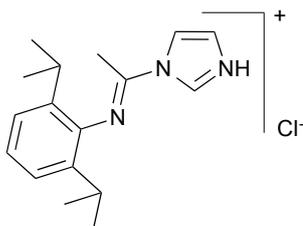


To a solution of **3**⁺[PF₆]⁻ (50 mg, 0.070 mmol) in CH₂Cl₂ (5 mL) at 0 °C, was added NaO*t*-Bu (7.0 mg, 0.073 mmol). The reaction mixture was stirred for 10 min at 0 °C. Then the reaction mixture was allowed to warm to room temperature and was stirred for another 20 min. After

filtration through Celite, the filtrate was evaporated to *ca.* 1 mL under reduced pressure. After Et₂O (2 mL) was added, the solution was cooled to -30 °C to yield dark red crystals that were collected by filtration and dried in vacuo (28 mg, 0.049 mmol, 70%). Anal. calcd for C₂₅H₃₄IrN₃ (%): C, 52.79; H, 6.03; N, 7.39. Found: C, 52.30; H, 6.24; N, 7.45. The spectroscopic analysis of the crystals at room temperature revealed a mixture of two complexes **4** and **5** with a molar ratio 14:86 in CD₂Cl₂ (by ¹H NMR integration of 1:3) and with a molar ratio 80:20 in toluene-*d*₈ (by ¹H NMR integration of 8:1), respectively. The assignment to **4** or **5** was made on the basis of the chemical shift of C=N in the ¹³C NMR spectrum, which is different for a coordinated and a dangling imine group. **4**: ¹H NMR (500 MHz, CD₂Cl₂): δ 7.65 (d, ³J = 1.5 Hz, 2H, NCHCHN_(imine)), 7.19 (m, 2H, aryl-*H*), 7.10 (m, 4H, aryl-*H*), 6.90 (d, ³J = 1.5 Hz, 2H, NCHCHN_(imine)), 4.48 (m, 2H, CH_(cod)), 3.55 (m, 2H, CH_(cod)), 3.49 (m, 4H, CH_(cod)), 3.02 (sept, ³J = 7.0 Hz, 2H, CH(CH₃)₂), 2.95 (s, 6H, CH₃_(imine)), 2.68 (sept, ³J = 7.0 Hz, 2H, CH(CH₃)₂), 2.51–2.29 (m, 12H, CH₂_(cod)), 2.22 (m, 4H, CH₂_(cod)), 1.32 (d, ³J = 7.0 Hz, 12H, CH(CH₃)₂), 1.13 (d, ³J = 7.0 Hz, 12H, CH(CH₃)₂). ¹³C{¹H} NMR (125 MHz, CD₂Cl₂): δ 174.8 (NCN_(imine)), 156.2 (C=N), 143.9 (*ipso*-C_(dipp)), 137.7 (*o*-C_(dipp)), 136.9 (*o*-C_(dipp)), 128.7 (*p*-C_(dipp)), 125.5 (NCHCHN_(imine)), 123.6 (*m*-C_(dipp)), 123.4 (*m*-C_(dipp)), 120.3 (NCHCHN_(imine)), 77.8

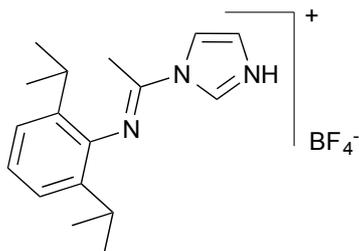
(CH_(cod)), 73.6 (CH_(cod)), 61.2 (CH_(cod)), 58.8 (CH_(cod)), 34.3 (CH_{2(cod)}), 33.3 (CH_{2(cod)}), 31.5 (CH_{2(cod)}), 30.1 (CH_{2(cod)}), 28.5 (CH(CH₃)₂), 28.4 (CH(CH₃)₂), 23.9 (CH(CH₃)₂), 23.8 (CH(CH₃)₂), 22.6 (CH(CH₃)₂), 20.8 (CH_{3(imine)}). **5**: ¹H NMR (500 MHz, CD₂Cl₂): δ 7.24 (m, 3H, aryl-*H*), 6.98 (d, ³*J* = 1.7 Hz, 1H, NCHCHN_(imine)), 6.88 (d, ³*J* = 1.7 Hz, 1H, NCHCHN_(imine)), 4.22 (m, 2H, CH_(cod)), 3.35 (m, 2H, CH_(cod)), 3.22 (sept, ³*J* = 6.7 Hz, 2H, CH(CH₃)₂), 2.25 (s, 3H, CH_{3(imine)}), 2.21–2.01 (m, 4H, CH_{2(cod)}), 1.90–1.68 (m, 4H, CH_{2(cod)}), 1.34 (d, ³*J* = 6.7 Hz, 6H, CH(CH₃)₂), 1.10 (d, ³*J* = 6.7 Hz, 6H, CH(CH₃)₂). ¹³C{¹H} NMR (125 MHz, CD₂Cl₂): δ 179.3 (NCN_(imine)), 166.3 (C=N), 142.1 (*o*-C_(dipp)), 139.6 (*ipso*-C_(dipp)), 133.4 (NCHCHN_(imine)), 127.7 (*p*-C_(dipp)), 124.2 (*m*-C_(dipp)), 114.3 (NCHCHN_(imine)), 83.3 (CH_(cod)), 62.6 (CH_(cod)), 32.8 (CH_{2(cod)}), 30.7 (CH_{2(cod)}), 28.5 (CH(CH₃)₂), 25.1 (CH(CH₃)₂), 23.5 (CH(CH₃)₂), 15.5 (CH_{3(imine)}).

