Supporting Information

for

Electrochemical C–H Bond Activation via Cationic Iridium Hydride Pincer Complexes

Brian M. Lindley[a,†] *Andrew G. Walden,*[a,b,†] *Ann Marie Brasacchio,*[a,c] *Andrea Casuras,*[d] *Nicholas Lease,*[d] *Alan S. Goldman,*[d] *and Alexander J. M. Miller*[a,]*

[a] Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States

[b] Oglethorpe University, Atlanta, Georgia 30319, United States (Current Address)

[c] High Point University, High Point, NC 27262, United States (Current Address)

[d] Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, United States

[†] These co-authors contributed equally.

Table of Contents

1. General Considerations. All procedures were carried out in a glovebox under an argon atmosphere, unless otherwise noted. Solvents were dried and degassed with argon using a Pure Process Technology solvent system. All deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc. and degassed by three freeze-pump-thaw cycles and stored over molecular sieves. The complexes (^{tBu4}PCP)Ir(H)$_n$ (n = 2 or n = 4, **1**),[1] and (^{tBu4}PCP)Ir(H)(Cl) (**2**),[2] were synthesized according to literature procedures. All other materials were commercially available and used as received, unless otherwise noted. ^{1}H and ^{31}P NMR spectra were recorded on a 600 MHz spectrometer at room temperature, unless otherwise noted. Chemical shifts are reported with respect to residual protio solvent for ^{1}H.[3] ^{31}P NMR spectra were referenced to an 85% H_3PO_4 external standard (0 ppm). NMR resonances appearing as triplets due to virtual coupling (arising from strong P–P coupling through the iridium center) have been accordingly labeled "vt".[4]

Cyclic voltammetry experiments were conducted in a single-compartment cell in a three-electrode configuration. Glassy carbon disc (3 mm diameter) working electrodes, platinum wire counter electrodes, and silver wire pseudo-reference electrodes were used. Potentials are provided relative to ferrocene added as an internal reference at the conclusion of the experiment. Experiments were performed in 1,2-difluorobenzene with [Bu_4N][PF_6] (200 mM) added as supporting electrolyte. Experiments performed under argon were conducted in an argon glovebox with a Pine Instruments WaveDriver 200 potentiostat.

Bulk electrolysis experiments were conducted in three-compartment cells. Reticulated vitreous carbon working electrodes, platinum coil counter electrodes and silver wire pseudo-reference electrodes were used. Experiments were performed in 1,2-difluorobenzene with [Bu_4N][PF_6] (200 mM) added as a supporting electrolyte.

2. Synthesis of Cationic Iridium Hydride Complexes

[(^{tBu4}PCP)Ir(H)(py)][BAr$^F_4$] (3$^+$). In an argon glovebox, 0.050 g (0.0802 mmol) of (^{tBu4}PCP)Ir(H)(Cl) (**2**) and 0.064 g (0.0802 mmol) of NaBAr$^F_4$ were added to a 20 mL vial with 2 mL of CH_2Cl_2. The reaction mixture took on a bright orange color with some undissolved white solids. Next 6.5 μL of pyridine (0.0810) mmol) were added via syringe. The vial was shaken to stir the reaction mixture and dissolve all of the components. The solution became homogenous and began to lighten to an orange/yellow color. Within a few minutes, the precipitation of colorless solids was observed. This solution was allowed to react overnight at room temperature. The mixture was then filtered into a 20mL vial and layered with 15 mL of pentane. Over the course of 48 hours, a large amount of deep red crystals grew. The light orange mother liquor was decanted away and the resulting crop of crystals (0.1009 g 87% yield) were allowed to dry. ^{1}H NMR (CD_2Cl_2, 600 MHz): δ 8.88 (br s, 2H, pyridine), 7.89 (t, J = 8 Hz, 1H, pyridine), 7.72 (br s, 8H, BAr$^F_4$), 7.56 (br s, 4H, BAr$^F_4$), 7.57 (br s, 2H, pyridine), 7.13 (d, J = 8 Hz, 2H, PCP Ar), 6.90 (t, J = 8 Hz, 1H, PCP Ar), 3.56 (m, 4H, CH_2), 1.13 (vt, J = 7 Hz, 18H, tBu), 1.11 (vt, J = 7 Hz, 18H, tBu), -45.39 (t, J = 12 Hz, 1H, hydride). ^{13}C{^{1}H} NMR (CD_2Cl_2, 150 MHz): δ 162.34 (q, J = 50 Hz), 152.47 (t, J = 8 Hz), 143.93, 143.89, 139.11, 135.38, 129.47 (qq, J = 32 Hz, 3 Hz), 127.72, 126.99, 125.15 (q, J = 272 Hz), 122.33 (t, J = 8 Hz), 118.06 (m), 39.31 (t, J = 11 Hz), 35.96 (t, J = 12 Hz), 35.75 (t, J = 15 Hz), 30.92 (t, J = 2 Hz), 29.06 (t, J = 2 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, 243 MHz): δ 66.54. Anal. for $C_{61}H_{61}BNF_{24}P_2Ir$ (calc.) C 47.91 H 4.02 N 0.92; (found) C 48.02 H 4.13 N 0.96.

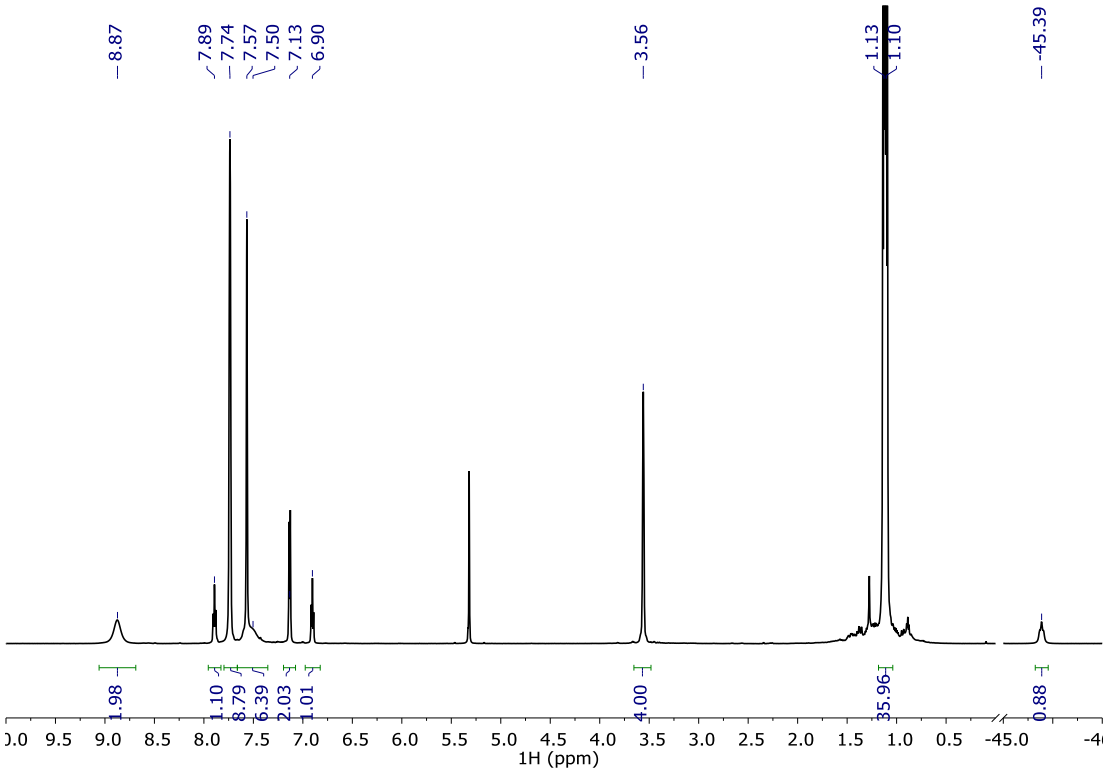


Figure S1. ^{1}H NMR spectrum of [(^{tBu4}PCP)Ir(H)(py)][BAr$^{F}_{4}$] (**3**$^{+}$).

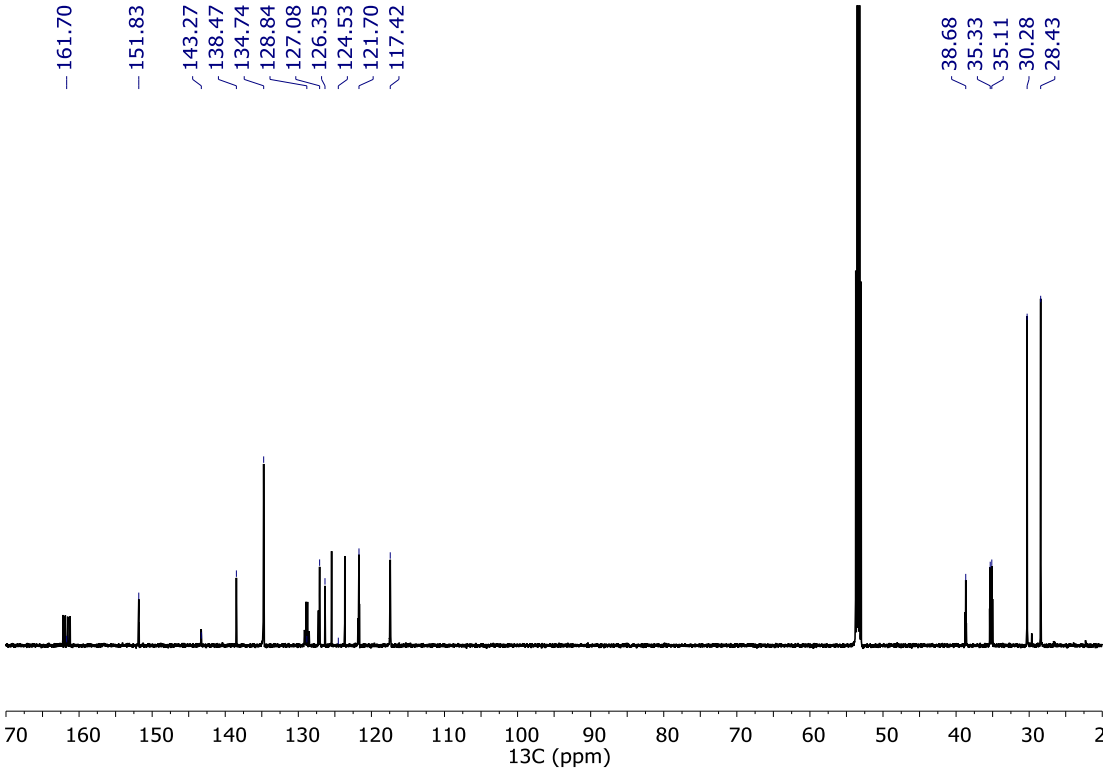


Figure S2. ^{13}C{^{1}H} NMR spectrum of [(^{tBu4}PCP)Ir(H)(py)][BAr$^{F}_{4}$] (**3**$^{+}$).

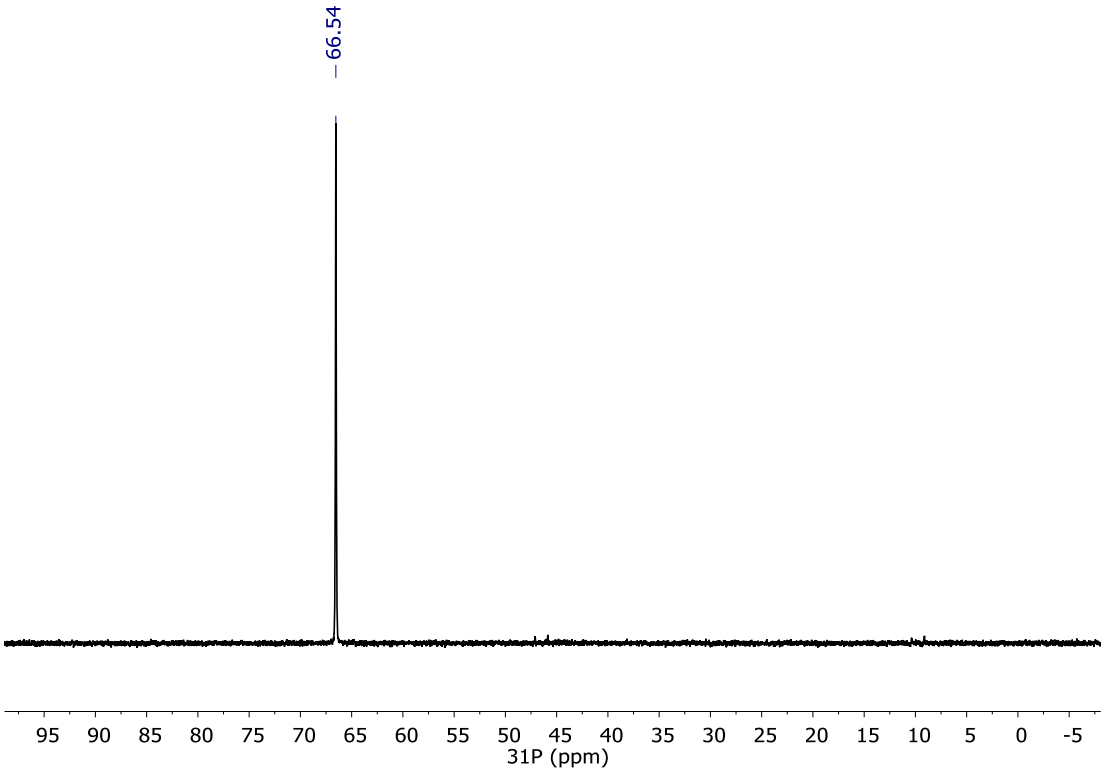


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of [(^{tBu4}PCP)Ir(H)(py)][BAr^{F}_{4}] (**3**$^{+}$).

[(^{tBu4}PCP)Ir(H)(lut)][BAr^{F}_{4}] (4^{+}). In an argon glovebox, 0.0492 g (0.0791 mmol) of (^{tBu4}PCP)Ir(H)(Cl) (**2**) and 0.064 g (0.0810 mmol) of $NaBAr^{F}_{4}$ were added to a 20 mL vial with 2 mL of CH_2Cl_2. The reaction mixture took on a bright orange color with some undissolved white solids. Next 9.31 μL of 2,6-lutidine were added via syringe. The vial was shaken to stir the reaction mixture and dissolve all of the components. The solution became homogenous and began to lighten to an orange/yellow color. Within a few minutes, the precipitation of clear solids was observed. This solution was allowed to react overnight at room temperature. The mixture was then filtered into a 20mL vial and layered with 15 mL of pentane. Over the course of 48 hours, a large amount of orange crystals grew. The light orange/pale mother liquor was decanted away and the resulting crop of crystals (0.1020 g 88% yield) were allowed to dry. ^{1}H NMR (CD_2Cl_2, 600 MHz): δ 7.75 (t, J = 8 Hz, 1H, lutidine), 7.72 (broad s, 8H, BAr^{F}_{4}), 7.56 (broad s, 4H, BAr^{F}_{4}), 7.26 (d, J

= 8 Hz 1H, lutidine), 7.01 (d, J = 8 Hz, 1H, lutidine), 6.95 (d, J = 7 Hz, 2H, aryl backbone), 6.87 (t, J = 7 Hz, 1H, aryl backbone), 3.40 (m, 4H, methylene linker), 2.28 (s, 3H, lutidine methyl), 1.71 (s, 3H, lutidine methyl) 1.23 (vt, J = 7 Hz 18H, tBu), 1.07 (vt, J = 7 Hz, 18H, tBu), -31.40 (t, J = 15, Hz 1H, hydride). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 150 MHz): δ 161.73 (q, 50 Hz), 157.81, 157.13, 147.44 (t, 7 Hz), 139.26, 134.77, 134.41, 128.84 (qq, 32 Hz, 4 Hz), 125.57, 125.53, 124.97, 124.57 (q, 272 Hz), 122.07 (t, 8 Hz), 117.46 (sept, 4 Hz), 38.11 (t, 10 Hz), 36.96 (t, 13 Hz), 34.66 (15 Hz), 29.63 (t, 2 Hz), 29.33 (t, 2 Hz), 22.25, 19.91. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 243 MHz): δ 63.97. Anal. for $C_{63}H_{65}BNF_{24}P_2Ir$ (calc.) C 48.59 H 4.21 N 0.90; (found) C 48.35 H 4.11 N 0.91.

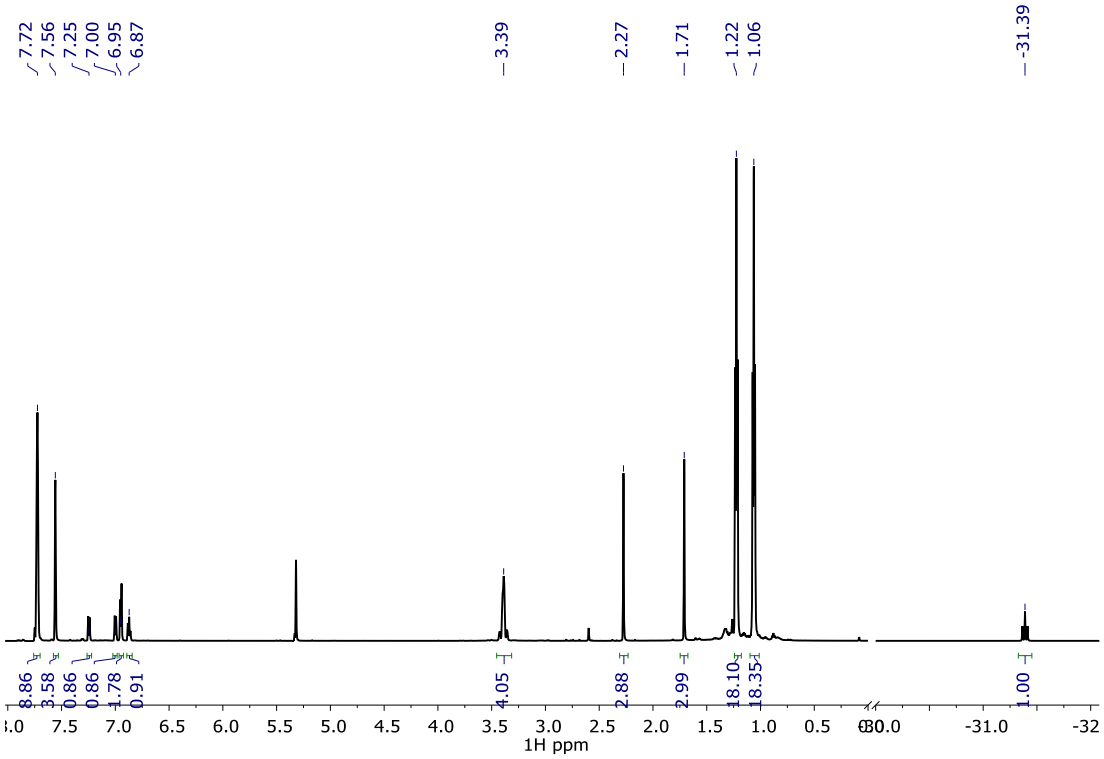


Figure S4. ^{1}H NMR spectrum of [(^{tBu4}PCP)Ir(H)(lut)][BAr^{F}_4] (**4**$^{+}$).

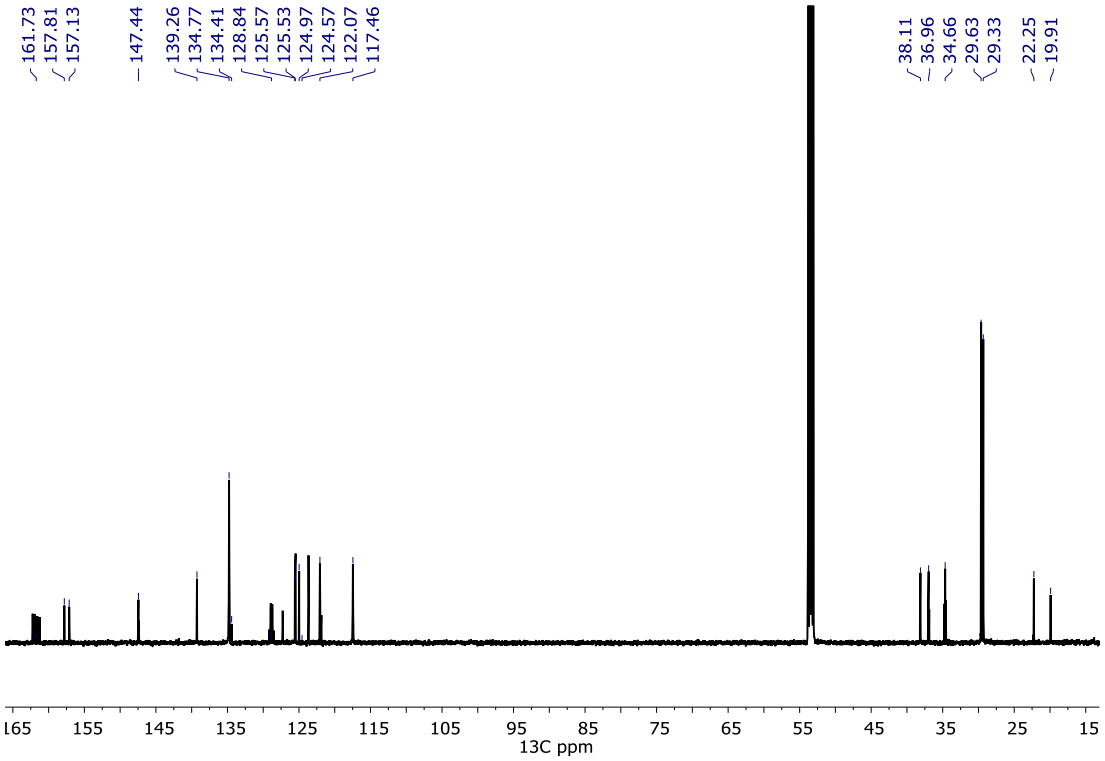


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum [(^{tBu4}PCP)Ir(H)(lut)][BAr^{F}_{4}] (**4**$^{+}$).