1.6 Synthesis of 6⁺Cl⁻



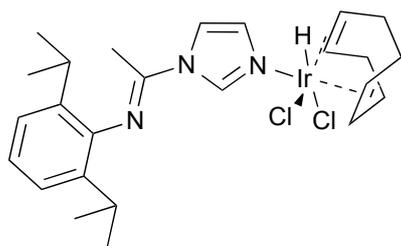
To a solution of 1-(2,6-diisopropylphenyl)imidazole ethylimidazole (540 mg, 2.0 mmol) in Et₂O (30 mL) was added dropwise a solution of HCl (1.0 M in Et₂O, 2.0 mL, 2.0 mmol). The reaction mixture was stirred for 1 h at room temperature. Then the resultant precipitate was collected by filtration, washed with Et₂O and dried in vacuo to obtain a white powder (520 mg, 1.7 mmol, 85%). ¹H NMR (500 MHz, CDCl₃): δ 15.02 (br s, 1H, NH), 10.73 (s, 1H, NCHN), 8.13 (s, 1H, NCHCHN_(imine)), 7.51 (s, 1H, NCHCHN_(imine)), 7.17 (m, 3H, aryl-*H*), 2.62 (sept, ³*J* = 6.9 Hz, 2H, CH(CH₃)₂), 2.54 (s, 3H, CH_{3(imine)}), 1.15 (d, ³*J* = 6.9 Hz, 6H, CH(CH₃)₂), 1.11 (d, ³*J* = 6.9 Hz, 6H, CH(CH₃)₂). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 147.7 (C=N), 139.9 (*ipso*-C_(dipp)), 135.6 (*o*-C_(dipp)), 135.1 (NCHN), 124.6 (*p*-C_(dipp)), 122.6 (*m*-C_(dipp)), 119.4 (NCHCHN_(imine)), 116.2 (NCHCHN_(imine)), 27.6 (CH(CH₃)₂), 22.3 (CH(CH₃)₂), 21.9 (CH(CH₃)₂), 16.1 (CH_{3(imine)}). IR: ν_{max}(pure, orbit diamond)/cm⁻¹ 3368 ν(N-H) and 1694 ν(C=N). Anal. calcd for C₁₇H₂₄ClN₃ (%): C, 66.76; H, 7.91; N, 13.74. Found: C, 66.44; H, 7.76; N, 13.89.

1.7 Synthesis of $6^+[\text{BF}_4]^-$



To a solution of 1-(2,6-diisopropylphenylimino)ethylimidazole (600 mg, 2.2 mmol) in Et₂O (30 mL) was added dropwise a solution of HBF₄·Et₂O (0.30 mL, 357 mg, 2.2 mmol) in Et₂O (5 mL). The reaction mixture was stirred for 12 h at room temperature. Then the resultant precipitate was collected by filtration, washed with Et₂O and dried in vacuo to obtain a white powder (572 mg, 1.6 mmol, 73%). ¹H NMR (500 MHz, CDCl₃): δ 12.45 (br s, 1H, NH), 9.43 (s, 1H, NCHN), 8.17 (s, 1H, NCHCHN_(imine)), 7.67 (s, 1H, NCHCHN_(imine)), 7.18 (m, 3H, aryl-H), 2.65 (sept, ³J = 6.9 Hz, 2H, CH(CH₃)₂), 2.38 (s, 3H, CH₃(imine)), 1.16 (d, ³J = 6.9 Hz, 6H, CH(CH₃)₂), 1.12 (d, ³J = 6.9 Hz, 6H, CH(CH₃)₂). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 148.2 (C=N), 140.8 (*ipso*-C_(dipp)), 136.8 (*o*-C_(dipp)), 135.3 (NCHN), 125.6 (*p*-C_(dipp)), 123.6 (*m*-C_(dipp)), 121.2 (NCHCHN_(imine)), 117.5 (NCHCHN_(imine)), 28.6 (CH(CH₃)₂), 23.4 (CH(CH₃)₂), 22.9 (CH(CH₃)₂), 15.8 (CH₃(imine)). IR: ν_{max} (pure, orbit diamond)/cm⁻¹ 3326 ν(N-H) and 1705 ν(C=N). Anal. calcd for C₁₇H₂₄BF₄N₃ (%): C, 57.16; H, 6.77; N, 11.76. Found: C, 57.38; H, 6.52; N, 12.30.