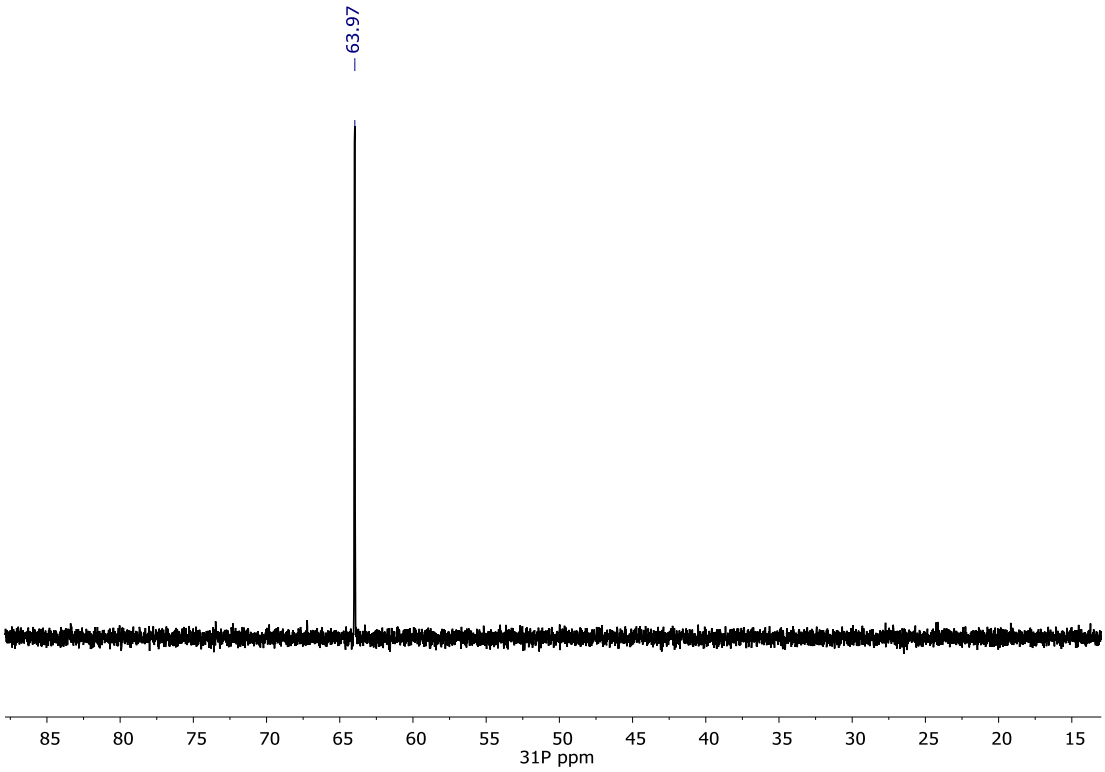


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum [(^{tBu4}PCP)Ir(H)(lut)][BAr^{F}_{4}] (**4**$^{+}$).

[(^{tBu4}PCP)Ir(H)(2-Phpy)][BAr^F_4] (5^+). In an argon glovebox, 0.0503 g (0.0808 mmol) of (^{tBu4}PCP)Ir(H)(Cl) (**2**) and 0.065 g (0.0816 mmol) of $NaBAr^F_4$ were added to a 20 mL vial with 2.5 mL of CH_2Cl_2. The reaction mixture took on a dark red orange color with some undissolved white solids. Next, 11.5 μL of 2-phenylpyridine were added via syringe. The vial was shaken to stir the reaction mixture and dissolve all of the components. The solution lightened to a bright orange color. Within a few minutes, the precipitation of clear solids was observed. This solution was allowed to react overnight at room temperature. The mixture was then filtered into a 20mL vial and the resulting homogenous solution was layered with 15 mL of pentane. Over the course of 24 hours, some orange crystals had grown, but the solution remained orange in color. An additional 5 mL pentane was added and allowed to sit for a another 24 hours. The light orange mother liquor was decanted away and the resulting crop of yellow/orange crystals (0.1050 g 86% yield) was allowed to dry. ^{1}H NMR (CD_2Cl_2, 600 MHz): δ 8.19 (d, J = 6 Hz, 1H, 2-Phpy), 7.97 (t, J = 8 Hz, 1H, 2-Phpy), 7.94 (t, J = 8 Hz, 1H, 2-Phpy), 7.91 (br s, 1H, 2-Phpy), 7.73 (br s, 8H, BAr^F_4), 7.72 (m, 1H, 2-Phpy), 7.56 (br s, 4H, BAr^F_4), 7.32 (t, J = 7 Hz, 1H, 2Phpy), 7.02 (d, J = 8 Hz, 2H, PCP Ar), 6.95 (t, J = 8 Hz, 1H, PCP Ar), 3.23 (dt, J = 17 Hz, 3 Hz, 2H, CH_2), 3.15 (dt, J = 17 Hz, 3 Hz, 2H, CH_2) 1.13 (vt, J = 7 Hz, 18H, tBu), 0.70 (vt, J = 7 Hz, 18H, tBu), -20.13 (s, 1H, hydride). ^{13}C{^{1}H} NMR (CD_2Cl_2, 150 MHz): δ 162.88, 162.33 (q, J = 50 Hz), 150.17, 147.08, 145.72 (t, J = 7 Hz), 139.65, 137.21, 135.37, 133.05, 129.45 (qq, J = 31 Hz, 3 Hz), 126.07, 125.88, 125.60, 125.17 (q, J = 272 Hz), 123.53 (t, J = 7 Hz), 118.04 (m), 38.73 (t, J = 10 Hz), 37.28 (t, J = 13 Hz), 34.18 (t, J = 14 Hz), 29.74, 29.13 (t, J = 2 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, 243 MHz): δ 53.34. Anal. for $C_{67}H_{65}BNF_{24}P_2Ir$ (calc.) C 50.13 H 4.08 N 0.87; (found) C 49.99 H 4.24 N 0.84.

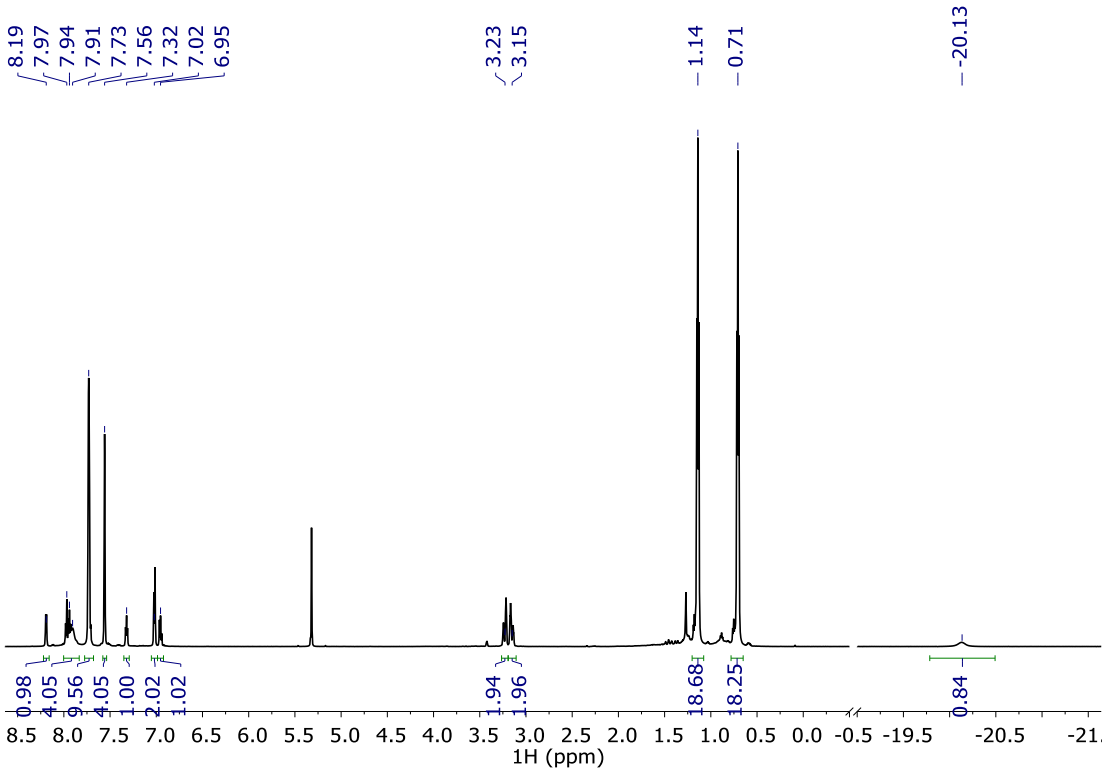


Figure S7. ^{1}H NMR spectrum of [(^{tBu4}PCP)Ir(H)(2-Phpy)][BAr$^{F}_{4}$] (**5**$^{+}$).

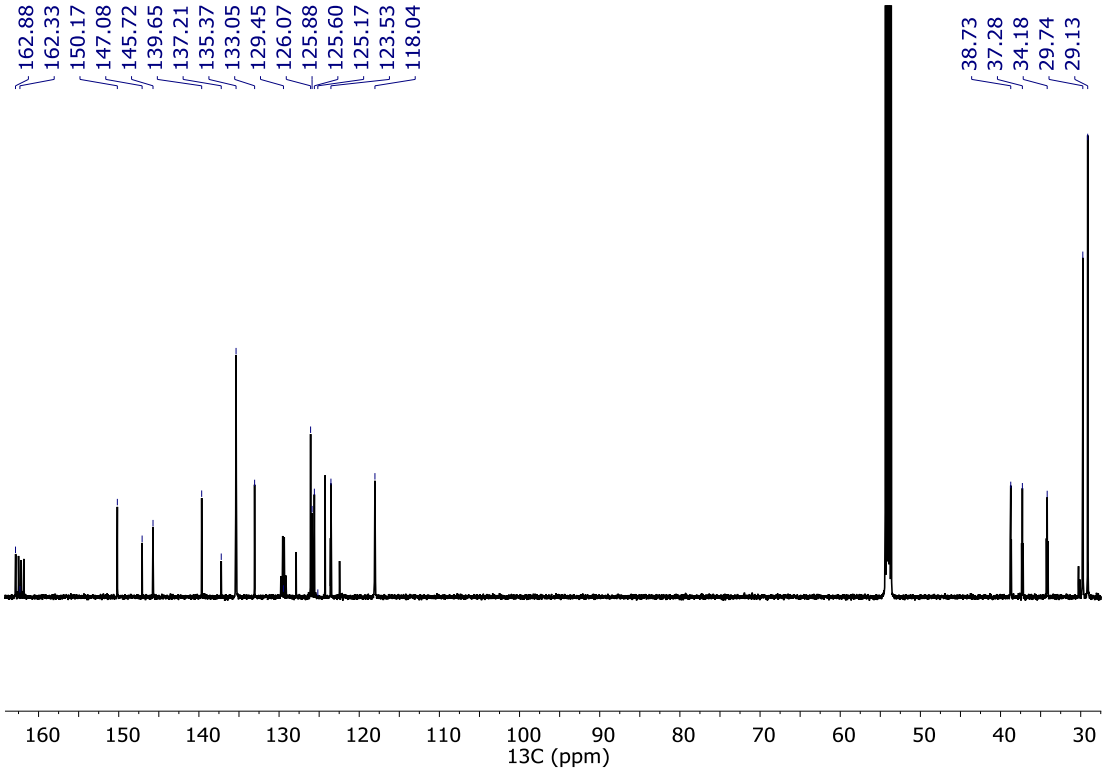


Figure S8. ^{13}C{^{1}H} NMR spectrum of [(^{tBu4}PCP)Ir(H)(2-Phpy)][BAr$^{F}_{4}$] (**5**$^{+}$).

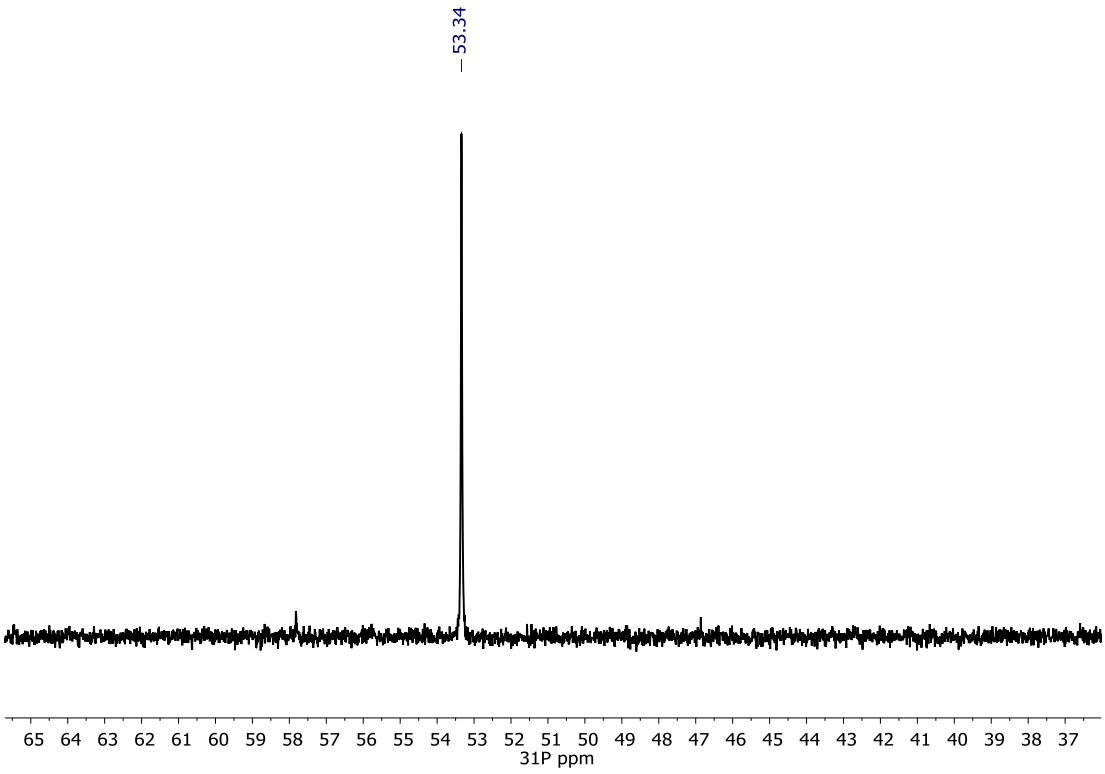


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of [(^{tBu4}PCP)Ir(H)(2-Phpy)][BAr$^{F}_{4}$] (**5**$^{+}$).

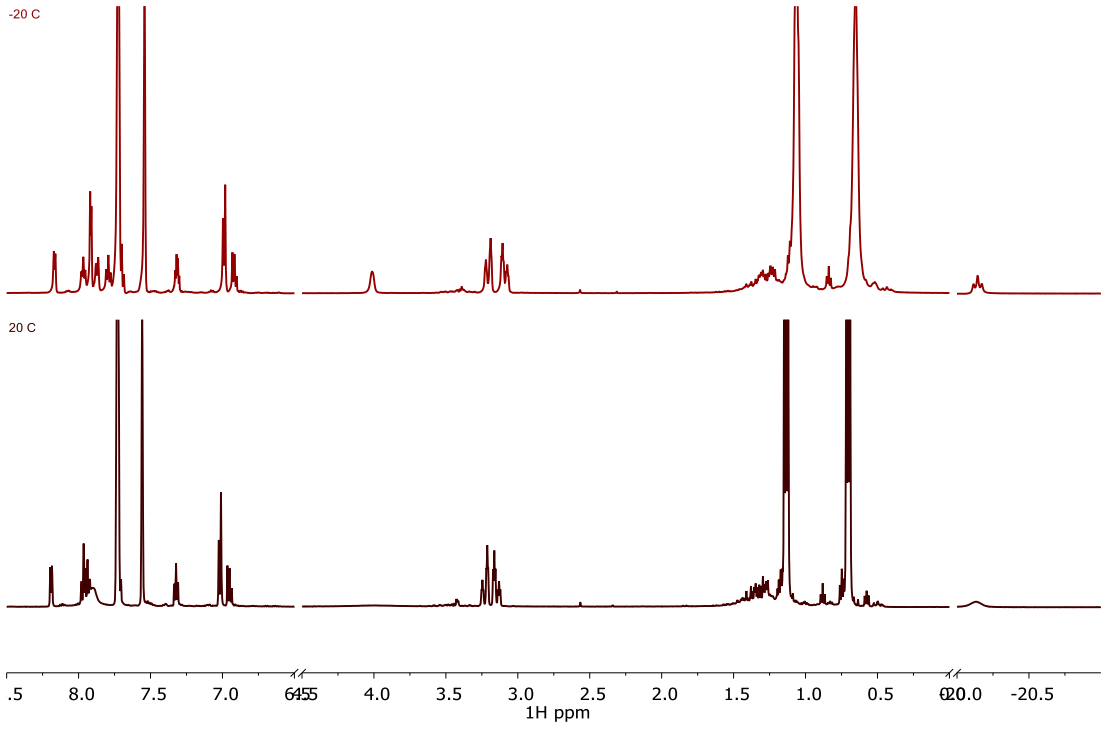


Figure S10. ^{1}H NMR spectrum of **5**$^{+}$ at 20 °C (bottom) and −20 °C (top).

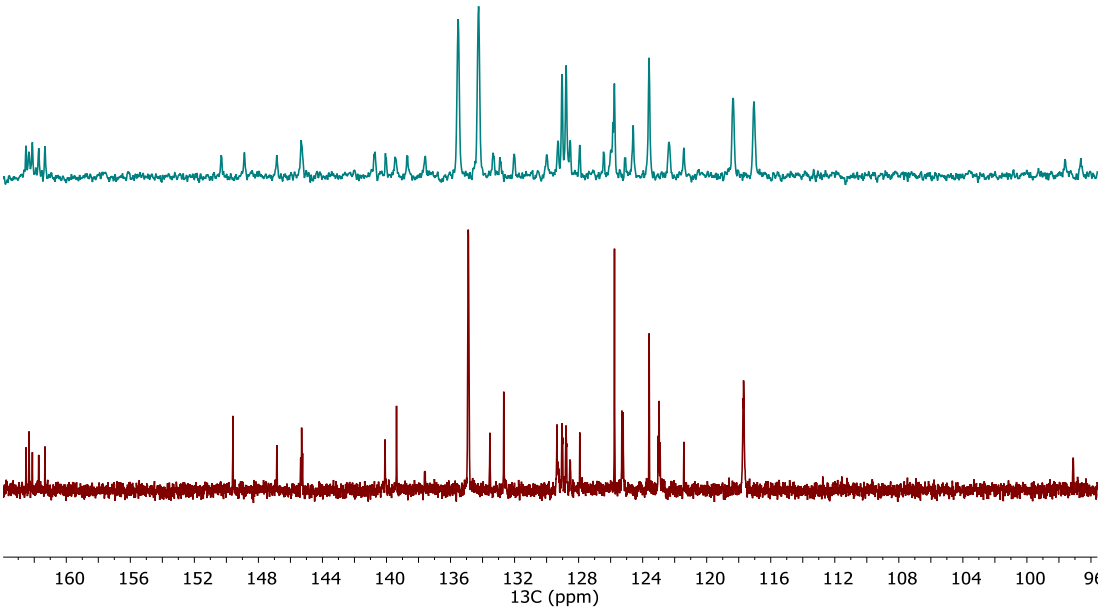


Figure S11. ^{13}C (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of $\mathbf{5}^{+}$ at −20 °C.