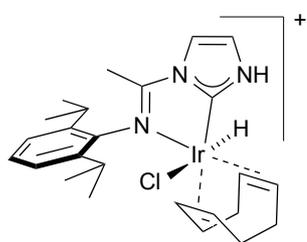
1.8 Synthesis of 7



To a solution of 6^+Cl^- (46 mg, 0.15 mmol) in THF (5 mL) was added a solution of [Ir(cod)(μ-Cl)]₂ (50 mg, 0.075 mmol) in THF (5 mL). The mixture was stirred for 4 h at room temperature and then was concentrated under reduced pressure to ca. 1 mL. A yellow precipitate was formed after 5 mL of pentane was added to the solution. The precipitate was filtered, washed with pentane (2 × 3 mL) and dried under vacuum to give a yellow solid (82 mg, 0.13 mmol, 85%). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.90 (s, 1H, NCHN), 7.83 (t, 1H, ³J = 1.6 Hz, NCHCHN_(imine)), 7.39 (t, 1H, ³J = 1.6 Hz, NCHCHN_(imine)), 7.16 (m, 3H, aryl-H), 4.88 (m, 1H, CH_(cod)), 4.76 (m, 1H, CH_(cod)), 4.37 (m, 1H, CH_(cod)), 4.26 (m, 1H, CH_(cod)), 3.07–2.79 (m, 2H, CH₂(cod)), 2.76–2.52 (m, 4H, CH₂(cod) and CH(CH₃)₂), 2.39–2.15 (m, 5H, CH₂(cod) and CH₃(imine)), 2.11–1.89 (m, 2H, CH₂(cod)), 1.15 (d, ³J = 6.9 Hz, 6H, CH(CH₃)₂), 1.11 (d, ³J = 6.9 Hz, 6H,

CH(CH₃)₂), -12.10 (s, 1H, Ir-H). ¹³C{¹H} NMR (125 MHz, CD₂Cl₂): δ 148.6 (C=N), 141.9 (*ipso*-C_(dipp)), 138.8 (NCHN), 137.2 (*o*-C_(dipp)), 131.8 (NCHCHN_(imine)), 125.2 (*p*-C_(dipp)), 123.7 (*m*-C_(dipp)), 117.3 (NCHCHN_(imine)), 83.5 (CH_(cod)), 81.7 (CH_(cod)), 79.5 (CH_(cod)), 76.2 (CH_(cod)), 35.3 (CH_{2(cod)}), 32.3 (CH_{2(cod)}), 29.9 (CH_{2(cod)}), 29.6 (CH_{2(cod)}), 28.7 (CH(CH₃)₂), 23.4 (CH(CH₃)₂), 23.0 (CH(CH₃)₂), 16.4 (CH_{3(imine)}). IR: ν_{max}(pure, orbit diamond)/cm⁻¹ 2206 ν(Ir-H), 1687 ν(C=N) and 294 ν(Ir-Cl). Anal. calcd for C₂₅H₃₆Cl₂IrN₃ (%): C, 46.79; H, 5.65; N, 6.55. Found: C, 46.32; H, 5.52; N, 6.52.

1.9 Synthesis of 8⁺[BF₄]⁻



To a solution of 6⁺[BF₄]⁻ (54 mg, 0.15 mmol) in THF (5 mL) was added to a solution of [Ir(cod)(μ-Cl)]₂ (50 mg, 0.075 mmol) in THF (5 mL). The mixture was stirred for 12 h at room temperature and then the volatiles was removed under reduced pressure. The residue was dissolved in 2 mL of dichloromethane and stratified with Et₂O to yield light green crystals, which were collected by filtration and dried in vacuo (85 mg, 0.12 mmol, 82%). ¹H NMR (500 MHz, CD₂Cl₂): δ 11.84 (br s, 1H, NH), 7.50 (t, ³J = 1.7 Hz, 1H, NHCHCHN_(imine)), 7.44–7.22 (m, 4H, NHCHCHN_(imine) and aryl-H), 5.21 (m, 1H, CH_(cod)), 4.78 (m, 1H, CH_(cod)), 4.45 (m, 1H, CH_(cod)), 4.10 (m, 1H, CH_(cod)), 3.72 (sept, ³J = 6.9 Hz, 1H, CH(CH₃)₂), 2.94 (m, 3H, CH(CH₃)₂ and CH_{2(cod)}), 2.36 (s, 3H, CH_{3(imine)}), 2.70–2.46 (m, 5H, CH_{3(imine)} and CH_{2(cod)}), 2.30–2.16 (m, 2H, CH_{2(cod)}), 1.90–1.76 (m, 2H, CH_{2(cod)}), 1.41 (d, ³J = 6.9 Hz, 3H, CH(CH₃)₂), 1.32 (d, ³J = 6.9 Hz, 3H, CH(CH₃)₂), 1.12 (d, ³J = 6.9 Hz, 3H, CH(CH₃)₂), 1.07 (d, ³J = 6.9 Hz, 3H, CH(CH₃)₂), -14.50 (d, ⁴J = 1.6Hz, 1H Ir-H). ¹³C{¹H} NMR (125 MHz, CD₂Cl₂): δ 167.3 (C=N), 161.3 (NHCHN_(imine)), 142.8 (*o*-C_(dipp)), 141.3 (*o*-C_(dipp)), 138.1 (*ipso*-C_(dipp)), 129.9 (*p*-C_(dipp)), 125.9 (*m*-C_(dipp)), 125.3 (*m*-C_(dipp)), 122.5 (NHCHCHN_(imine)), 117.8 (NHCHCHN_(imine)), 99.8 (CH_(cod)), 98.4 (CH_(cod)), 78.9 (CH_(cod)), 77.6 (CH_(cod)), 37.5 (CH_{2(cod)}), 29.1 (CH_{2(cod)}), 28.3 (CH_{2(cod)}), 28.2 (CH(CH₃)₂), 28.0 (CH_{2(cod)}), 27.9 (CH(CH₃)₂), 25.6 (CH(CH₃)₂), 25.4 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 23.3 (CH(CH₃)₂), 16.9 (CH_{3(imine)}). IR: ν_{max} (pure, orbit diamond)/cm⁻¹ 3241 ν(N-H), 2211 ν(Ir-H), 1627 ν(C=N) and 445 ν(Ir-Cl). Anal. calcd