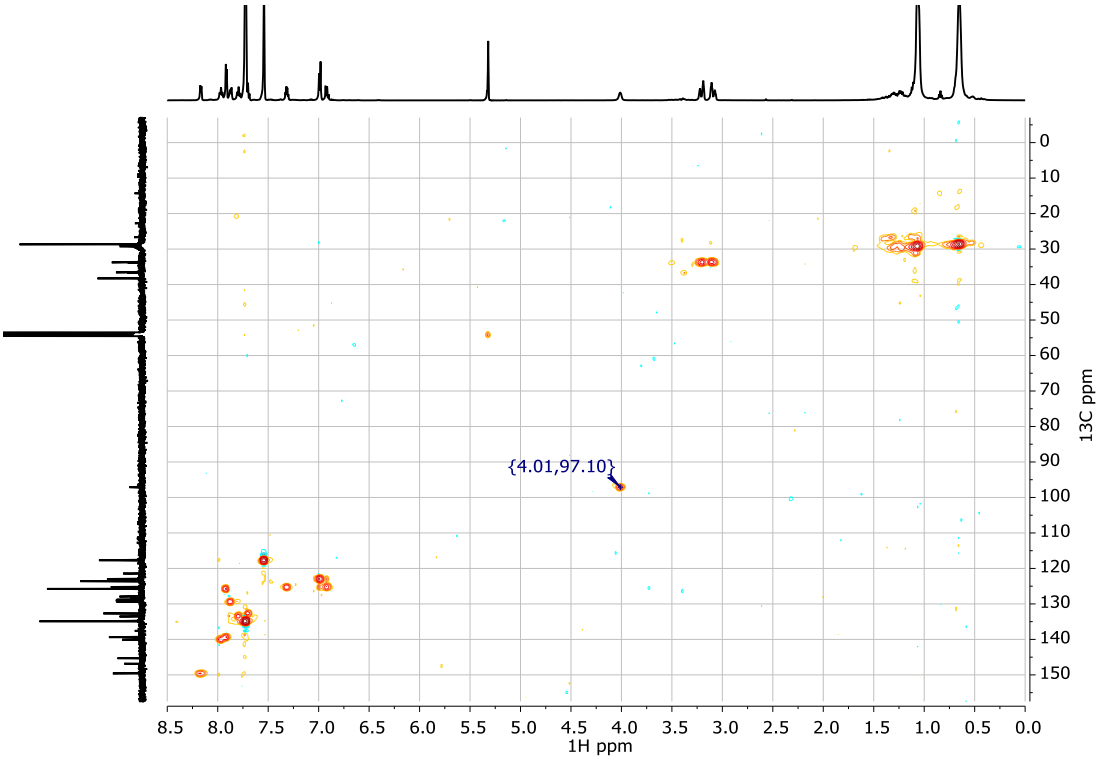


Figure S12. ^{13}C-^{1}H HSQC spectrum of $\mathbf{5}^{+}$ at −20 °C.

3. Pyridine Binding Studies of 1 and 3^+

General Procedure for Testing Pyridine Adduct Formation with Dihydride 1. Under an argon atmosphere, 0.003 g of (^{tBu4}PCP)Ir(H)$_2$ (**1**) was dissolved in THF-d_8 in a 4 mL vial. To this solution, pyridine was added via syringe, either in large excess or 5-10 equivalents relative to **1**. These solutions were then transferred to J Young tubes and analyzed by ^{1}H and ^{31}P NMR spectroscopy.

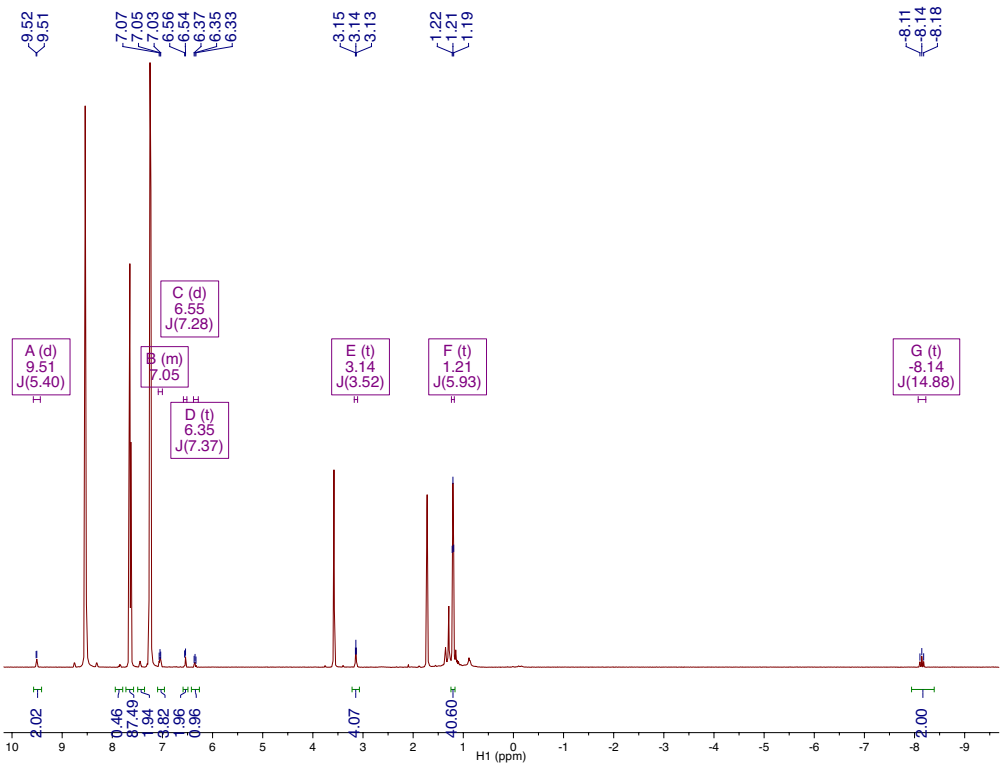


Figure S13. ^{1}H NMR spectrum of addition of excess pyridine to (^{tBu4}PCP)Ir(H)$_2$ (**1**).

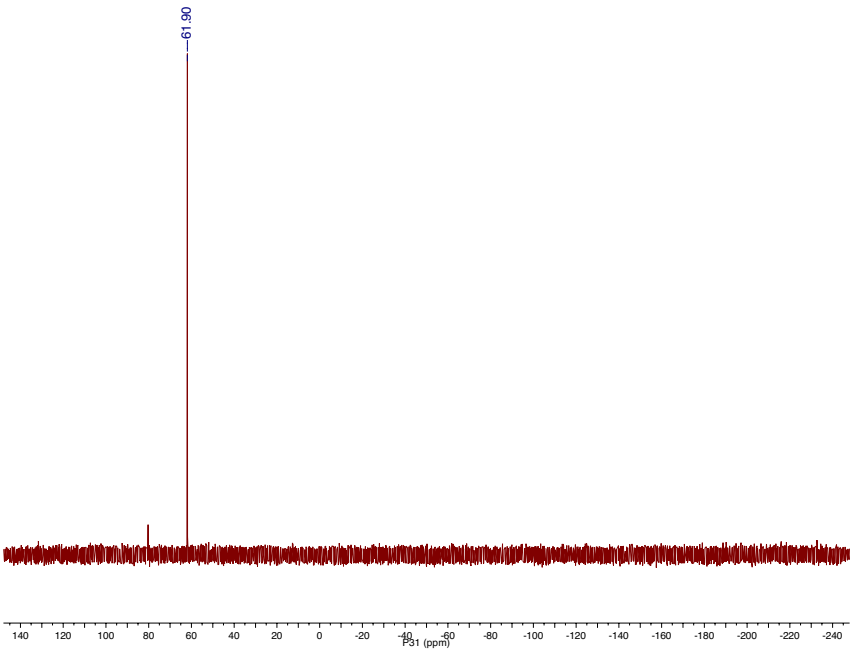
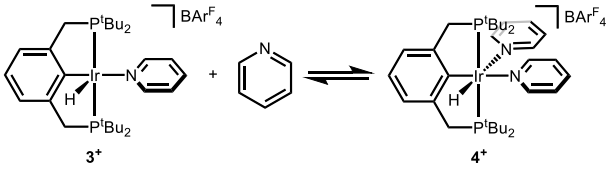


Figure S14. $^{31}P\{^{1}H\}$ NMR spectrum of addition of excess pyridine to (^{tBu4}PCP)Ir(H)$_2$ (**1**).

Establishing Pyridine Binding Equilibrium with 3$^+$. Treatment of isolated **3**$^+$ with increasing amounts of pyridine resulted in NMR spectral changes. The ^{31}P NMR resonance shifts upfield from 64.4 ppm to 54.2 ppm with one additional equiv pyridine, with a further upfield shift to 47.6 ppm with five more equiv pyridine. The hydride signal in the ^{1}H NMR spectrum shifts downfield as more pyridine is added, reaching –23.4 in the presence of excess pyridine. A change in solution symmetry is also evident by ^{1}H NMR, as the *tert*-butyl resonances resolve from a broad multiplet (C_{2v} symmetry) to two sharp triplets (C_s symmetry) with increasing pyridine concentration. This behavior is consistent a change from five-coordinate to six-coordinate geometry in an equilibrium between monopyridine complex **3**$^+$ and bis(pyridine) complex [(PCP)IrH(py)$_2$][BAr$^F{}_4$] (**4**$^+$) (Scheme S1).

Scheme S1. Equilibrium between $\mathbf{3}^{+}$ and $\mathbf{4}^{+}$ in the presence of free pyridine



4. Deprotonation of 4^+ and Subsequent CO Binding

Reaction of 4^+ with ^{t}BuP$_1$(pyrr) in 1,2-DFB. [(^{tBu4}PCP)IrH(lut)][BAr$^F{}_4$] (**4**$^+$, 10.0 mg, 6.4×10^{-6} mol), ^{t}BuP$_1$(pyrr) (4.0 µL, 1.3×10^{-5} mol, 2 equiv.), mesitylene (2.0 µL, 1.4×10^{-5} mol), and 0.60 mL 1,2-DFB were added to a vial with stirbar, resulting in an immediate dark orange solution. The mixture was stirred for 2 hr, then added to a J-Young tube with C_6D_6 capillary and analyzed by ^{1}H and ^{31}P{^{1}H} NMR. A mixture of rotamers (^{tBu4}PCP)Ir(H)(CO)(2,3-$C_6F_2H_3$), **6a** and **6b** (1.4:1 ratio), was formed in 91% yield.

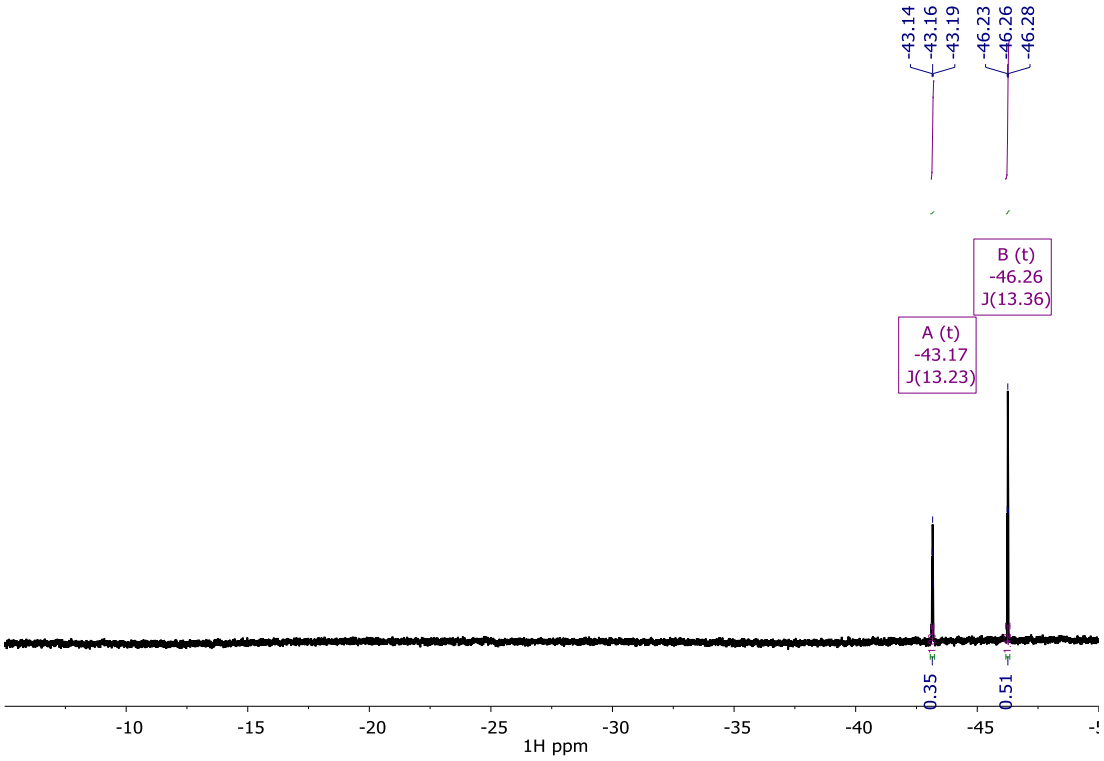


Figure S15. ^{1}H NMR spectrum for reaction of **4**$^+$ and ^{t}BuP$_1$(pyrr) in 1,2-DFB.

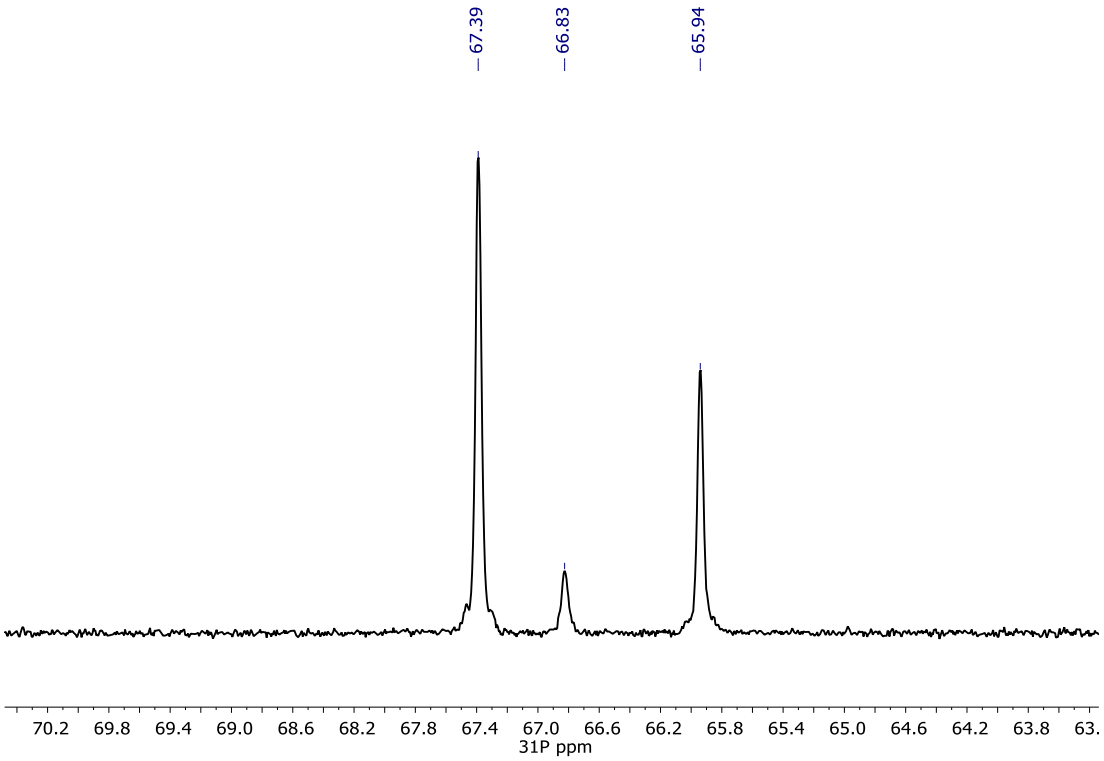


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum for reaction of $\mathbf{4}^{+}$ and $^{t}BuP_1(pyrr)$ in 1,2-DFB.

Reaction of 6a-b with CO. A solution of **6a-b** in 1,2-DFB in a J-Young tube was freeze-pump-thaw degassed 3 times, then backfilled with 1 atm CO. Mixing the contents of the tube resulted in an immediate bleach from dark orange to pale yellow. ^{1}H, ^{19}F, and ^{31}P NMR spectra agreed with the previously reported (^{tBu4}PCP)Ir(H)(CO)(2,3-$C_6F_2H_3$).[13]

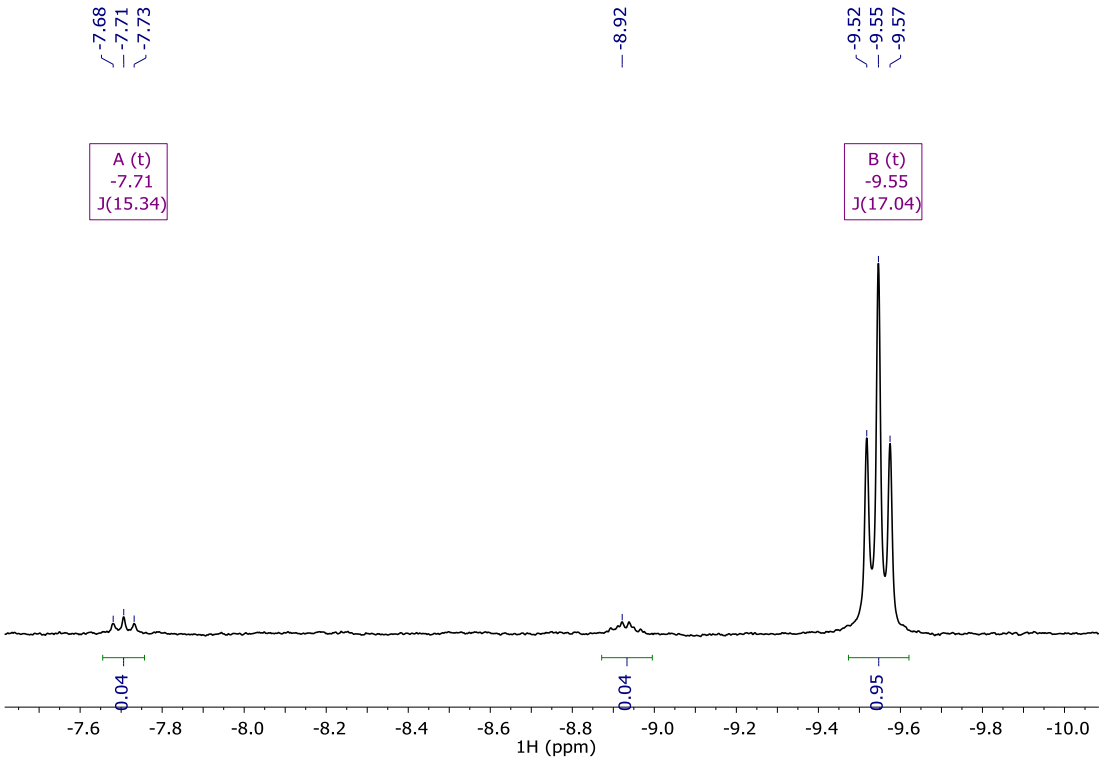


Figure S17. ^{1}H NMR spectrum (hydride region) after reaction of **6a-b** with CO in 1,2-DFB.

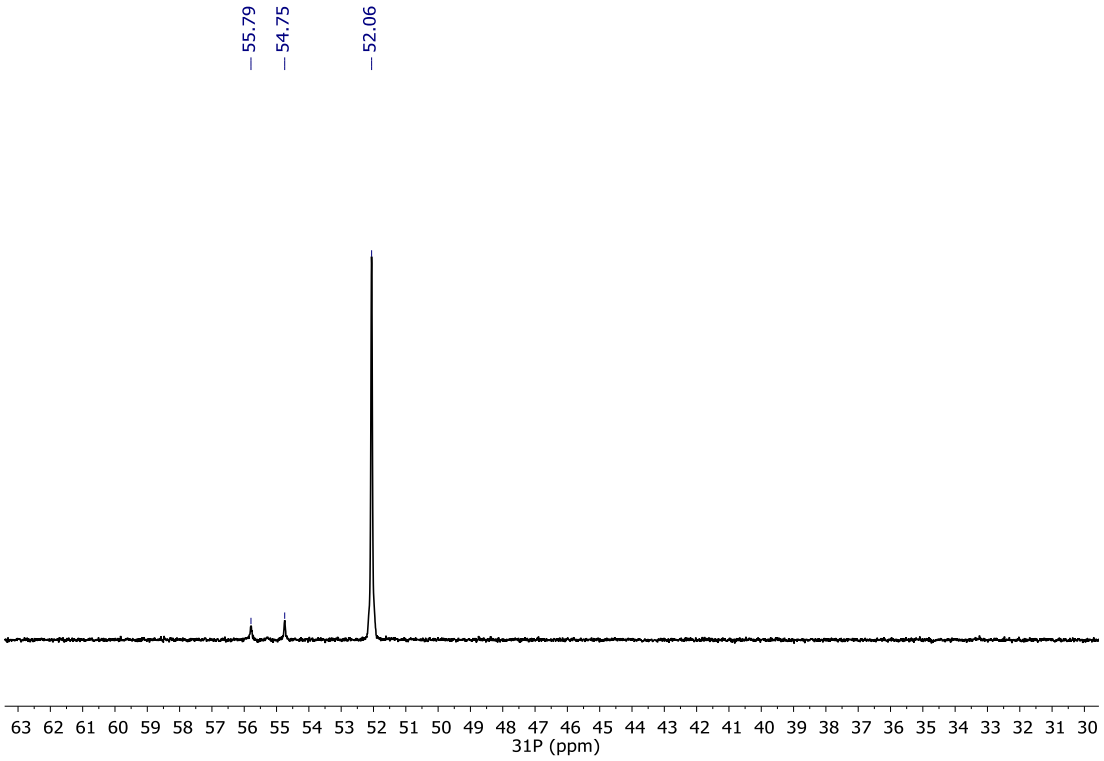


Figure S18. ^{31}P{^{1}H} NMR spectrum after reaction of **6a-b** with CO in 1,2-DFB.