for C₂₅H₃₆BClF₄IrN₃ (%): C, 43.33; H, 5.24; N, 6.06. Found: C, 42.97; H, 5.25; N, 6.02.

2 X-ray crystallography

2.1 General methods

Suitable crystals for the X-ray analysis of all compounds were obtained as described above. Data for **1**, **2**, **3** and **8** were collected on an APEX-II CCD (graphite-monochromated Mo-K α radiation, $\lambda = 0.71073$ Å) at 173(2) K, data for **4** was collected on a Kappa CCD diffractometer (graphite-monochromated Mo-K α radiation, $\lambda = 0.71073$ Å) at 173(2) K. Crystallographic and experimental details for these structures are summarized in Table S1. The structures were solved by direct methods (SHELXS-97¹) and refined by full-matrix least-squares procedures (based on F^2 , SHELXL-97) with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures).

CCDC 1039710-1039714

The following specific comments apply for the structures:

Complex 3: Instead of placed in a calculated position, the hydrogen atom H1N was found.

Complex 4: The SQUEEZE instruction in PLATON was applied for **4**. The residual electron density was assigned to four molecules of disordered diethyl ether for **4**.

Complex 8: Instead of placed in a calculated position, the hydrogen atom H1N and the hydride atom H1 on the iridium atom were found. The SQUEEZE instruction in PLATON was applied for **8**. The residual electron density was assigned to one molecule of disordered diethyl ether for **8**.

2.2 Summary of crystal data

Table S1. Crystal data and structure refinement for **1**, **2**, **3**, **4** and **8**

Compound number	1	2	3	4	8
Internal code	pbad121109	pbmw140303	pbfh140623	pbfh140901	pbfh141126
CDC	1039710	1039712	1039714	1039713	1039711
Empirical formula	C ₂₅ H ₃₅ ClIrN ₃	C ₃₃ H ₄₇ Cl ₂ Ir ₂ N ₃	C ₂₅ H ₃₅ F ₆ IrN ₃ P	C ₅₀ H ₆₈ Ir ₂ N ₆	C ₂₅ H ₃₆ BClF ₄ IrN ₃
<i>M</i> _w	605.21	941.03	714.73	1137.50	693.03
<i>T</i> /K	173(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	P -1	P 21/c	P -1	P -1	C 2/c
<i>a</i> /Å	8.5409(4)	8.7044(3)	10.2750(4)	12.2904(3)	22.1698(9)
<i>b</i> /Å	11.3926(5)	21.9069(8)	10.7121(4)	13.3290(5)	20.5501(8)
<i>c</i> /Å	13.7162(6)	19.1631(6)	13.6503(5)	19.4944(6)	14.5843(6)
α /°	69.6340(10)	90	105.8340(10)	86.542(2)	90
β /°	87.7630(10)	115.4070(10)	110.0360(10)	72.600(2)	110.9360(10)
γ /°	71.5300(10)	90	97.4030(10)	62.575(4)	90
<i>V</i> /Å ³	1182.94(9)	3300.7(2)	1316.23(9)	2693.61(17)	6205.8(4)
<i>Z</i>	2	4	2	2	8
μ /mm ⁻¹	5.773	8.243	5.195	4.970	4.429
No. of rflns collected	23224	34723	21762	29513	50764
No. unique rflns	8245	11428	8346	12243	12686
<i>R</i> _{int}	0.0211	0.0243	0.0264	0.0503	0.0252
Goodness of fit on <i>F</i> ²	1.100	1.042	1.036	1.083	1.069
Final <i>R</i> indices	<i>R</i> 1 = 0.0202	<i>R</i> 1 = 0.0309	<i>R</i> 1 = 0.0329	<i>R</i> 1 = 0.0380	<i>R</i> 1 = 0.0333
[<i>I</i> > 2σ(<i>I</i>)]	w <i>R</i> 2 = 0.0434	w <i>R</i> 2 = 0.0601	w <i>R</i> 2 = 0.0744	w <i>R</i> 2 = 0.1102	w <i>R</i> 2 = 0.0756
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0253	<i>R</i> 1 = 0.0450	<i>R</i> 1 = 0.0448	<i>R</i> 1 = 0.0528	<i>R</i> 1 = 0.0469
	w <i>R</i> 2 = 0.0455	w <i>R</i> 2 = 0.0660	w <i>R</i> 2 = 0.0786	w <i>R</i> 2 = 0.1169	w <i>R</i> 2 = 0.0812