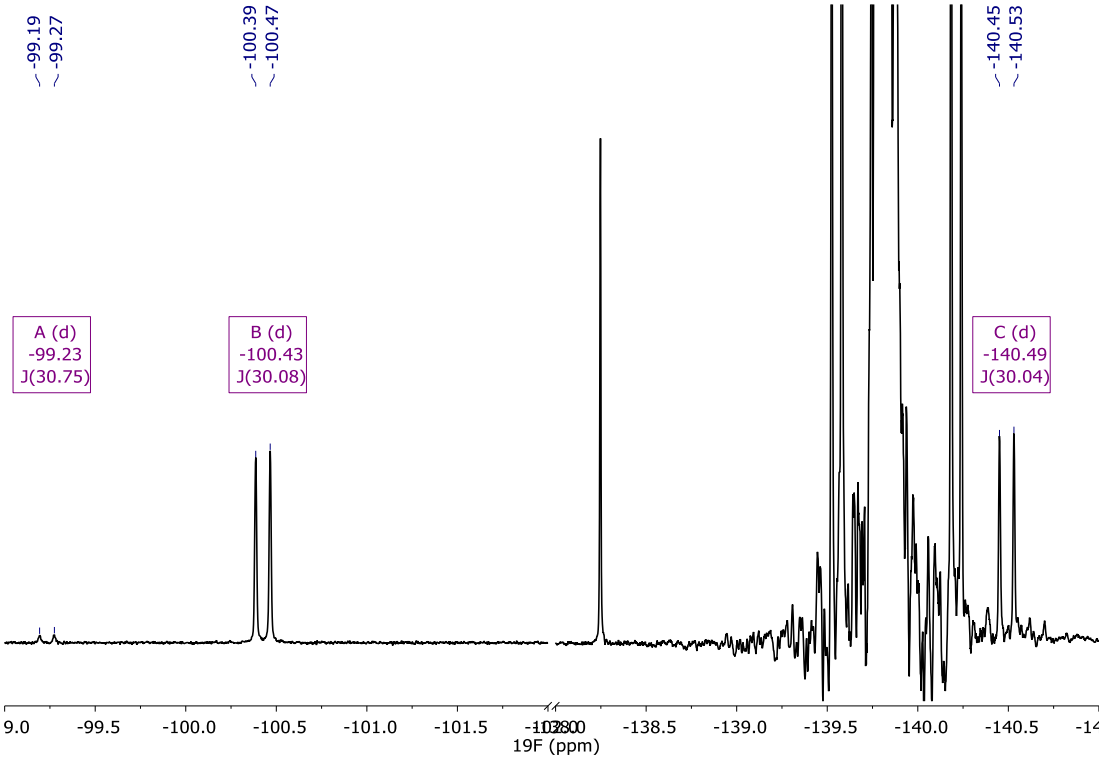


Figure S19. $^{19}F\{^{1}H\}$ NMR spectrum after reaction of **6a-b** with CO in 1,2-DFB.

Reaction of 5^+ with ^{t}BuP$_1$(pyrr) in 2-phenylpyridine. A Teflon-sealed NMR tube was charged with 10 mg $\mathbf{5}^+$, 0.6 mL 2-phenylpyridine, and 0.1 mL of a C_6D_6 solution containing hexamethyldisiloxane internal standard. By syringe, 10.5 µL (5.5 equiv) ^{t}BuP$_1$(pyrr) was slowly added. The tube was sealed and shaken to mix, and monitored by NMR spectroscopy. Two unidentified hydride-containing products were formed within 30 minutes, consistent with C–H activation at the pyridyl ring of 2-phenylpyridine. Heating at 50 ºC lead to formation of the two isomers of cyclometallated 2-phenylpyridine (identified by comparison to authentic samples).[5,6,7]

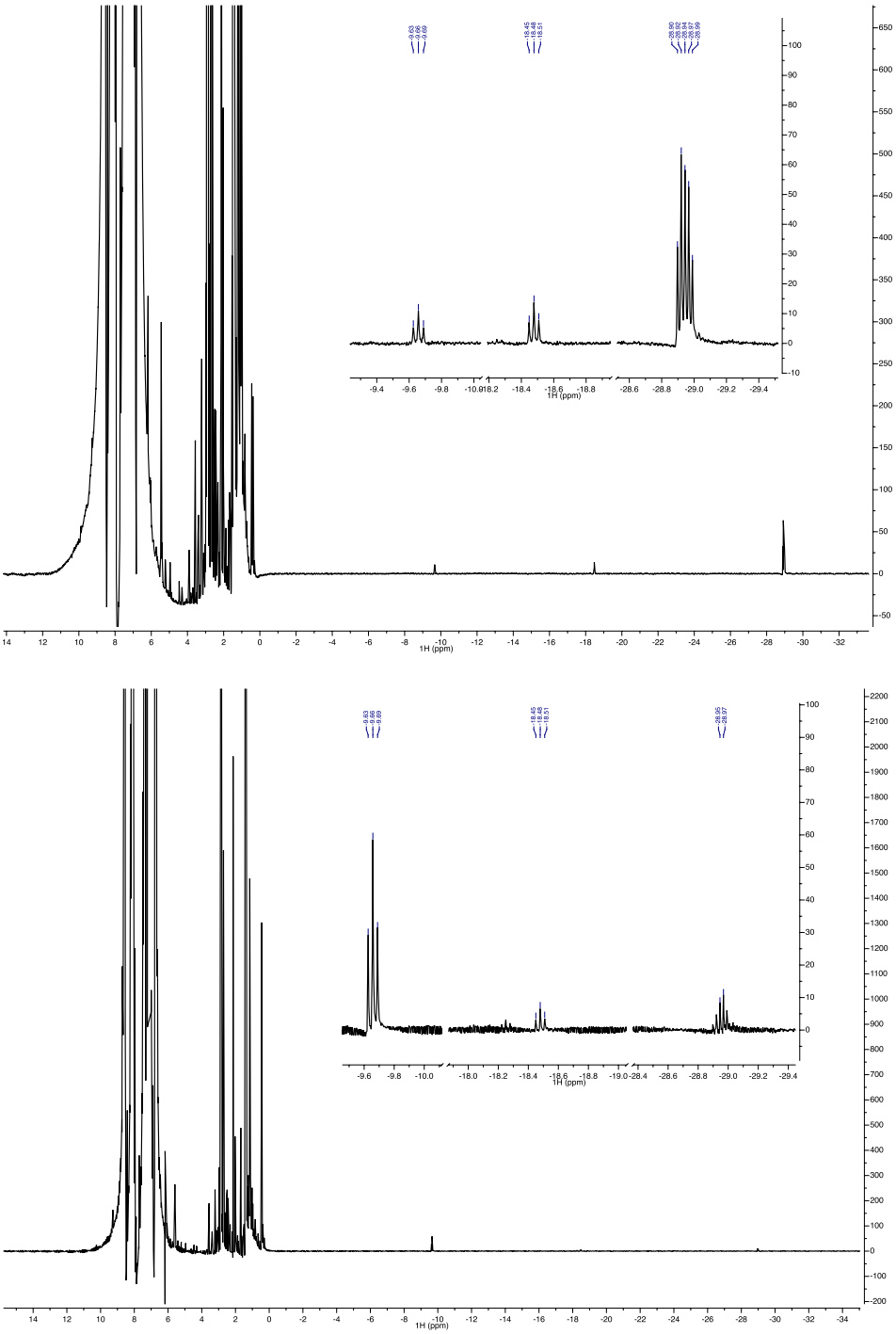


Figure S20. ^{1}H NMR spectra after reaction of $\mathbf{4}^{+}$ with ^{t}BuP$_1$(pyrr) in 2-phenylpyridine after 6 hours at room temperature (top) and after 12 hours heating at 50 ºC (bottom).

5. Electrochemistry Experiments

Electrosynthesis of 4^+ in 1,2-DFB and Subsequent Deprotonation. A 4 mL solution of (^{tBu4}PCP)IrH$_4$ (**1**, 10.2 mg, 1.74×10^{-5} mol) and 2,6-lutidine (20.5 mg, 1.91×10^{-4} mol, 11 equiv.) in 0.2 M [nBu$_4$N][PF$_6$] in 1,2-DFB was added to the working compartment of the three-compartment cell. The solution was electrolyzed at 0.90 V vs. the Ag wire pseudoreference electrode. Over the course of 1.5 hr, 3.54 C of current, amounting to 2.1 e^- per Ir, was passed, resulting in a color change from pale yellow to dark yellow. After reducing the volume of the solution to 1 mL, mesitylene (5 µL, 3.6×10^{-5} mol) was added and the solution was added to a J-Young tube with a C_6D_6 capillary. The yield of $\mathbf{4}^+$ was determined to be 83%. ^{t}BuP$_1$(pyrr) (26.5 µL, 8.7×10^{-5} mol, 5.0 equiv) was added via microsyringe to the tube, resulting in an immediate color change to orange. The yield of **6a-b** was determined to be 78% relative to (^{tBu4}PCP)IrH$_4$ starting material (94% yield relative to $\mathbf{4}^+$).

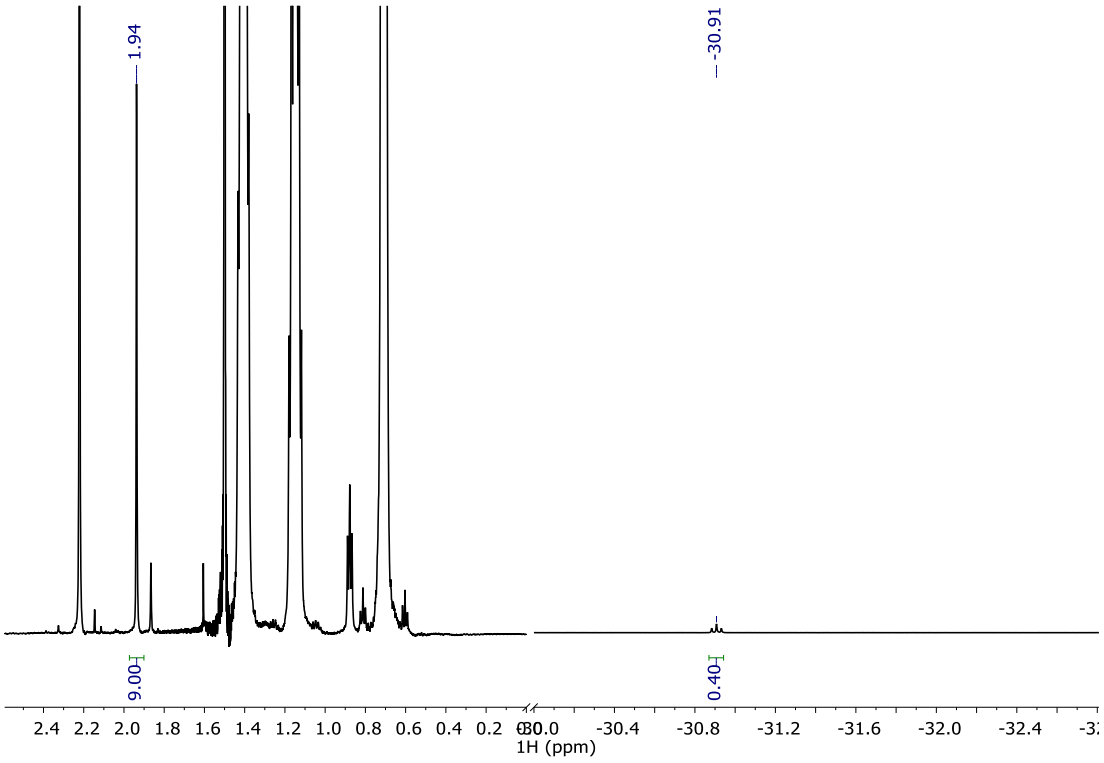


Figure S21. ^{1}H NMR spectrum for electrochemically generated $\mathbf{4}^+$ in 1,2-DFB.

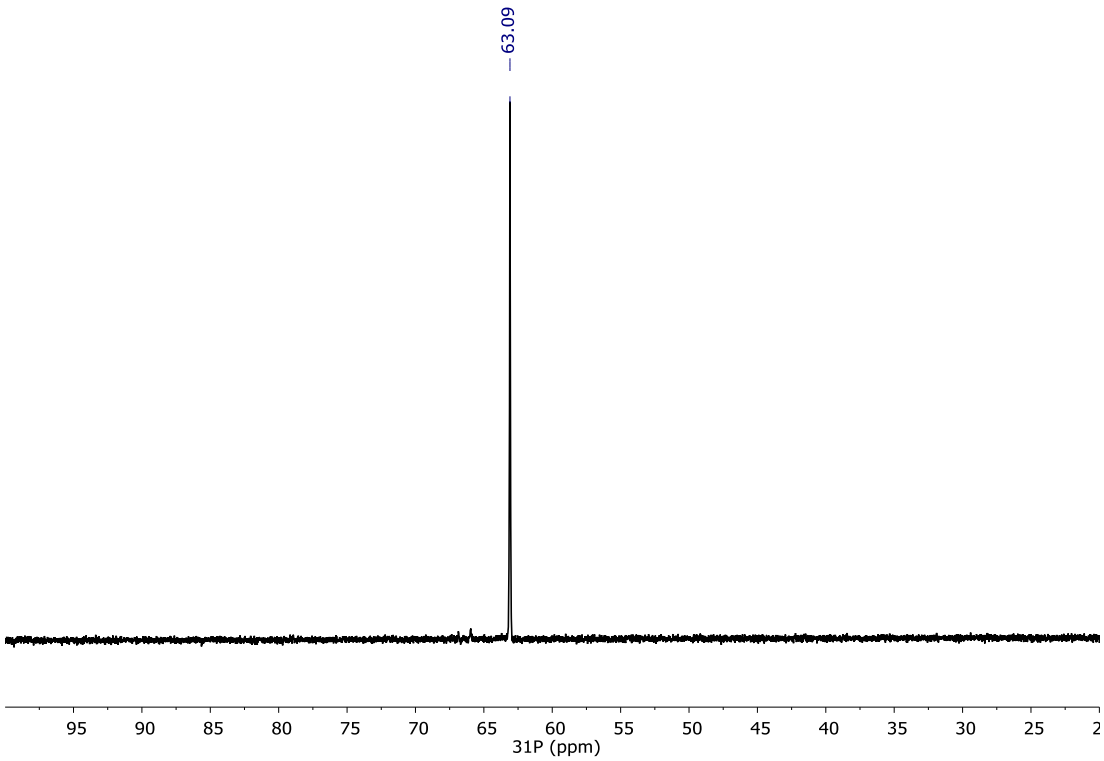


Figure S22. $\{^{31}P\}^{1}H$ NMR spectrum for electrochemically generated $\mathbf{4}^{+}$ in 1,2-DFB.

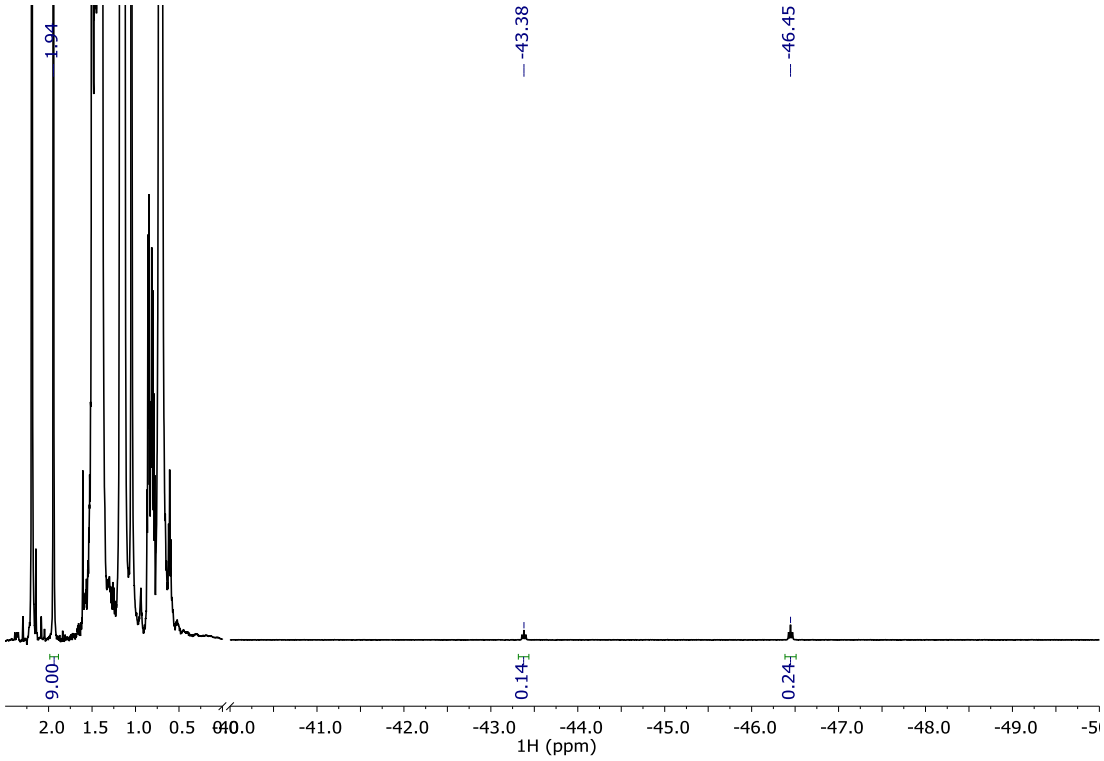


Figure S23. ^{1}H NMR spectrum for **6a-b** from electrochemically generated $\mathbf{4}^{+}$ + $^{t}BuP_{1}$(pyrr).

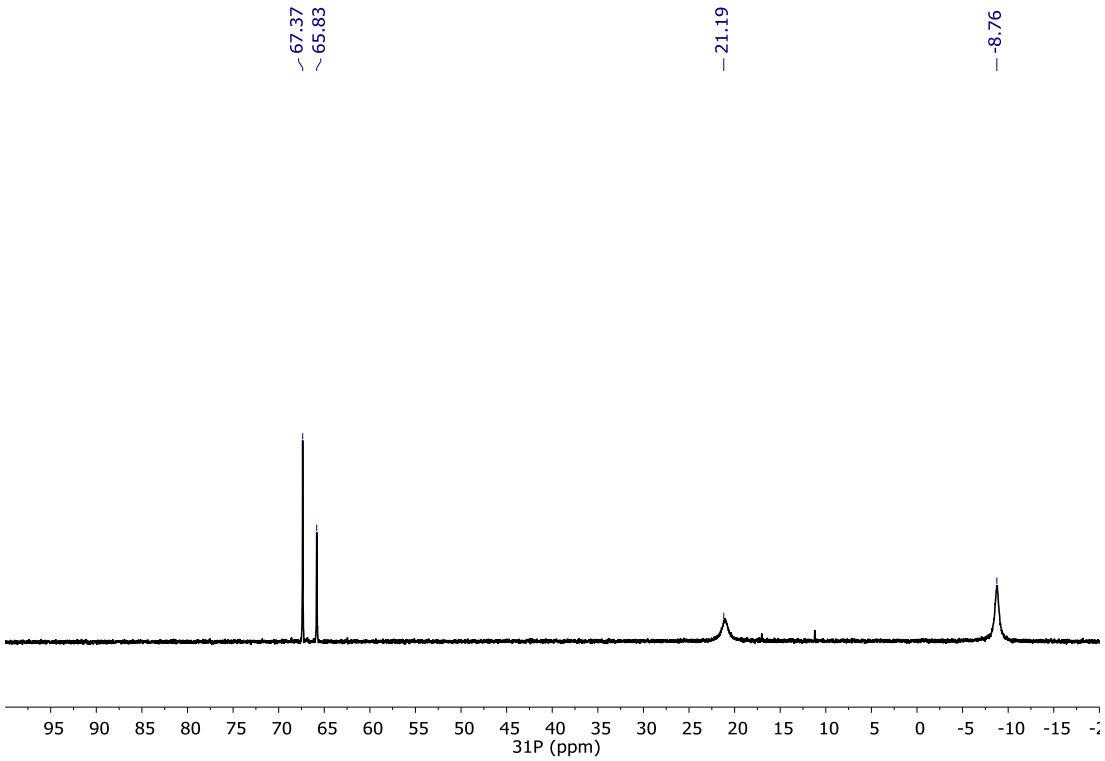


Figure S24. $^{31}P\{^{1}H\}$ NMR Spectrum for **6a-b** from electrochemically generated $\mathbf{4}^{+}$ + $^{t}BuP_1(pyrr)$. Note: resonances at δ 21.19 and −8.76 correspond to $[H^{t}BuP_1(pyrr)]^{+}$ and $^{t}BuP_1(pyrr)$, respectively.

Electrolysis of 1 with $^{t}BuP_1(pyrr)$. A 4 mL solution of (^{tBu4}PCP)IrH_4 (10.9 mg, 1.7×10^{-5} mol) and $^{t}BuP_1(pyrr)$ (28.8 mg, 9.22×10^{-5} mol, 5.4 equiv.) in 0.2 M $[nBu_4N][PF_6]$ in 1,2-DFB was added to the working compartment of the three-compartment cell. The solution was electrolyzed at 1.05 V vs. the Ag wire pseudoreference electrode. Over the course of 2 hr, 4.86 C of current, amounting to 2.7 e^{-} per Ir, was passed, resulting in a color change from light orange to dark orange. The solution in the working electrode compartment was concentrated to 1 mL and added to a J-Young tube with mesitylene (5 μL) and a C_6D_6 capillary. ^{1}H and $^{31}P\{^{1}H\}$ showed (^{tBu4}PCP)IrH_4 and (^{tBu4}PCP)IrH_2, as well as the C-H activated products **6a** and **6b** in 32% yield.