2.3 Crystal structure of **1**

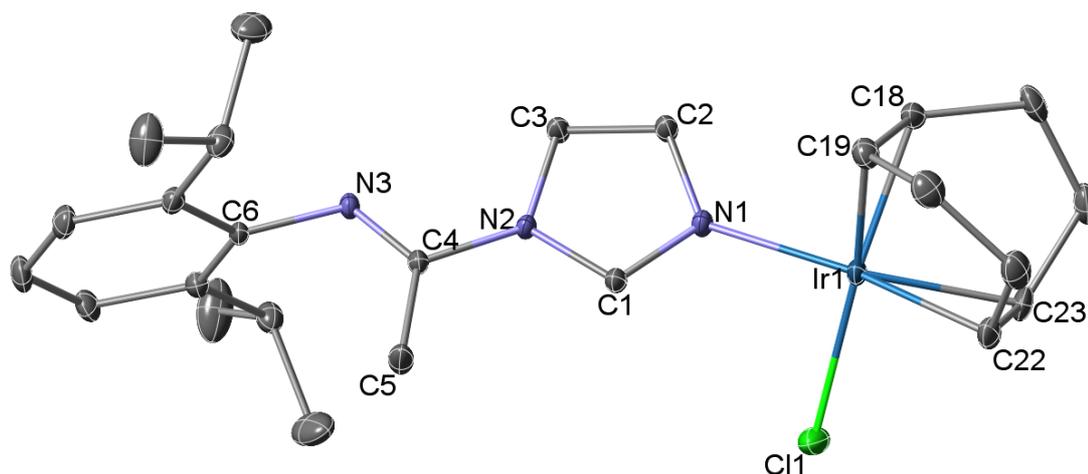


Figure S1. Molecular structure of **1**. H atoms omitted for clarity. Thermal ellipsoids are at the 30% level. Selected bond lengths (Å) and angles (°): C1–N1 1.321(2), C1–N2 1.360(2), C2–N1 1.387(3), C2–C3 1.358(3), C3–N2 1.381(2), C4–N2 1.427(2), C4–N3 1.261(2), C4–C5 1.494(3), C6–N3 1.427(2), Ir1–N1 2.0903(16), Ir1–C11 2.3605(6), Ir1–C18 2.111(2), Ir1–C19 2.096(2), Ir1–C22 2.130(2), Ir1–C23 2.121(2), C18–C19 1.418(3), C22–C23 1.405(4); N1–C1–N2 110.79(17), Ir1–C23 2.121(2), C18–C19 1.418(3), C22–C23 1.405(4); N1–C1–N2 110.79(17), N1–Ir1–C11 87.98(5), N1–Ir1–C18 93.71(7), N1–Ir1–C19 90.42(8), C11–Ir1–C22 92.51(7), C11–Ir1–C23 91.22(7).