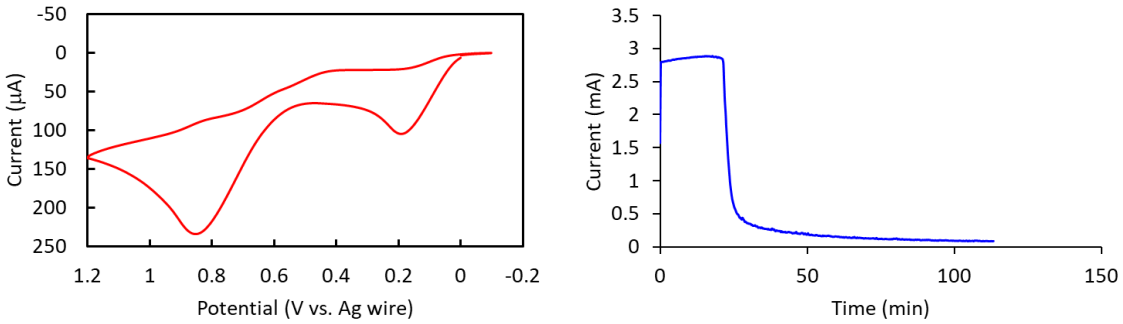


Figure S25. CV and bulk electrolysis trace for **1** + ^{t}BuP$_1$(pyrr).

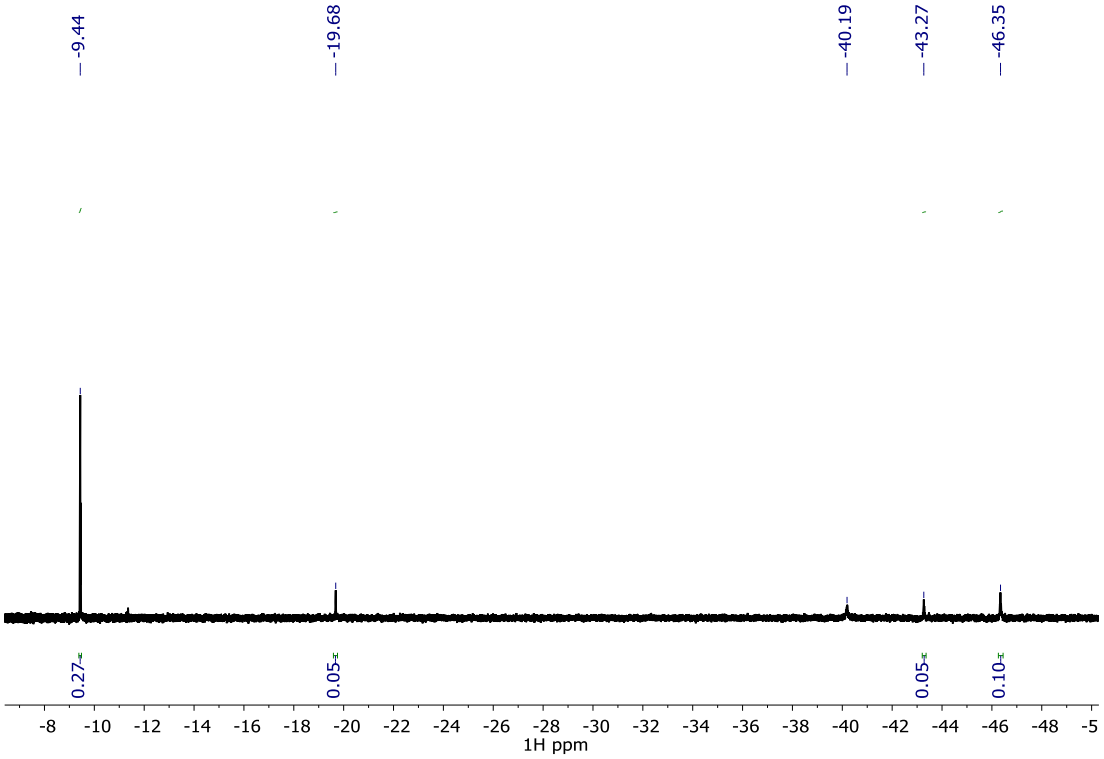


Figure S26. ^{1}H NMR spectrum for **1** + ^{t}BuP$_1$(pyrr) electrolysis.

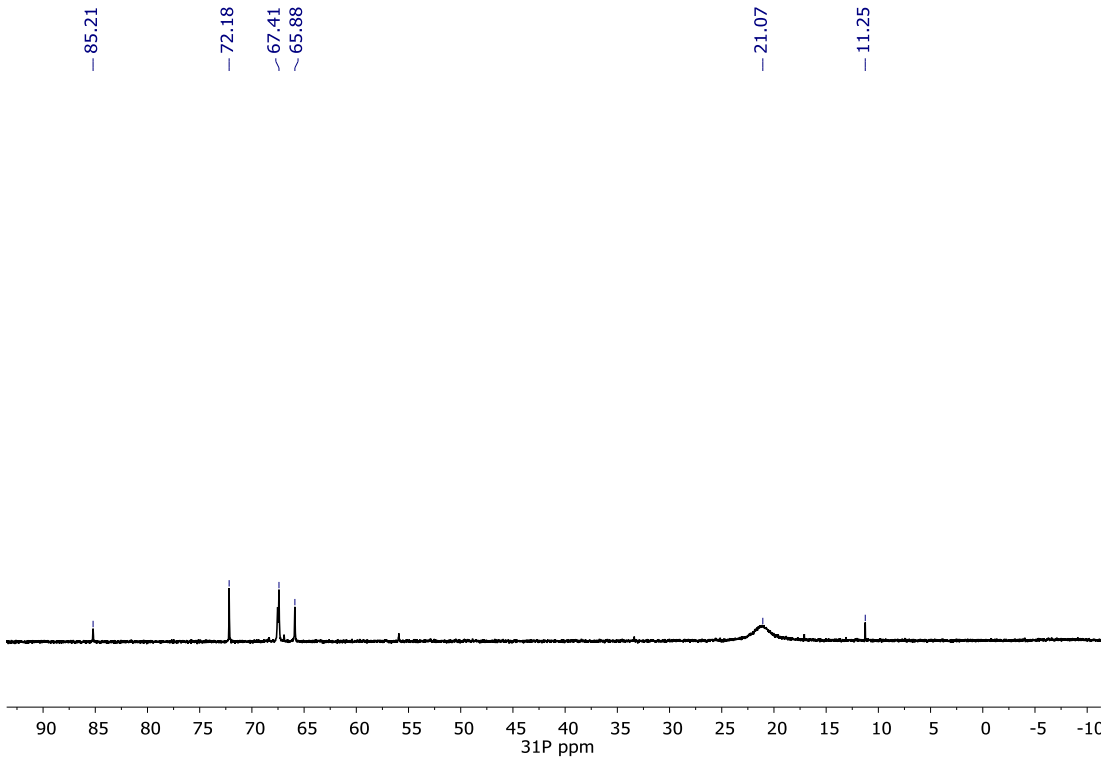


Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum for **1** + $^{t}BuP_1$(pyrr) electrolysis.

Electrolysis of 1 with ^{t}BuP$_1$(pyrr) and 2,6-lutidine. A 4 mL solution of (^{tBu4}PCP)IrH$_4$ (9.8 mg, 1.7×10^{-5} mol) and $^{t}BuP_1$(pyrr) (29.0 mg, 9.28×10^{-5} mol, 5.6 equiv.) in 0.2 M [nBu$_4$N]PF$_6$ in 1,2-DFB was added to the working compartment of the three-compartment cell. The solution was electrolyzed at 1.05 V vs. the Ag wire pseudoreference electrode. Over the course of 3 hr, 4.41 C of current, amounting to 2.7 e$^-$ per Ir, was passed, resulting in a color change from light orange to dark orange. The solution in the working electrode compartment was concentrated to 1 mL and added to a J-Young tube with mesitylene (5 μL) and a C_6D_6 capillary. ^{1}H and $^{31}P\{^{1}H\}$ showed (^{tBu4}PCP)IrH$_4$ and (^{tBu4}PCP)IrH$_2$, as well as the C-H activated products **6a** and **6b** in 19% yield.

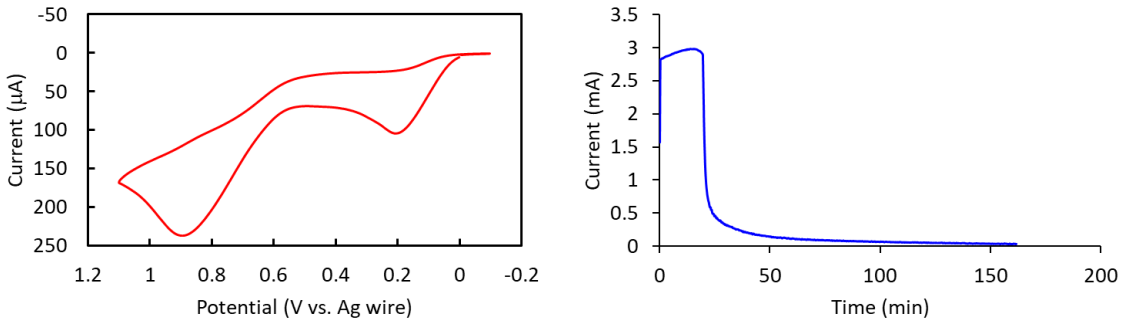


Figure S28. CV and bulk electrolysis trace for **1** + ^{t}BuP$_1$(pyrr) + 2,6-lutidine.

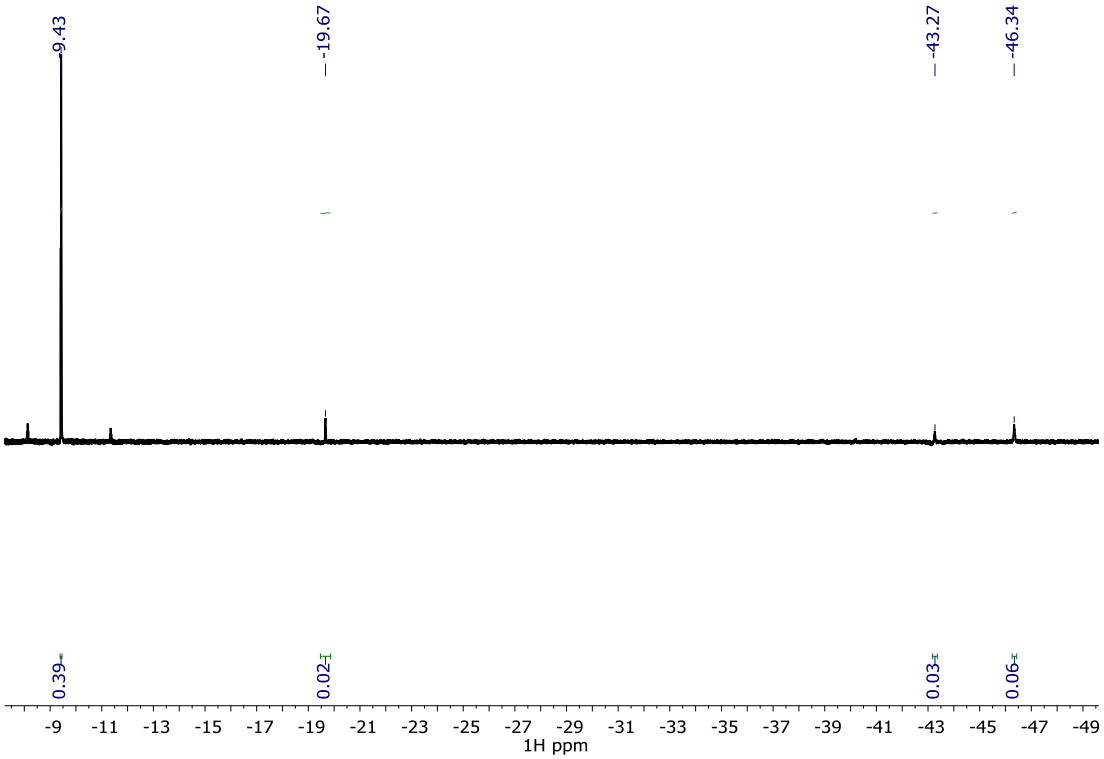


Figure S29. ^{1}H NMR spectrum for **1** + ^{t}BuP$_1$(pyrr) + 2,6-lutidine electrolysis.

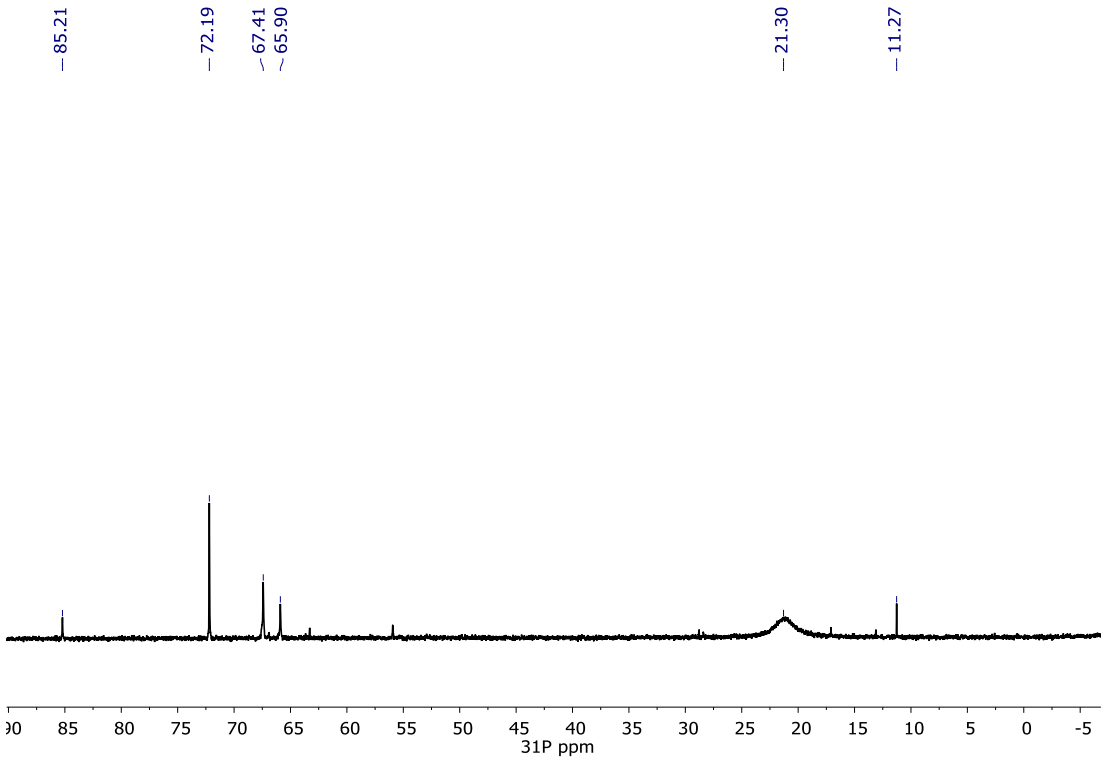


Figure S30. $^{31}P\{^{1}H\}$ NMR for **1** + $^{t}BuP_1$(pyrr) + 2,6-lutidine electrolysis.

One-pot Synthesis of 6a-b from (^{tBu4}PCP)IrH$_4$. A 4 mL solution of (^{tBu4}PCP)IrH$_4$ (11.1 mg, 1.89×10^{-5} mol) and 2,6-lutidine (20.2 mg, 1.89×10^{-4} mol, 10 equiv.) in 0.2 M [nBu$_4$N]PF$_6$ in 1,2-DFB was added to the working compartment of the three-compartment cell. The solution was electrolyzed at 0.87 V vs. the Ag wire pseudoreference electrode. Over the course of 1.5 hr, 5.33 C of current, amounting to 2.9 e$^-$ per Ir, was passed, resulting in a color change from pale yellow to dark yellow. $^{t}BuP_1$(pyrr) (25 µL, 8.2×10^{-5} mol, 4.3 equiv) was added via microsyringe to the working electrode compartment solution, resulting in a color change to orange. The solution was stirred for 1 hr, then reduced in volume to 1 mL. Mesitylene (5 µL, 3.6×10^{-5} mol) was added and the solution was added to a J-Young tube with a C_6D_6 capillary. The yield of **6a-b** was determined to be 61%.

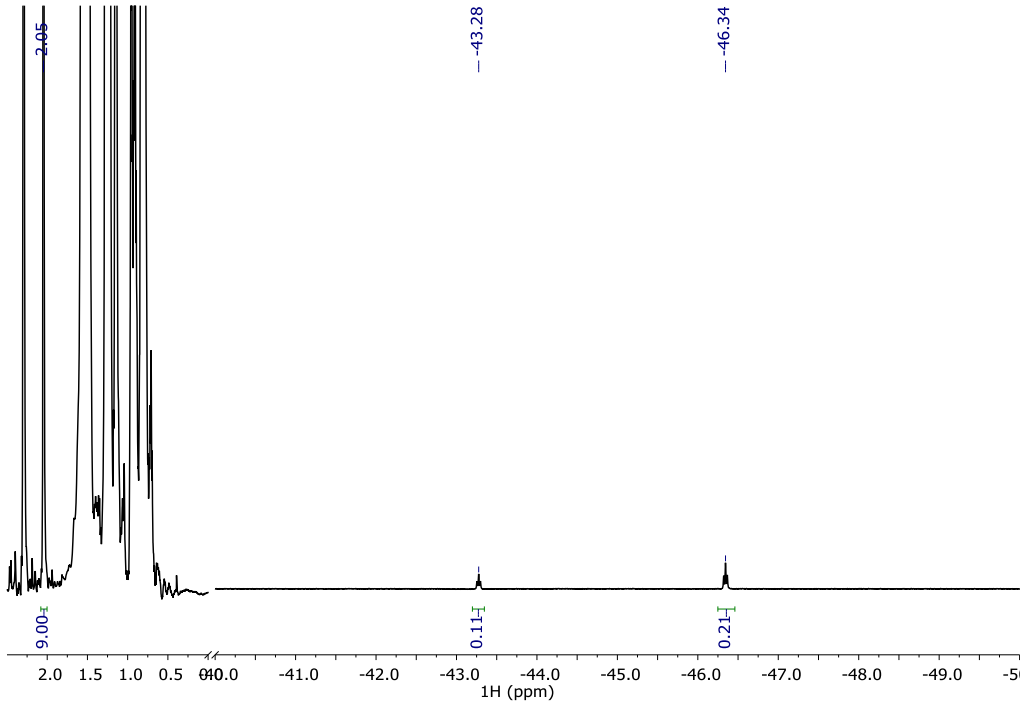


Figure S31. ^{1}H NMR spectrum for one-pot reaction of **1** + 2,6-lutidine electrolysis in 1,2-DFB followed by treatment with ^{t}BuP$_1$(pyrr).

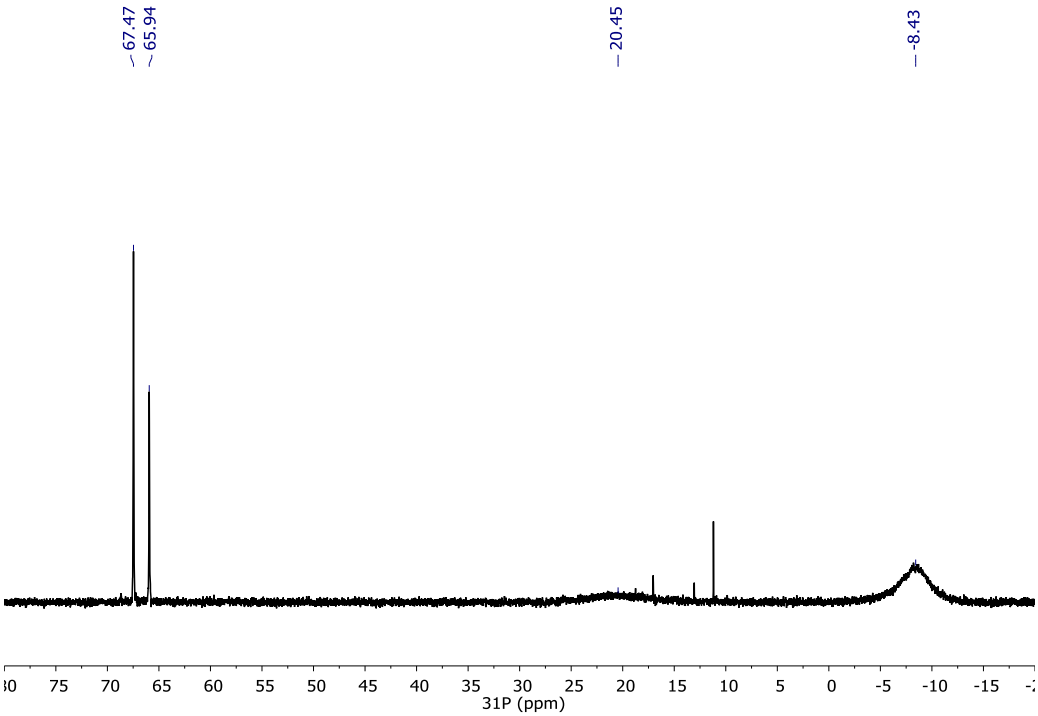


Figure S32. $\{^{31}P\}^{1}H$ NMR spectrum for one-pot reaction of **1** + 2,6-lutidine electrolysis in 1,2-DFB followed by treatment with ^{t}BuP$_1$(pyrr).