2.4 Crystal structure of 2

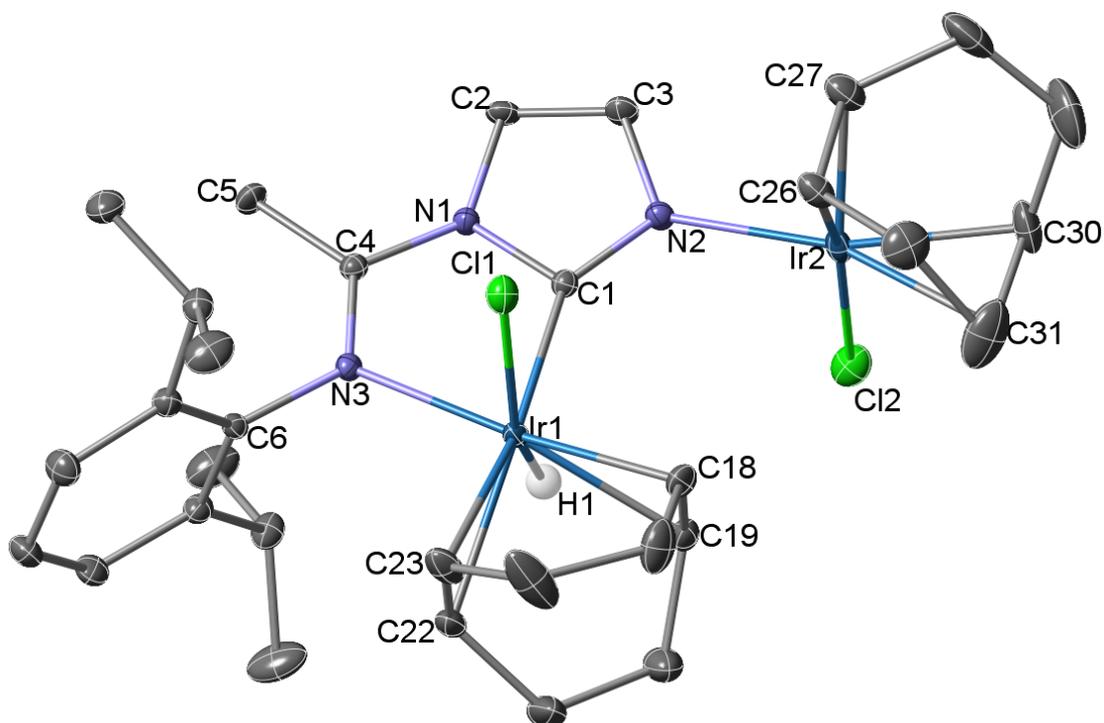


Figure S2. Molecular structure of **2**. H atoms omitted for clarity, except H1(Ir). Thermal ellipsoids are at the 30% level. Selected bond lengths (Å) and angles (°): C1–N1 1.400(4), C1–N2 1.330(5), C2–N1 1.394(5), C2–C3 1.344(5), C3–N2 1.406(5), C4–N1 1.374(5), C4–N3 1.295(5), C4–C5 1.482(5), C6–N3 1.454(4), Ir1–Cl1 2.5017(10), Ir1–C1 2.024(3), Ir1–N3 2.115(3), Ir1–C18 2.186(4), Ir1–C19 2.221(4), Ir1–C22 2.276(4), Ir1–C23 2.258(4), C18–C19 1.391(6), C22–C23 1.363(7), Ir2–Cl2 2.3627(11), Ir2–N2 2.083(3), Ir2–C26 2.108(4), Ir2–C27 2.100(5), Ir2–C30 2.127(4), Ir2–C31 2.118(4), C26–C27 1.412(6), C30–C31 1.394(7); N1–C1–N2 106.6(3), C1–Ir1–N3 78.43(13), C1–Ir1–C18 100.85(15), C1–Ir1–C19 98.67(14), N3–Ir1–C22 95.44(13), N3–Ir1–C23 96.99(15), C1–Ir1–Cl1 80.92(10), N3–Ir1–Cl1 87.03(8), N2–Ir2–Cl2 88.52(9), N2–Ir2–C26 92.18(15), N2–Ir2–C27 91.08(16), Cl2–Ir2–C30 91.80(16), Cl2–Ir2–C31 91.42(16).