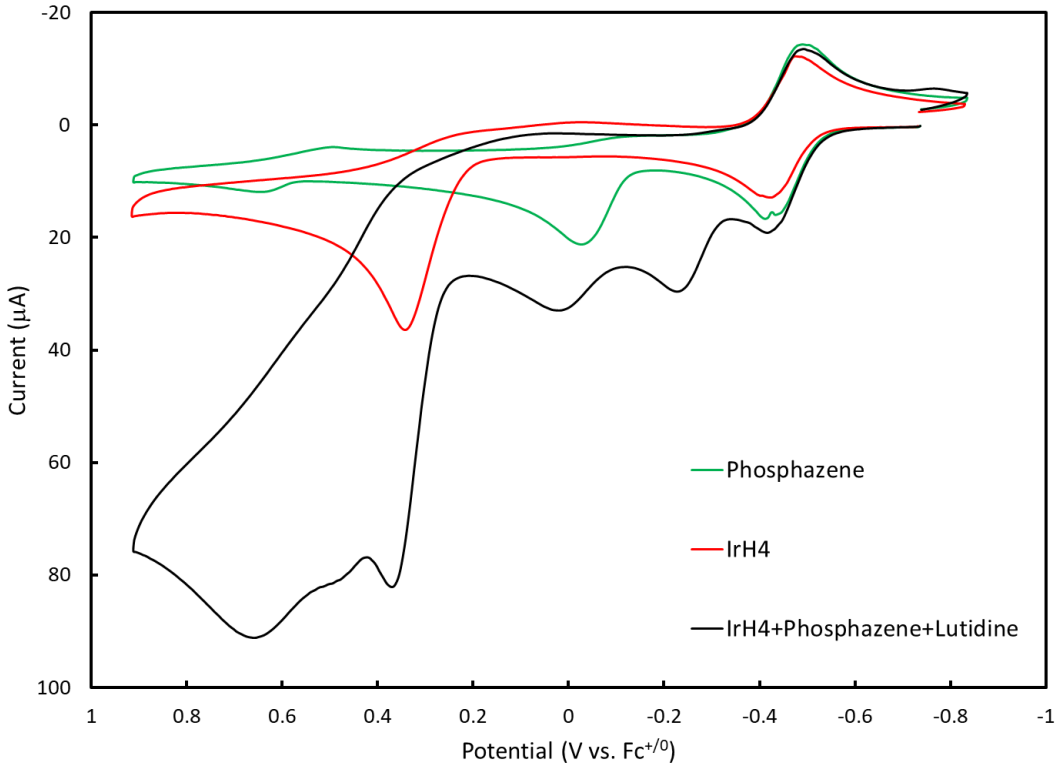


Figure S33. CVs of ^{t}BuP$_1$(pyrr), (^{tBu4}PCP)IrH$_4$, and ^{t}BuP$_1$(pyrr)/(^{tBu4}PCP)IrH$_4$/2,6-lutidine mixture in 1,2-DFB with 0.2 M [^{n}Bu$_4$N][PF$_6$] at 100 mV/s. All cyclic voltammograms contain decamethylferrocene as an internal standard ($E°$ = −0.45 V vs. Fc$^{+/0}$).

6. Reaction of 1 with H_2 Acceptor

Reaction of (^{tBu4}PCP)IrH_4 with *tert*-butylethylene. A J-Young tube was charged with (^{tBu4}PCP)IrH_4 (8.1 mg, 1.4×10^{-5} mol), *tert*-butylethylene (3.5 μL, 2.7×10^{-5} mol, 2.0 equiv.), mesitylene (5 μL, as internal standard) and 1,2-difluorobenzene (600 μL). The tube was heated at 55 °C and monitored by ^{1}H and ^{31}P NMR over 17 h.

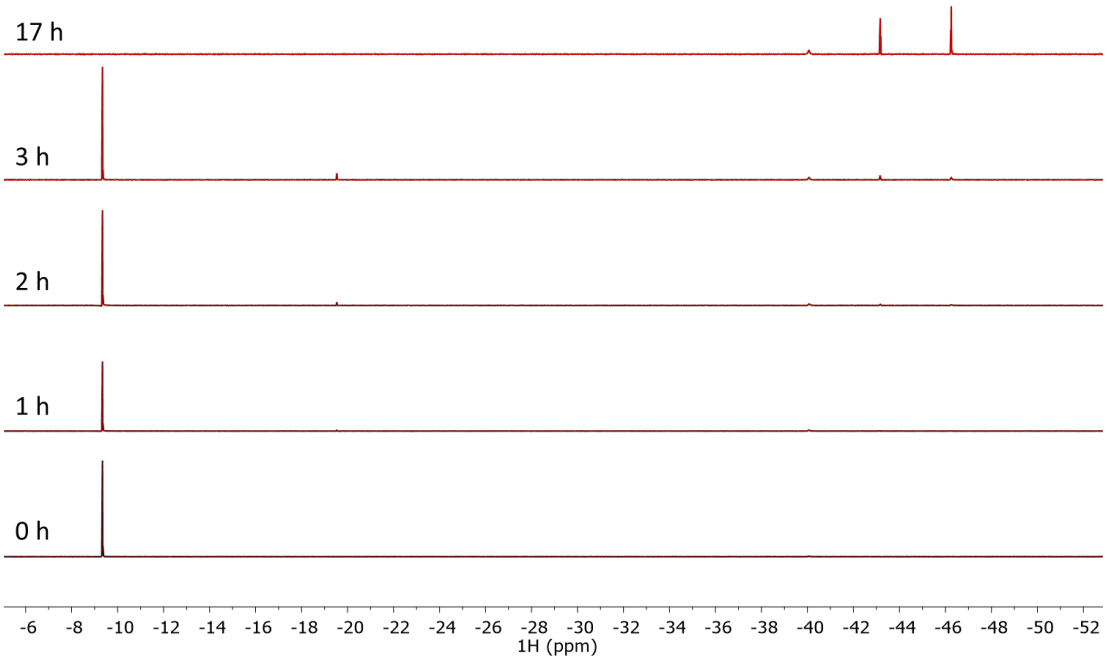


Figure S34. ^{1}H NMR time course for reaction of **1** with *tert*-butylethylene.

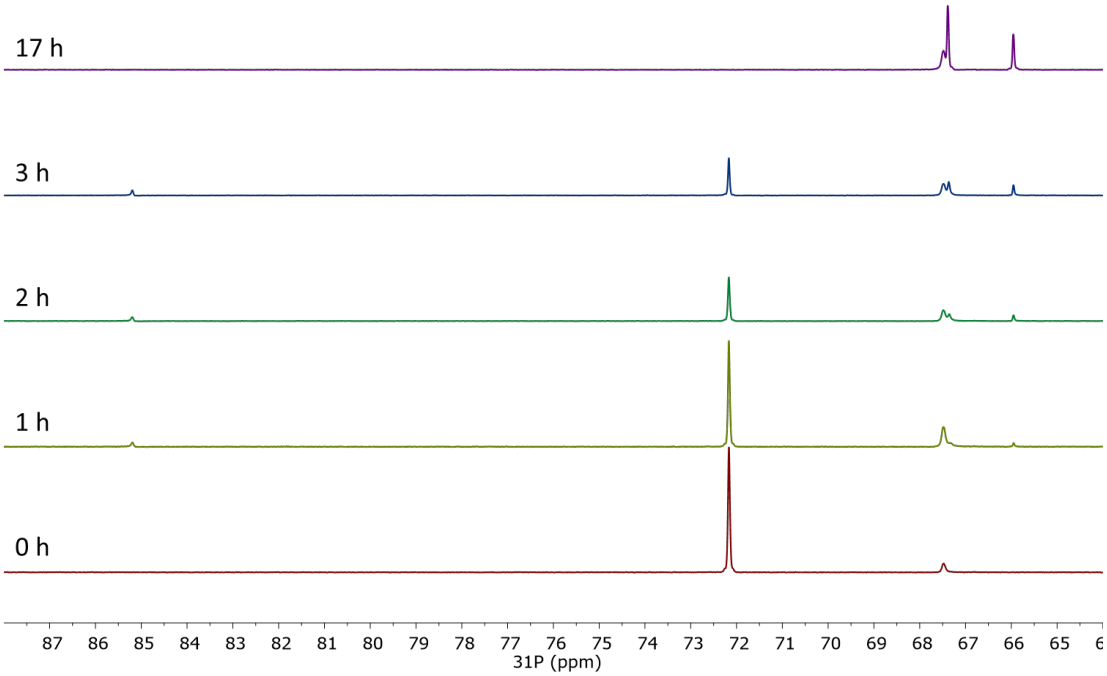


Figure S35. $^{31}P\{^{1}H\}$ NMR time course for reaction of **1** with *tert*-butylethylene.

7. Computational Details

Geometry optimization of 3^+, 4^+, and 5^+. The gas-phase geometries of 3^+, 4^+, and 5^+ were optimized in Gaussian 16[8] using the PBE functional,[9,10,11] with the LANL2DZ basis set[12,13,14] for Ir and 6-311G[15,16] for other atoms. The coordinates from the X-ray structures of 3^+ and 5^+ were used as the input for the computations. For 5^+, methyl groups were added to the coordinates of 3^+ using Gaussview.[17]

Sample Input File:

```
%chk=/nas/longleaf/home/brianml/chk/PCPIrH-py.chk
%mem=16000MB
%nprocshared=8
# opt PBEPBE pop=full scf=(conver=8,cycle=400)

PCPIrH-py geometry optimization

1 1
 Ir          7.11780000   7.11780000  17.32860000
 P           8.73120000   5.89590000  18.43410000
 C           8.59630000   8.59630000  17.32860000
 N           5.58030000   5.58030000  17.32860000
 C          10.56430000  10.56430000  17.32860000
 C           8.88370000   6.12660000  20.24320000
 C           3.64600000   3.64600000  17.32860000
 C           8.99160000   4.12220000  17.83450000
 C          10.36880000   3.55290000  18.24000000
 C           9.90610000   8.25640000  17.53650000
 C          10.27570000   6.77940000  17.78260000
 C           7.43900000   5.87700000  20.84630000
 C          10.91910000   9.26540000  17.50530000
 C           9.13320000   7.55640000  20.61400000
 C           9.66470000   5.10410000  20.99180000
 C           8.85800000   4.10190000  16.36160000
 C           4.34470000   3.90630000  16.20570000
 C           7.93810000   3.24130000  18.52080000
 C           5.30910000   4.90180000  16.25420000
 H          11.23610000  11.23610000  17.32860000
 H           2.97430000   2.97430000  17.32860000
 H          10.99330000   3.65540000  17.49490000
```

H	10.71000000	4.03310000	19.02680000
H	10.27840000	2.60330000	18.47220000
H	11.00810000	6.71740000	18.44800000
H	10.57920000	6.35990000	16.94040000
H	6.79830000	6.50150000	20.44770000
H	7.16250000	4.96380000	20.65560000
H	11.83230000	9.02800000	17.60930000
H	9.96810000	7.86390000	20.20510000
H	8.39000000	8.10670000	20.30910000
H	9.19930000	7.63460000	21.58790000
H	9.33420000	4.20980000	20.75960000
H	10.61290000	5.17970000	20.75960000
H	9.56350000	5.24710000	21.95530000
H	8.25510000	4.81550000	16.07740000
H	9.73880000	4.23550000	15.95270000
H	8.49790000	3.23730000	16.07740000
H	4.18290000	3.42070000	15.40510000
H	8.25510000	2.98100000	19.41140000
H	7.09510000	3.73640000	18.61090000
H	7.78300000	2.44150000	17.98010000
H	5.79610000	5.09740000	15.46050000
P	5.89590000	8.73120000	16.22300000
C	6.12660000	8.88370000	14.41390000
C	4.12220000	8.99160000	16.82260000
C	3.55290000	10.36880000	16.41710000
C	8.25640000	9.90610000	17.12060000
C	6.77940000	10.27570000	16.87450000
C	5.87700000	7.43900000	13.81090000
C	9.26540000	10.91910000	17.15180000
C	7.55640000	9.13320000	14.04310000
C	5.10410000	9.66470000	13.66530000
C	4.10190000	8.85800000	18.29550000
C	3.24130000	7.93810000	16.13640000
H	3.65540000	10.99330000	17.16220000
H	4.03310000	10.71000000	15.63040000
H	2.60330000	10.27840000	16.18490000
H	6.71740000	11.00810000	16.20910000
H	6.35990000	10.57920000	17.71670000
H	6.50150000	6.79830000	14.20940000
H	4.96380000	7.16250000	14.00150000
H	6.01600000	7.45920000	12.84050000
H	9.02800000	11.83230000	17.04780000
H	7.86390000	9.96810000	14.45200000
H	8.10670000	8.39000000	14.34800000
H	7.63460000	9.19930000	13.06920000
H	4.20980000	9.33420000	13.89750000

H	5.17970000	10.61290000	13.89750000
H	5.24710000	9.56350000	12.70180000
H	4.81550000	8.25510000	18.57970000
H	4.23550000	9.73880000	18.70440000
H	3.23730000	8.49790000	18.57970000
H	2.98100000	8.25510000	15.24570000
H	3.73640000	7.09510000	16.04620000
H	2.44150000	7.78300000	16.67700000
C	3.90630000	4.34470000	18.45140000
C	4.90180000	5.30910000	18.40290000
H	3.42070000	4.18290000	19.25200000
H	5.09740000	5.79610000	19.19660000
H	7.18901325	6.96509053	15.95611181

H C N P 0
6-311G(d,p)
****
Ir 0
Lanl2dz
****

Ir 0
Lanl2dz
****

XYZ Coordinates for Optimized Structure of 3^+

Ir	0.00114500	0.00780000	-0.01011900
P	-2.34091500	-0.33134300	-0.13569400
C	0.00692500	-2.03917800	-0.02295600
N	-0.01147800	2.23073700	0.00732800
C	0.00144700	-4.88901900	-0.02196700
C	-3.17731200	-0.51269200	1.58671800
C	-0.02238900	5.05544200	-0.00006800
C	-3.39568900	0.71574700	-1.34700300
C	-4.68614900	-0.00634500	-1.78523800
C	-1.14321900	-2.78144900	-0.41894800
C	-2.38025700	-2.03907700	-0.86370400
C	-2.87339600	0.73712600	2.43410300
C	-1.14105800	-4.18252900	-0.40740700
C	-2.54203700	-1.72904000	2.29249100
C	-4.69786700	-0.73086000	1.50466400
C	-2.52490100	0.94133700	-2.60083100

C	0.28245100	4.33328300	-1.15679700
C	-3.73976800	2.08218700	-0.72659300
C	0.27797000	2.94017400	-1.11254600
H	-0.00095000	-5.98094500	-0.02064900
H	-0.02632100	6.14685200	-0.00316000
H	-4.48002400	-0.97296700	-2.26769800
H	-5.38923400	-0.17407400	-0.96103000
H	-5.19979800	0.62302100	-2.53129200
H	-3.30853100	-2.57527000	-0.61044400
H	-2.37669000	-1.90787100	-1.95965300
H	-1.79379700	0.81427600	2.63909000
H	-3.21187700	1.67338000	1.96895200
H	-2.03938400	-4.72776400	-0.71086900
H	-2.77669200	-2.68053500	1.79549000
H	-1.44686800	-1.65015600	2.36015900
H	-2.94453400	-1.78018400	3.31805200
H	-5.23532900	0.15739900	1.14450400
H	-4.96640200	-1.58769400	0.86869400
H	-5.07451400	-0.94962400	2.51808500
H	-1.62441800	1.52595400	-2.37148800
H	-2.21461700	-0.00205900	-3.07646400
H	-3.11452000	1.50282700	-3.34455000
H	0.52512100	4.83647600	-2.09397700
H	-4.44397400	1.99487400	0.11314300
H	-2.84314800	2.61631400	-0.37775400
H	-4.22393900	2.71147900	-1.49184000
H	0.52102700	2.35337200	-1.99730000
P	2.35204500	-0.31935400	0.10616600
C	3.27693500	-0.42530300	-1.56895500
C	3.30424500	0.69960000	1.42072600
C	4.60349200	0.02497000	1.90249300
C	1.15882000	-2.78443900	0.35819500
C	2.40838600	-2.05116600	0.78363000
C	3.01352300	0.84813000	-2.39365100
C	1.14757400	-4.18684300	0.35651600
C	2.69667600	-1.63050100	-2.33824100
C	4.79292700	-0.62607200	-1.39620600
C	2.33845800	0.80424500	2.62099800
C	3.61289400	2.11244300	0.89352000
H	4.43221100	-0.98853600	2.29372000
H	5.37174400	-0.03159100	1.12218100
H	5.02071500	0.62370800	2.72981700
H	3.32754100	-2.57771200	0.48080600
H	2.44760800	-1.96042700	1.88243700
H	1.94780600	0.93255200	-2.65297400
H	3.32650400	1.76913000	-1.88179700

H	3.57767500	0.78387200	-3.33876700
H	2.04514800	-4.73485900	0.65722600
H	2.93062000	-2.59172800	-1.85920700
H	1.60488600	-1.56714300	-2.45068100
H	3.14458800	-1.64446300	-3.34579700
H	5.29052100	0.26411700	-0.98633000
H	5.03601600	-1.49013300	-0.75970400
H	5.23569300	-0.81910600	-2.38756000
H	1.40153200	1.31000700	2.34520500
H	2.09046000	-0.17854600	3.05148200
H	2.81515200	1.39712900	3.41944700
H	4.36183600	2.09876500	0.08848000
H	2.71250700	2.62493500	0.52374100
H	4.02897400	2.72060500	1.71405700
C	-0.32244700	4.33815900	1.16067700
C	-0.30751200	2.94479400	1.12184400
H	-0.56974400	4.84420100	2.09507400
H	-0.54903500	2.36569400	2.01330100
H	0.05348200	0.00456700	-1.55213100
H	-3.38214200	0.64382700	3.40792800

XYZ Coordinates for Optimized Structure of 4^+

Ir	0.02394500	0.00840100	-0.04043000
P	-2.31016600	0.50419300	0.28514300
C	0.09731700	1.99741800	-0.52374400
N	-0.10245900	-2.22811200	-0.22577000
C	0.12844900	4.66801600	-1.50630600
C	-3.54444000	0.20762500	-1.16183000
C	-0.42297200	-4.92000400	-0.94732500
C	-3.08644000	0.00195600	1.97444500
C	-4.27595100	0.90102700	2.37150000
C	-1.02157700	2.85663000	-0.36160200
C	-2.21747600	2.35677800	0.40677000
C	-3.63683000	-1.29750500	-1.48190200
C	-1.00637500	4.16520100	-0.86434200
C	-2.96197700	0.97628000	-2.36877300
C	-4.96584300	0.73987800	-0.90163300
C	-1.99763800	0.17376800	3.05312900
C	-0.22227800	-4.55305300	0.38100500
C	-3.53893300	-1.46946800	1.94048300
C	-0.05745800	-3.20322800	0.72489900
H	0.13517700	5.68817800	-1.89532700
H	-0.55529200	-5.96777800	-1.22368400
H	-3.99604200	1.96212500	2.44292800
H	-5.13089300	0.81450900	1.69194100

H	-4.62137100	0.59215800	3.37243700
H	-3.15741900	2.83008500	0.08428500
H	-2.09740500	2.59630100	1.47760900
H	-2.65508100	-1.78310600	-1.54123500
H	-4.22757400	-1.84199700	-0.73342000
H	-1.88778400	4.80122300	-0.74147800
H	-3.01923300	2.06542200	-2.23040400
H	-1.91061100	0.73055000	-2.56950200
H	-3.55219300	0.72454600	-3.26567100
H	-5.51289700	0.13200500	-0.16818700
H	-4.98181000	1.78987900	-0.57386200
H	-5.53211900	0.68927200	-1.84708300
H	-1.13886500	-0.48752100	2.88263000
H	-1.62917900	1.20949700	3.11891000
H	-2.43225900	-0.07773100	4.03502100
H	-0.18308300	-5.30686400	1.16935000
H	-4.44737900	-1.60592000	1.33734800
H	-2.76038700	-2.13927100	1.54510400
H	-3.77931800	-1.79830600	2.96528900
P	2.38958100	0.33262800	0.01745900
C	2.97329700	1.09361600	1.69663800
C	3.67897400	-0.95643500	-0.61140000
C	4.99888900	-0.30497000	-1.07477100
C	1.26005200	2.54709900	-1.13070700
C	2.52191100	1.71902100	-1.21317500
C	2.59950000	0.15682200	2.86145500
C	1.26212300	3.86161700	-1.62225000
C	2.25673500	2.44235300	1.91334500
C	4.48987600	1.36319700	1.72856300
C	3.05847200	-1.65837200	-1.83316700
C	3.95432300	-2.01976700	0.46712100
H	4.84054200	0.42012400	-1.88660900
H	5.55128800	0.19204400	-0.27062400
H	5.65012600	-1.09953500	-1.47657000
H	3.42594000	2.32930400	-1.05580900
H	2.62893700	1.24401800	-2.20442100
H	1.50877300	0.04739900	2.95517700
H	3.04513700	-0.84354100	2.77481200
H	2.96446100	0.60122900	3.80232500
H	2.16488900	4.25777300	-2.09626900
H	2.53814800	3.19729100	1.16583100
H	1.16314000	2.34782800	1.89949500
H	2.55512500	2.82645600	2.90319200
H	5.08895900	0.44290000	1.73939700
H	4.82393800	1.99639700	0.89311900
H	4.72112900	1.90923700	2.65814800

H	2.18461100	-2.25875600	-1.55351000
H	2.77271400	-0.95031100	-2.62646300
H	3.80879300	-2.34149300	-2.26491700
H	4.50909000	-1.61882800	1.32651000
H	3.02455700	-2.48129300	0.83442700
H	4.57062600	-2.82234300	0.02857900
C	-0.42547800	-3.91943200	-1.92002300
C	-0.25780900	-2.58866300	-1.53310900
H	-0.54618400	-4.15895400	-2.97823500
H	0.09921000	0.47974500	1.42785100
H	-4.14193100	-1.42912000	-2.45360100
C	-0.21966400	-1.49340300	-2.56714400
H	-1.19067400	-1.36391900	-3.06465100
H	0.07706200	-0.49818500	-2.15258700
H	0.52780400	-1.71743200	-3.34278000
C	0.18784200	-2.80983400	2.14989500
H	-0.75720900	-2.74815700	2.71327600
H	0.67677700	-1.82867200	2.19436800
H	0.81773700	-3.55586000	2.65574500

XYZ Coordinates for Optimized Structure of 5^{+}

Ir	0.12136400	-0.11324900	-0.20472500
P	-2.07057500	-1.10835100	-0.33826800
N	-0.13521600	1.12872000	1.61859800
C	0.59151300	-1.87581300	0.69395600
C	-0.65442700	2.38924900	1.51752300
C	1.84871600	-2.04598400	1.33110100
C	-1.11147200	2.83911400	0.18565600
C	-0.73952400	3.22070800	2.64949900
H	-1.11287400	4.23921100	2.54020000
C	-3.82100300	-2.30639200	-2.30431900
H	-3.22094300	-3.22799700	-2.30592900
H	-4.26912100	-2.21408900	-3.30787100
H	-4.64380200	-2.43018100	-1.59128700
C	-1.88710300	-0.98313200	-3.14389900
H	-1.27256300	-0.07724500	-3.06364500
H	-2.39025000	-0.97698800	-4.12542200
H	-1.21448400	-1.85447500	-3.12394400
C	-0.32664900	2.75579200	3.89527100
H	-0.38857800	3.39979300	4.77448100
C	-2.65964800	-1.42961100	2.37693000
H	-2.49577600	-2.51607700	2.35453000
H	-3.31651500	-1.21079600	3.23560000
H	-1.69238900	-0.94493500	2.56030500
C	-0.30622300	-2.97113200	0.67850000

C	-4.63586700	-1.71649800	0.88127000
H	-5.26443100	-1.30760200	0.07852700
H	-5.22826300	-1.67040500	1.81082500
H	-4.44554000	-2.78021900	0.67458100
C	0.25641500	0.68367600	2.83468600
H	0.63915400	-0.33992100	2.85749900
C	0.17263700	1.45285300	3.99171500
H	0.49938800	1.03378600	4.94435100
C	-2.09152700	3.84321300	0.05218900
H	-2.54792500	4.28073400	0.94232600
C	-3.34400400	-0.90663000	1.09683900
C	-2.96586300	-1.04755100	-2.04500200
C	2.13212600	-3.23180900	2.03023600
H	3.10197300	-3.34482400	2.52334700
C	-2.51859500	4.26812000	-1.20759600
H	-3.27946800	5.04745700	-1.28367800
C	-1.54369400	-2.88373900	-0.17803700
H	-2.36008700	-3.52675400	0.18395300
H	-1.29890700	-3.22023900	-1.20097600
C	-1.01994200	2.68834400	-2.25789700
H	-0.57803600	2.24852200	-3.15431800
C	2.91142400	-0.98082700	1.18257400
H	3.92210600	-1.41593300	1.13337300
H	2.91212700	-0.27302500	2.03134600
C	-1.97820900	3.69981400	-2.36834100
H	-2.30219100	4.04413200	-3.35246000
C	-0.60318600	2.25073700	-0.99429500
H	0.35980900	1.65089400	-0.98316900
C	2.64692500	-0.31795300	-3.13512100
H	3.00315700	-0.91998900	-3.98738200
H	2.96853700	0.71787100	-3.30748300
H	1.54749200	-0.34843800	-3.13944600
C	1.19987000	-4.26955100	2.08203100
H	1.42490600	-5.18498400	2.63269300
C	2.77669000	-2.39487800	-1.74376800
H	1.68512600	-2.50278300	-1.70136800
H	3.20627600	-2.91226900	-0.87409300
H	3.13663600	-2.91086800	-2.64945400
C	3.48219900	1.67721800	-0.05511100
C	-3.70707800	0.57523500	1.30128100
H	-2.83066500	1.17026800	1.58315300
H	-4.43622600	0.64754600	2.12592900
H	-4.16473700	1.03287400	0.41461000
C	2.71242600	2.53123200	0.96962300
H	2.54715100	2.00965700	1.92389200
H	1.74394600	2.86919100	0.57952700

H	3.31121300	3.43089600	1.18898300
C	3.21882500	-0.91971800	-1.83539700
C	4.89250200	1.41878900	0.51637600
H	5.38626600	2.39376800	0.66592600
H	5.53330600	0.82679200	-0.14624200
H	4.85702400	0.92358000	1.49802700
C	-3.84975300	0.20980900	-2.14297200
H	-4.73314200	0.15067600	-1.49201600
H	-4.21695100	0.30544800	-3.17854100
H	-3.29582700	1.12849300	-1.90182800
C	-0.00641500	-4.14360700	1.38697200
H	-0.71917900	-4.97323700	1.37914900
C	3.57815500	2.48174900	-1.36494700
H	2.59078100	2.65637500	-1.82075100
H	4.22694200	2.00552900	-2.11189800
H	4.01205800	3.47021700	-1.13981300
C	4.75877100	-0.89710800	-1.88464700
H	5.08527800	-1.55279100	-2.70867800
H	5.21574800	-1.28938700	-0.96332400
H	5.16951000	0.10096700	-2.08720800
P	2.50444500	0.03399300	-0.32155600
H	0.27231100	-0.90600400	-1.56115200

8. Crystallographic Details

[(^{tBu4}PCP)Ir(H)(py)][BAr$^{F}_{4}$] (3^{+}). The sample was submitted by Andrew Walden (research group of Miller, Department of Chemistry, the University of North Carolina at Chapel Hill). A block crystal (approximate dimensions 0.228 x 0.108 x 0.052 mm^3) was placed onto the tip of MiTeGen and mounted on a Bruker SMART Apex II diffractometer and measured at 100 K.

Data collection

A preliminary set of cell constants was calculated from reflections harvested from three sets of 12 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 134 reflections. The data collection was carried out using Cu Kα radiation (graphite monochromator) with a frame time of 10 seconds and a detector distance of 4.0 cm. A randomly oriented region of reciprocal space was surveyed to achieve complete data with a redundancy of 4. Sections of frames were collected with 0.50º steps in ω and ϕ scans. Data to a resolution of 0.84 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 8727 strong reflections from the actual data collection after integration (SAINT).[18] The intensity data were corrected for absorption (SADABS).[19] Please refer to Table S1 for additional crystal and refinement information.

Structure solution and refinement

The space group $P4_32_12$ was determined based on intensity statistics and systematic absences. The structure was solved using Superflip[20] and refined (full-matrix-least squares) using the Oxford University Crystals for Windows system.[21] The charge-flipping solution provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were

performed, which located the remaining non-hydrogen atoms. Structure $\mathbf{3}^{+}$ exhibits whole molecule disorder on the Ir complex, which was resolved successfully. The overall geometry of the complex enables the whole molecule disorder to occur, as the two-part disorder, approximately 3:1 ratio, were upside-down against each other. Additional two-part disorder on the BAr^{F}_{4} was also observed and resolved successfully. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms. The final full matrix least squares refinement converged to R1 = 0.0307 and wR2 = 0.0729 (F^2, all data).

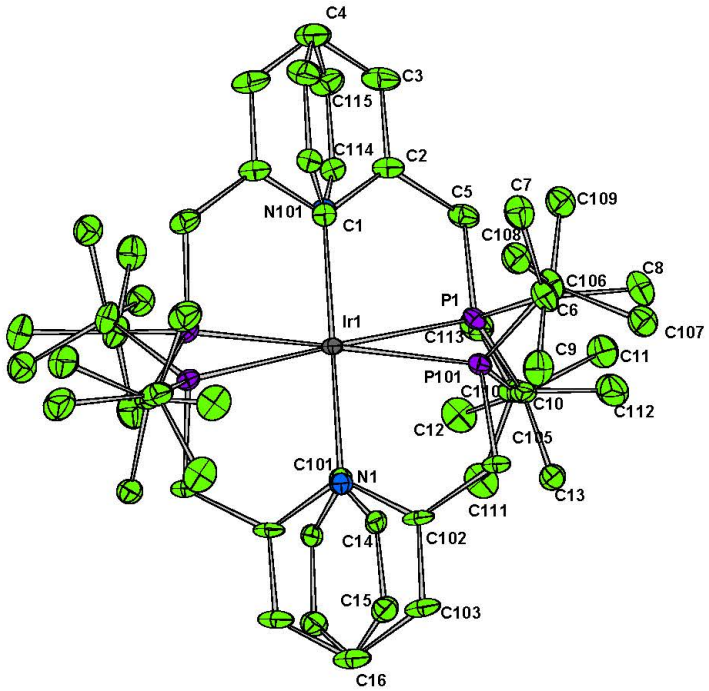


Figure S36. Molecular structure with labels on the asymmetric unit. BAr^{F}_{4} ions omitted for clarity.

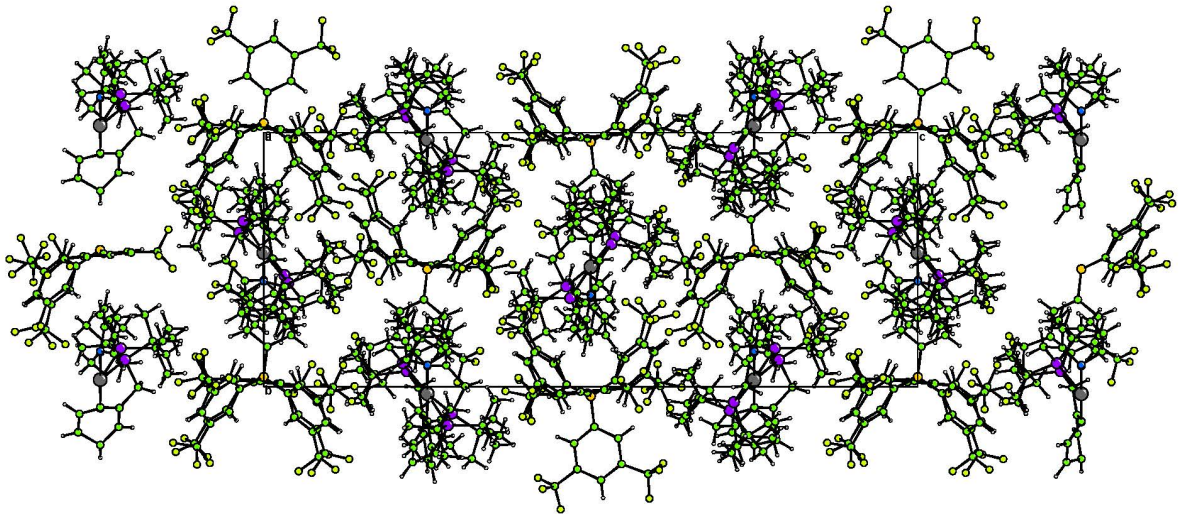


Figure S37. Cell plot, viewed along a- axis

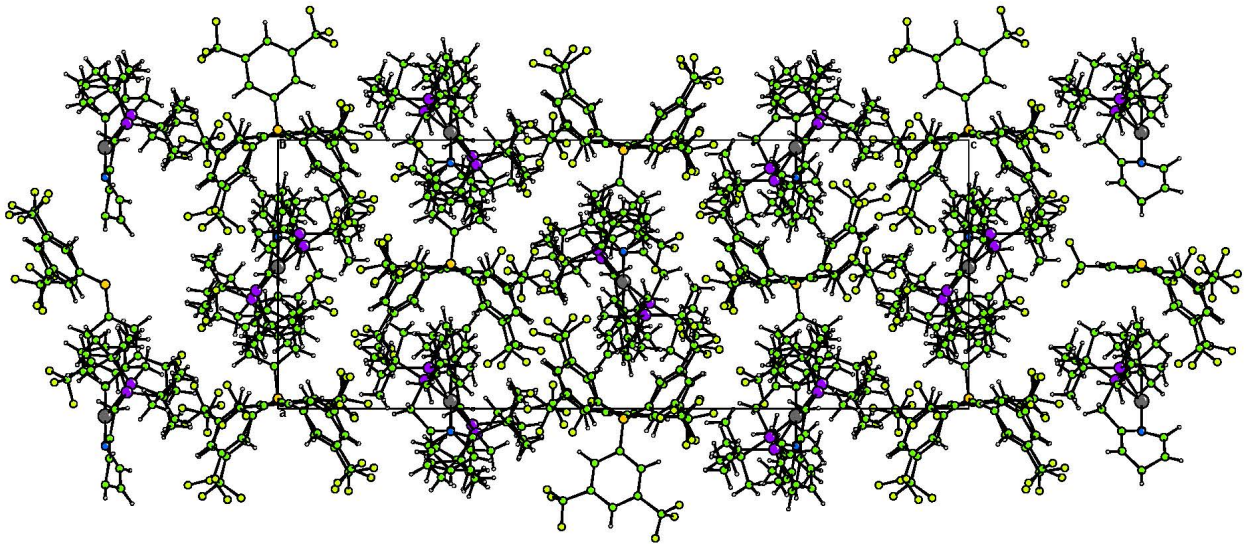


Figure S38. Cell plot, viewed along b- axis

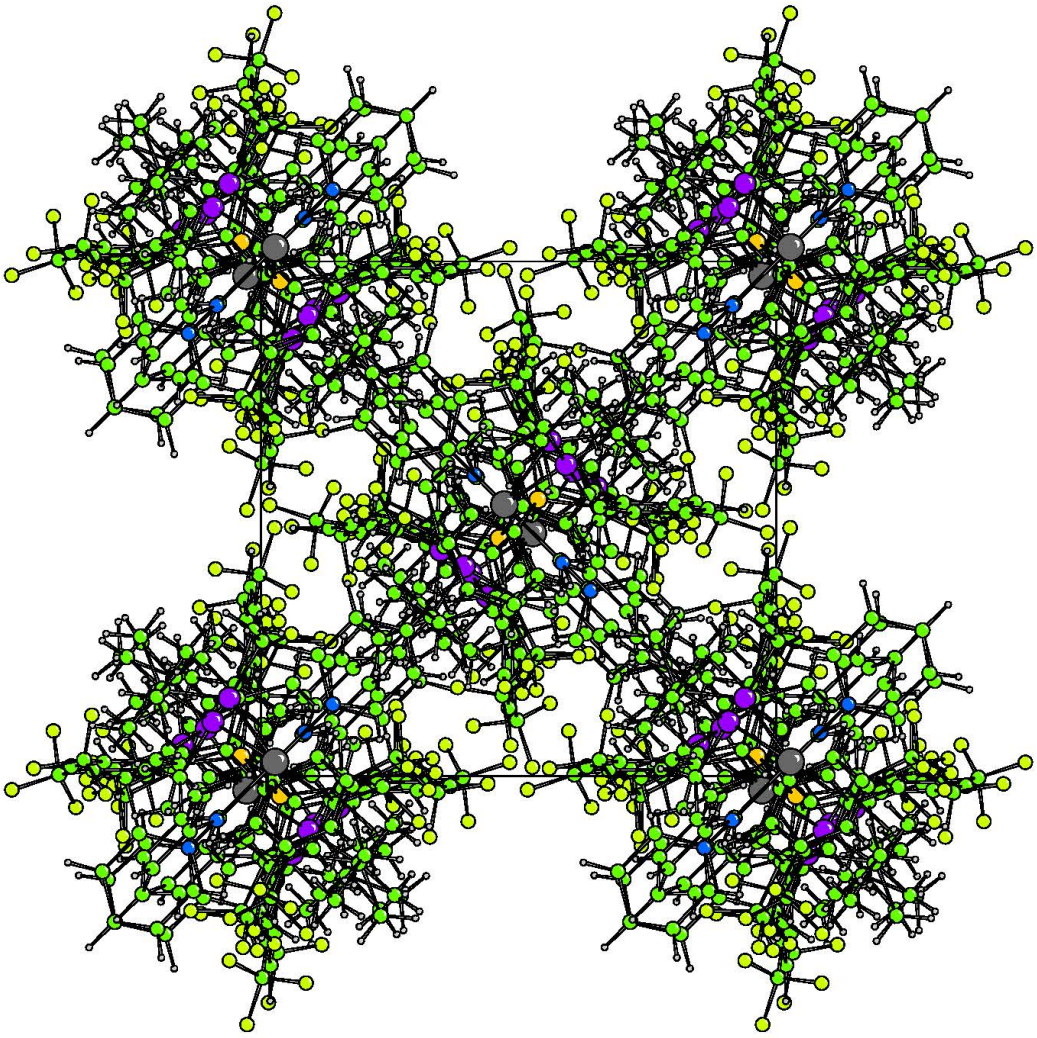


Figure S39. Cell plot, viewed along c- axis

Table S1. Crystal data and structure refinement for [(^{tBu4}PCP)Ir(H)(py)][BAr$^{F}_{4}$] (**3**$^{+}$).

Empirical formula	C61.00 H60.00 B1 F24 Ir1 N1 P2	
Formula weight	1528.08	
Crystal color, shape, size	block, 0.228 x 0.108 x 0.052 mm^3	
Temperature	100 K	
Wavelength	1.54180 Å	
Crystal system, space group	Tetragonal, $P4_32_12$	
Unit cell dimensions	a = 13.4887(4) Å	α= 90°.
	b = 13.4887(4) Å	β= 90°.
	c = 34.6571(12) Å	γ = 90°.
Volume	6305.7(4) Å^3	
Z	4	
Density (calculated)	1.610 Mg/m^3	
Absorption coefficient	5.573 mm^{-1}	

F(000)	3044.000
Data collection	
Diffractometer	Bruker Apex Kappa Duo, Bruker
Theta range for data collection	3.516 to 70.181°.
Index ranges	-15<=h<=12, -14<=k<=15, -37<=l<=42
Reflections collected	30251
Independent reflections	5711 [R(int) = 0.044]
Observed Reflections	5398
Completeness to theta = 59.654°	99.5 %
Solution and Refinement	
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.75 and 0.55
Solution	Charge Flipping
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = [\sigma^2 Fo^2 + AP^2 + BP]^{-1}$, with
	$P = (Fo^2 + 2\,Fc^2)/3$, A = 0.035, B = 11.510
Data / restraints / parameters	5686 / 529 / 668
Goodness-of-fit on F^2	0.9920
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0713
R indices (all data)	R1 = 0.0330, wR2 = 0.0729
Largest diff. peak and hole	0.57 and -0.42 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)

for $\mathbf{3}^+$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir1	5277(1)	5277(1)	5000	22
P1	6513(1)	4389(1)	5314(1)	29
P101	6055(5)	4075(5)	5376(1)	28
F34	6182(3)	1723(3)	6458(1)	83
F36	4651(3)	1991(2)	6394(1)	60
F37	5150(3)	598(2)	6604(1)	91
F45	5878(3)	977(3)	8237(1)	92
F46	4393(3)	1415(3)	8307(1)	83
F47	4734(3)	173(2)	7961(1)	83
F56	5851(4)	7029(4)	8714(2)	75
F57	5126(5)	8000(4)	8325(2)	65
F58	4424(4)	7568(4)	8846(2)	72
F60	2327(7)	3834(6)	8488(3)	79
F61	1671(5)	4658(6)	8033(2)	84
F62	1739(4)	5266(6)	8594(2)	90
F156	5018(13)	7207(9)	8887(3)	88
F157	5593(9)	7764(10)	8363(4)	67
F158	4112(9)	8065(8)	8520(4)	86
F160	2382(14)	3645(9)	8408(5)	64
F161	1612(10)	4937(15)	8232(4)	93
F162	2153(8)	4824(10)	8804(3)	61
N1	4146(2)	4146(2)	5000	32
N101	6396(4)	6396(4)	5000	36
C1	6360(2)	6360(2)	5000	37
C2	7356(3)	6112(3)	5065(2)	40
C3	8072(3)	6854(4)	5062(3)	59
C4	7833(3)	7833(3)	5000(1)	67
C5	7622(5)	5030(5)	5138(2)	44
C6	6522(3)	4560(3)	5849(1)	50
C7	6797(6)	5624(5)	5957(2)	56
C8	7285(5)	3858(6)	6045(2)	62
C9	5501(5)	4338(5)	6023(1)	57
C10	6664(3)	3076(3)	5155(1)	37
C11	7712(4)	2670(4)	5260(2)	59
C12	6539(5)	2983(4)	4720(2)	58
C13	5887(4)	2394(4)	5348(2)	43

C14	3932(4)	3619(4)	4682(1)	34
C15	3207(5)	2899(4)	4662(1)	50
C16	2706(2)	2706(2)	5000(1)	56
C17	5231(3)	3423(3)	7447(1)	22
C18	5313(4)	2973(3)	7082(1)	24
C19	5277(3)	1962(3)	7028(1)	28
C20	5189(4)	1327(3)	7344(1)	30
C21	5116(3)	1750(3)	7706(1)	28
C22	5129(3)	2767(3)	7756(1)	23
C23	5317(2)	1572(2)	6624(1)	42
C24	5030(2)	1084(2)	8051(1)	40
C25	4747(2)	5078(2)	7870(1)	24
C26	5090(6)	5912(8)	8073(4)	23
C27	4525(4)	6355(4)	8359(2)	28
C28	3587(8)	6011(11)	8445(5)	39
C29	3233(4)	5196(7)	8248(2)	36
C30	3802(7)	4736(9)	7965(4)	25
C31	4979(3)	7232(3)	8560(1)	36
C32	2249(3)	4744(4)	8340(2)	59
C101	4189(4)	4189(4)	5000	30
C102	4165(10)	3464(10)	5291(4)	38
C103	3425(11)	2730(11)	5283(4)	48
C105	4980(13)	3432(14)	5580(6)	34
C106	6790(8)	4507(9)	5802(2)	45
C107	6919(16)	3668(15)	6101(4)	52
C108	6274(13)	5379(14)	6006(5)	52
C109	7835(9)	4857(15)	5680(5)	52
C110	6697(8)	3095(8)	5086(3)	47
C111	5944(13)	2448(12)	4864(5)	54
C112	7313(15)	2403(12)	5348(6)	70
C113	7408(13)	3558(14)	4788(5)	61
C114	6305(9)	7227(9)	5210(5)	47
C115	7005(11)	7969(10)	5226(6)	66
C126	5020(20)	5993(17)	8027(9)	28
C127	4462(10)	6444(9)	8318(4)	31
C128	3640(20)	5980(20)	8470(9)	36
C129	3339(9)	5091(13)	8314(4)	32
C130	3898(19)	4629(16)	8025(9)	23
C131	4793(7)	7364(6)	8521(3)	38
C132	2377(7)	4628(8)	8438(3)	47
B1	5378(3)	4622(3)	7500	20

Table S3. Bond lengths [Å] and angles [°] for $\mathbf{3}^{+}$.