2.5 Crystal structure of 3

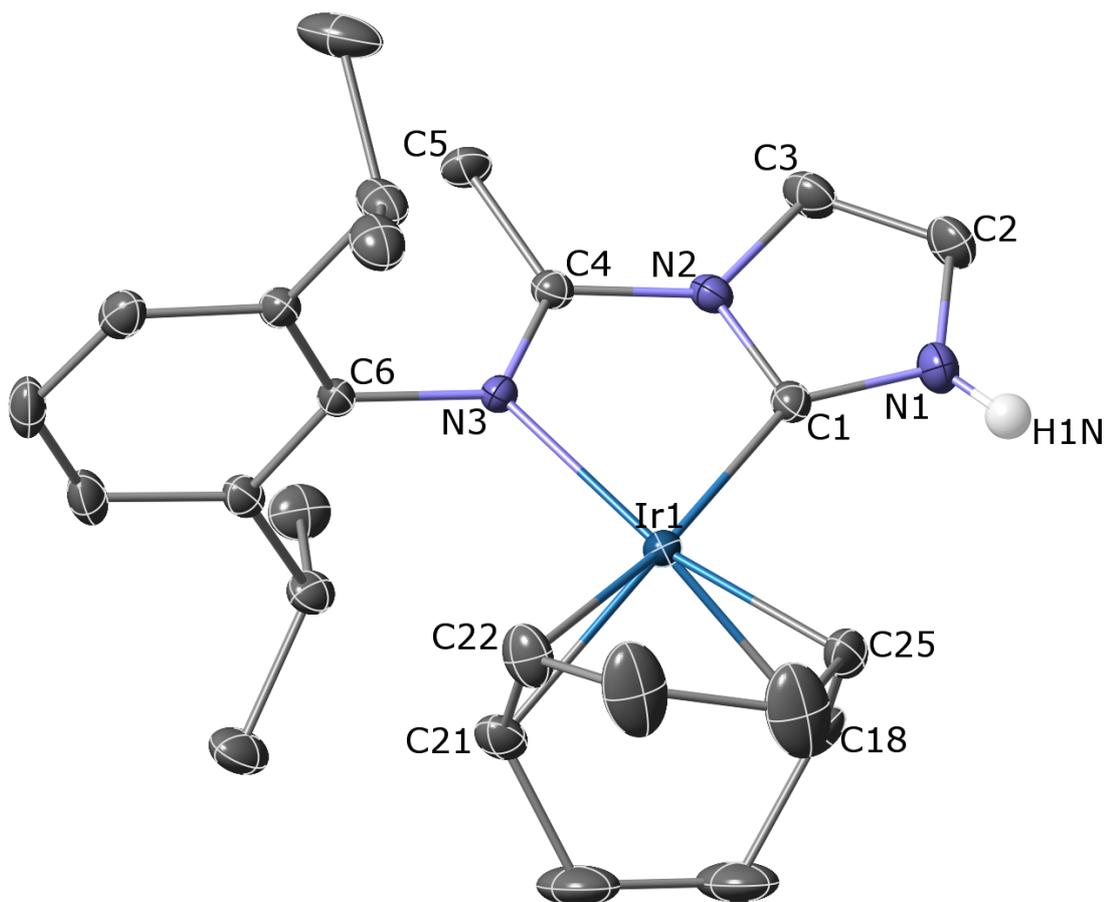


Figure S3. Molecular structure of the cation in $3^+[\text{PF}_6]^-$. H atoms omitted for clarity, except H1(N1). Thermal ellipsoids are at the 30% level. Selected bond lengths (Å) and angles (°): C1–N1 1.340(4), C1–N2 1.366(5), C2–N1 1.395(6), C2–C3 1.332(6), C3–N2 1.400(4), C4–N2 1.395(4), C4–N3 1.293(4), C4–C5 1.485(5), C6–N3 1.448(4), Ir1–C1 1.984(3), Ir1–N3 2.115(3), Ir1–C18 2.116(4), Ir1–C21 2.232(4), Ir1–C22 2.225(4), Ir1–C25 2.129(4), C18–C25 1.403(7), C21–C22 1.365(7), N1–H1N 0.84(5); N1–C1–N2 103.5(3), C1–Ir1–N3 77.15(13), C1–Ir1–C18 95.60(16), C1–Ir1–C25 96.52(15), N3–Ir1–C21 97.65(13), N3–Ir1–C22 100.53(15).

2.6 Crystal structure of 4

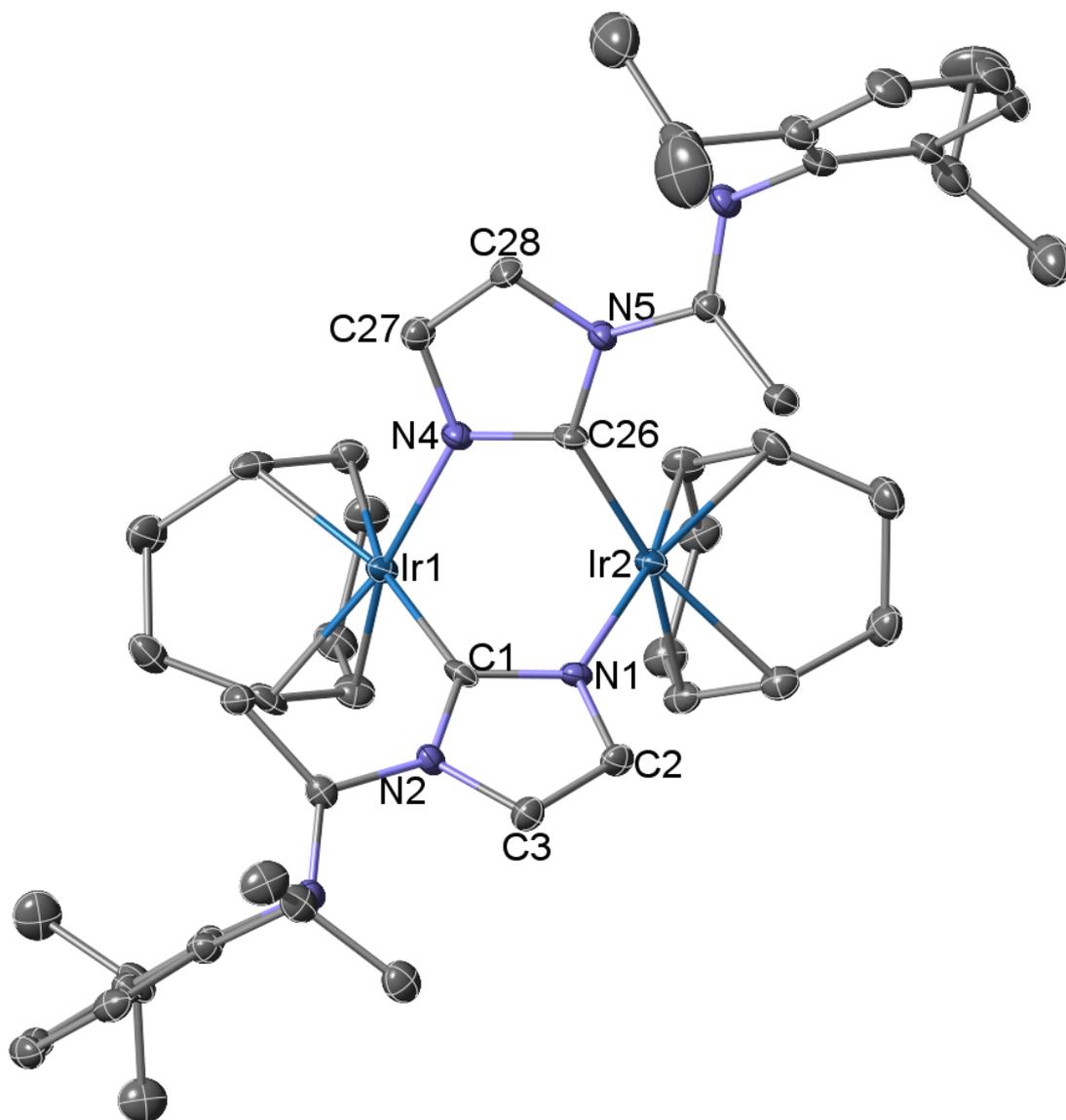


Figure S4. Molecular structure of **4**. H atoms omitted for clarity. Thermal ellipsoids are at the 30% level. Selected bond lengths (Å) and angles (°): C1–N1 1.357(7), C1–N2 1.392(6), C2–N1 1.394(7), C2–C3 1.356(8), C3–N2 1.399(7), C26–N4 1.347(7), C26–N5 1.383(6), C27–N4 1.387(6), C27–C28 1.338(8), C28–N5 1.387(6), Ir1–C1 2.046(5), Ir1–N4 2.066(4), Ir2–C26 2.050(4), Ir2–N1 2.058(4), Ir1···Ir2 3.1844(3); N1–C1–N2 105.3(4), N4–C26–N5 106.3(4), C1–Ir1–N4 88.11(18), C26–Ir2–N1 87.95(18).

2.7 Crystal structure of 8

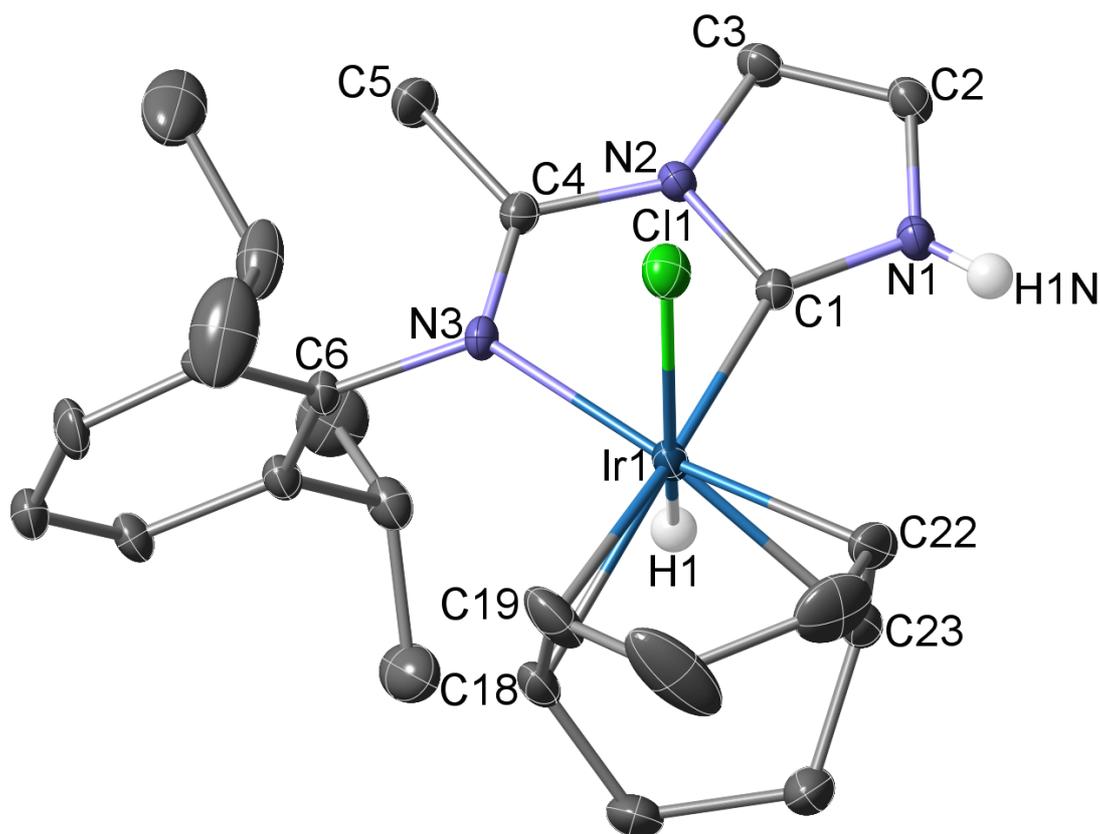


Figure S5. Molecular structure of 8^+ in $8^+[\text{BF}_4]^-$. H atoms omitted for clarity, except H1(N1) and H1(Ir). Thermal ellipsoids are at the 30% level. Selected bond lengths (\AA) and angles ($^\circ$): C1–N1 1.327(3), C1–N2 1.371(3), C2–N1 1.397(4), C2–C3 1.345(4), C3–N2 1.392(3), C4–N2 1.391(3), C4–N3 1.290(3), C4–C5 1.486(4), C6–N3 1.452(3), Ir1–Cl1 2.4901(8), Ir1–C1 1.983(2), Ir1–N3 2.125(2), Ir1–C18 2.281(3), Ir1–C19 2.287(3), Ir1–C22 2.180(3), Ir1–C23 2.191(3), C18–C19 1.367(6), C22–C23 1.375(6); N1–C1–N2 105.0(2), C1–Ir1–N3 77.45(9), C1–Ir1–C22 97.10(12), C1–Ir1–C23 97.03(11), N3–Ir1–C18 95.69(10), N3–Ir1–C19 103.11(14), C1–Ir1–Cl1 82.23(8), N3–Ir1–Cl1 87.35(6).

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