Ir1-P1#1	2.3235(17)	Ir1-P1	2.3235(17)
Ir1-N1	2.157(4)	Ir1-C1	2.066(5)
Ir1-P101#1	2.329(5)	Ir1-P101	2.329(5)
Ir1-N101	2.135(7)	Ir1-C101	2.074(7)
P1-C5	1.832(7)	P1-C6	1.868(4)
P1-C10	1.867(4)	P101-C105	1.832(19)
P101-C106	1.873(6)	P101-C110	1.871(7)
F34-C23	1.317(4)	F36-C23	1.326(4)
F37-C23	1.336(4)	F45-C24	1.320(4)
F46-C24	1.313(4)	F47-C24	1.329(4)
F56-C31	1.318(5)	F57-C31	1.334(5)
F58-C31	1.320(5)	F60-C32	1.334(6)
F61-C32	1.323(5)	F62-C32	1.320(5)
F156-C131	1.323(7)	F157-C131	1.325(7)
F158-C131	1.318(7)	F160-C132	1.330(7)
F161-C132	1.323(7)	F162-C132	1.331(6)
N1-C14#1	1.343(4)	N1-C14	1.343(4)
N101-C114#1	1.341(5)	N101-C114	1.341(5)
C1-C2#1	1.403(4)	C1-C2	1.403(4)
C2-C3	1.391(6)	C2-C5	1.524(8)
C3-C4	1.376(5)	C3-H31	0.950
C4-H41	0.950	C4-C115#1	1.376(5)
C4-C115	1.376(5)	C4-H42	0.950
C5-H51	0.950	C5-H52	0.950
C6-C7	1.529(6)	C6-C8	1.554(6)
C6-C9	1.533(5)	C7-H71	0.950
C7-H72	0.950	C7-H73	0.950
C8-H81	0.950	C8-H82	0.950
C8-H83	0.950	C9-H91	0.950
C9-H92	0.950	C9-H93	0.950
C10-C11	1.559(5)	C10-C12	1.520(5)
C10-C13	1.546(5)	C11-H111	0.950
C11-H112	0.950	C11-H113	0.950
C12-H121	0.950	C12-H122	0.950
C12-H123	0.950	C13-H131	0.950
C13-H132	0.950	C13-H133	0.950
C14-C15	1.380(6)	C14-H141	0.950
C15-C16	1.378(4)	C15-H151	0.950
C16-H161	0.950	C16-C103#1	1.380(6)
C16-C103	1.380(6)	C16-H162	0.950
C17-C18	1.407(5)	C17-C22	1.397(6)

C17-B1	1.641(5)	C18-C19	1.377(5)
C18-H181	0.950	C19-C20	1.395(6)
C19-C23	1.500(4)	C20-C21	1.379(6)
C20-H201	0.950	C21-C22	1.383(6)
C21-C24	1.502(4)	C22-H221	0.950
C25-C26	1.404(4)	C25-C30	1.395(5)
C25-B1	1.658(4)	C25-C126	1.399(6)
C25-C130	1.403(6)	C25-B1	1.658(4)
C26-C27	1.386(4)	C26-H261	0.950
C27-C28	1.381(5)	C27-C31	1.505(4)
C28-C29	1.379(5)	C28-H281	0.950
C29-C30	1.392(5)	C29-C32	1.496(4)
C30-H301	0.950	C101-C102#1	1.406(5)
C101-C102	1.406(5)	C102-C103	1.406(8)
C102-C105	1.49(2)	C103-H1031	0.950
C105-H1051	0.950	C105-H1052	0.950
C106-C107	1.543(7)	C106-C108	1.538(7)
C106-C109	1.546(7)	C107-H1071	0.950
C107-H1072	0.950	C107-H1073	0.950
C108-H1081	0.950	C108-H1082	0.950
C108-H1083	0.950	C109-H1091	0.950
C109-H1092	0.950	C109-H1093	0.950
C110-C111	1.545(7)	C110-C112	1.543(7)
C110-C113	1.542(7)	C111-H1111	0.950
C111-H1112	0.950	C111-H1113	0.950
C112-H1121	0.950	C112-H1122	0.950
C112-H1123	0.950	C113-H1131	0.950
C113-H1132	0.950	C113-H1133	0.950
C114-C115	1.376(8)	C114-H1141	0.950
C115-H1151	0.950	C126-C127	1.397(6)
C126-H1261	0.950	C127-C128	1.383(6)
C127-C131	1.495(6)	C128-C129	1.376(6)
C128-H1281	0.950	C129-C130	1.399(6)
C129-C132	1.504(6)	C130-H1301	0.950

P1#1-Ir1-P1	163.55(10)	P1#1-Ir1-N1	98.22(5)
P1-Ir1-N1	98.22(5)	P1#1-Ir1-C1	81.78(5)
P1-Ir1-C1	81.78(5)	N1-Ir1-C1	179.994
P101#1-Ir1-P101	160.0(3)	P101#1-Ir1-N101	99.99(17)
P101-Ir1-N101	99.99(17)	P101#1-Ir1-C101	80.01(17)
P101-Ir1-C101	80.01(17)	N101-Ir1-C101	179.994

Ir1-P1-C5	100.7(2)	Ir1-P1-C6	113.98(13)
C5-P1-C6	105.5(3)	Ir1-P1-C10	115.38(13)
C5-P1-C10	105.1(3)	C6-P1-C10	114.21(18)
Ir1-P101-C105	100.8(7)	Ir1-P101-C106	117.6(4)
C105-P101-C106	105.1(7)	Ir1-P101-C110	113.6(4)
C105-P101-C110	103.9(7)	C106-P101-C110	113.5(6)
Ir1-N1-C14#1	121.77(5)	Ir1-N1-C14	121.77(5)
C14#1-N1-C14	116.46(9)	Ir1-N101-C114#1	121.75(5)
Ir1-N101-C114	121.75(5)	C114#1-N101-C114	116.49(10)
Ir1-C1-C2#1	120.57(5)	Ir1-C1-C2	120.57(5)
C2#1-C1-C2	118.85(9)	C1-C2-C3	119.47(8)
C1-C2-C5	118.7(3)	C3-C2-C5	121.8(3)
C2-C3-C4	121.98(8)	C2-C3-H31	118.6
C4-C3-H31	119.4	C3-C4-C3#1	118.25(9)
C3-C4-H41	120.9	C3#1-C4-H41	120.9
C115#1-C4-C115	122.60(10)	C115#1-C4-H42	118.7
C115-C4-H42	118.7	C2-C5-P1	108.4(4)
C2-C5-H51	110.3	P1-C5-H51	110.5
C2-C5-H52	109.2	P1-C5-H52	108.9
H51-C5-H52	109.5	P1-C6-C7	111.12(6)
P1-C6-C8	111.27(6)	C7-C6-C8	107.71(7)
P1-C6-C9	111.14(6)	C7-C6-C9	107.73(7)
C8-C6-C9	107.70(7)	C6-C7-H71	109.4
C6-C7-H72	109.2	H71-C7-H72	109.5
C6-C7-H73	109.7	H71-C7-H73	109.5
H72-C7-H73	109.5	C6-C8-H81	109.1
C6-C8-H82	109.9	H81-C8-H82	109.5
C6-C8-H83	109.5	H81-C8-H83	109.5
H82-C8-H83	109.5	C6-C9-H91	109.1
C6-C9-H92	109.3	H91-C9-H92	109.5
C6-C9-H93	110.0	H91-C9-H93	109.5
H92-C9-H93	109.5	P1-C10-C11	111.26(6)
P1-C10-C12	111.06(6)	C11-C10-C12	107.71(7)
P1-C10-C13	111.21(6)	C11-C10-C13	107.71(7)
C12-C10-C13	107.71(7)	C10-C11-H111	109.4
C10-C11-H112	109.2	H111-C11-H112	109.5
C10-C11-H113	109.8	H111-C11-H113	109.5
H112-C11-H113	109.5	C10-C12-H121	108.7
C10-C12-H122	109.7	H121-C12-H122	109.5
C10-C12-H123	110.0	H121-C12-H123	109.5
H122-C12-H123	109.5	C10-C13-H131	109.4
C10-C13-H132	109.5	H131-C13-H132	109.5
C10-C13-H133	109.4	H131-C13-H133	109.5

H132-C13-H133	109.5	N1-C14-C15	124.52(8)
N1-C14-H141	117.2	C15-C14-H141	118.3
C14-C15-C16	115.93(8)	C14-C15-H151	122.1
C16-C15-H151	122.0	C15-C16-C15#1	122.58(9)
C15-C16-H161	118.7	C15#1-C16-H161	118.7
C103#1-C16-C103	118.20(10)	C103#1-C16-H162	120.9
C103-C16-H162	120.9	C18-C17-C22	115.1(4)
C18-C17-B1	121.1(3)	C22-C17-B1	123.4(3)
C17-C18-C19	123.0(4)	C17-C18-H181	118.4
C19-C18-H181	118.6	C18-C19-C20	120.4(4)
C18-C19-C23	118.1(3)	C20-C19-C23	121.5(3)
C19-C20-C21	117.7(4)	C19-C20-H201	121.4
C21-C20-H201	121.0	C20-C21-C22	121.6(4)
C20-C21-C24	118.8(3)	C22-C21-C24	119.5(3)
C17-C22-C21	122.1(4)	C17-C22-H221	119.0
C21-C22-H221	118.9	C19-C23-F37	112.66(9)
C19-C23-F36	112.80(9)	F37-C23-F36	106.01(9)
C19-C23-F34	112.70(9)	F37-C23-F34	106.22(9)
F36-C23-F34	105.88(9)	C21-C24-F47	112.80(9)
C21-C24-F45	112.75(9)	F47-C24-F45	105.94(9)
C21-C24-F46	112.70(9)	F47-C24-F46	106.06(9)
F45-C24-F46	106.01(9)	C26-C25-C30	116.61(6)
C26-C25-B1	121.0(2)	C30-C25-B1	121.9(2)
C126-C25-C130	116.58(7)	C126-C25-B1	119.5(4)
C130-C25-B1	123.7(4)	C25-C26-C27	121.49(6)
C25-C26-H261	119.1	C27-C26-H261	119.4
C26-C27-C28	120.93(6)	C26-C27-C31	116.6(3)
C28-C27-C31	122.5(3)	C27-C28-C29	118.52(6)
C27-C28-H281	120.8	C29-C28-H281	120.6
C28-C29-C30	120.93(6)	C28-C29-C32	121.8(3)
C30-C29-C32	117.2(3)	C25-C30-C29	121.48(6)
C25-C30-H301	118.9	C29-C30-H301	119.6
C27-C31-F57	112.76(6)	C27-C31-F58	112.75(6)
F57-C31-F58	106.00(7)	C27-C31-F56	112.76(6)
F57-C31-F56	106.00(7)	F58-C31-F56	105.99(7)
C29-C32-F60	112.74(6)	C29-C32-F61	112.79(6)
F60-C32-F61	105.97(7)	C29-C32-F62	112.74(6)
F60-C32-F62	106.03(7)	F61-C32-F62	105.97(7)
Ir1-C101-C102#1	120.57(5)	Ir1-C101-C102	120.57(5)
C102#1-C101-C102	118.87(10)	C101-C102-C103	119.47(8)
C101-C102-C105	119.1(8)	C103-C102-C105	121.2(8)
C102-C103-C16	121.99(8)	C102-C103-H1031	118.6
C16-C103-H1031	119.2	C102-C105-P101	108.2(12)

C102-C105-H1051	112.4	P101-C105-H1051	110.0
C102-C105-H1052	107.4	P101-C105-H1052	109.3
H1051-C105-H1052	109.5	P101-C106-C107	111.19(7)
P101-C106-C108	111.16(7)	C107-C106-C108	107.71(7)
P101-C106-C109	111.19(7)	C107-C106-C109	107.71(7)
C108-C106-C109	107.71(7)	C106-C107-H1071	109.5
C106-C107-H1072	110.2	H1071-C107-H1072	109.5
C106-C107-H1073	108.7	H1071-C107-H1073	109.5
H1072-C107-H1073	109.5	C106-C108-H1081	108.1
C106-C108-H1082	109.8	H1081-C108-H1082	109.5
C106-C108-H1083	110.5	H1081-C108-H1083	109.5
H1082-C108-H1083	109.5	C106-C109-H1091	109.9
C106-C109-H1092	109.0	H1091-C109-H1092	109.5
C106-C109-H1093	109.4	H1091-C109-H1093	109.5
H1092-C109-H1093	109.5	P101-C110-C111	111.17(7)
P101-C110-C112	111.19(7)	C111-C110-C112	107.71(7)
P101-C110-C113	111.18(7)	C111-C110-C113	107.70(7)
C112-C110-C113	107.71(7)	C110-C111-H1111	108.9
C110-C111-H1112	108.6	H1111-C111-H1112	109.5
C110-C111-H1113	110.9	H1111-C111-H1113	109.5
H1112-C111-H1113	109.5	C110-C112-H1121	108.4
C110-C112-H1122	108.2	H1121-C112-H1122	109.5
C110-C112-H1123	111.7	H1121-C112-H1123	109.5
H1122-C112-H1123	109.5	C110-C113-H1131	110.3
C110-C113-H1132	110.7	H1131-C113-H1132	109.5
C110-C113-H1133	107.5	H1131-C113-H1133	109.5
H1132-C113-H1133	109.5	N101-C114-C115	124.52(8)
N101-C114-H1141	117.2	C115-C114-H1141	118.3
C114-C115-C4	115.92(8)	C114-C115-H1151	122.1
C4-C115-H1151	122.0	C25-C126-C127	121.46(7)
C25-C126-H1261	118.3	C127-C126-H1261	120.1
C126-C127-C128	120.93(7)	C126-C127-C131	122.6(7)
C128-C127-C131	115.8(7)	C127-C128-C129	118.51(7)
C127-C128-H1281	120.0	C129-C128-H1281	121.3
C128-C129-C130	120.91(7)	C128-C129-C132	120.0(8)
C130-C129-C132	119.0(8)	C25-C130-C129	121.45(7)
C25-C130-H1301	119.6	C129-C130-H1301	119.0
C127-C131-F157	112.75(6)	C127-C131-F156	112.76(6)
F157-C131-F156	106.00(7)	C127-C131-F158	112.75(6)
F157-C131-F158	106.01(7)	F156-C131-F158	105.98(7)
C129-C132-F162	112.76(6)	C129-C132-F160	112.76(6)
F162-C132-F160	106.00(7)	C129-C132-F161	112.76(6)
F162-C132-F161	106.00(7)	F160-C132-F161	105.98(7)

C25-B1-C25#2	102.7(4)	C25-B1-C17	112.99(18)
C25#2-B1-C17	111.98(18)	C25-B1-C17#2	111.98(18)
C25#2-B1-C17#2	112.99(18)	C17-B1-C17#2	104.5(4)

Symmetry transformations used to generate equivalent atoms:

#1 y,x,-z+1 #2 -y+1,-x+1,-z+3/2

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $\mathbf{3}^+$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir1	19(1)	19(1)	27(1)	-1(1)	1(1)	-3(1)
P1	20(1)	36(1)	32(1)	-2(1)	0(1)	1(1)
P101	21(2)	32(2)	33(2)	-2(2)	3(2)	0(2)
F34	74(3)	117(4)	59(2)	-34(2)	28(2)	2(3)
F36	88(3)	60(2)	32(2)	-10(1)	-14(2)	2(2)
F37	196(5)	29(2)	48(2)	-17(1)	6(3)	-16(3)
F45	107(4)	93(4)	77(3)	41(3)	-51(3)	-9(3)
F46	129(4)	54(3)	68(2)	29(2)	43(3)	12(2)
F47	169(4)	30(2)	50(2)	14(2)	-22(2)	-31(3)
F56	73(4)	45(3)	107(5)	-32(3)	-41(4)	1(3)
F57	97(5)	39(3)	58(3)	5(2)	-10(4)	-22(3)
F58	75(4)	69(4)	74(4)	-48(3)	32(3)	-17(3)
F60	64(4)	77(4)	96(5)	2(4)	30(4)	-26(3)
F61	34(3)	113(6)	105(6)	-21(5)	3(4)	-19(3)
F62	58(4)	100(6)	111(4)	-40(4)	40(4)	-17(4)
F156	115(10)	69(7)	79(8)	-19(6)	-30(7)	-18(7)
F157	71(7)	50(6)	79(6)	-40(5)	4(5)	-21(5)
F158	84(7)	62(6)	112(7)	-49(6)	8(6)	1(5)
F160	56(5)	61(6)	75(6)	-31(5)	36(5)	-29(5)
F161	27(6)	144(10)	107(10)	19(9)	-13(8)	-15(7)
F162	53(8)	82(9)	49(6)	-6(7)	36(5)	-23(7)
N1	30(2)	30(2)	38(4)	0(3)	0(3)	-2(3)
N101	34(6)	34(6)	39(8)	3(6)	-3(6)	-4(8)
C1	35(3)	35(3)	40(4)	3(3)	-3(3)	-3(4)
C2	34(4)	36(4)	49(5)	-11(3)	10(3)	-10(3)
C3	35(4)	62(6)	80(7)	-13(5)	12(4)	-17(3)
C4	61(4)	61(4)	79(6)	3(4)	-3(4)	-28(4)
C5	28(4)	46(5)	59(4)	-10(3)	4(3)	-1(3)
C6	48(5)	63(5)	39(3)	-8(3)	-11(3)	4(4)
C7	65(6)	60(5)	45(4)	-9(4)	-5(4)	9(4)
C8	56(6)	75(6)	55(4)	0(4)	-19(4)	9(4)
C9	64(6)	71(5)	37(3)	3(3)	10(3)	9(4)
C10	25(4)	31(4)	56(4)	0(3)	1(3)	-2(3)
C11	34(6)	56(6)	86(6)	-1(5)	5(4)	18(4)
C12	60(6)	67(6)	46(4)	-22(4)	9(4)	11(4)
C13	28(4)	40(4)	62(4)	9(3)	3(3)	3(3)
C14	29(4)	25(3)	47(3)	1(3)	-8(3)	4(3)

C15	43(5)	31(4)	77(5)	-2(4)	-16(4)	1(4)
C16	31(2)	31(2)	105(6)	-13(4)	13(4)	-9(3)
C17	16(2)	21(2)	29(2)	-2(2)	-2(2)	4(2)
C18	22(2)	23(2)	25(2)	-2(2)	2(2)	-3(2)
C19	25(2)	24(2)	36(2)	-4(2)	6(2)	1(2)
C20	27(2)	16(2)	46(2)	-5(2)	-3(2)	2(2)
C21	28(3)	24(2)	33(2)	5(2)	-6(2)	-3(2)
C22	23(2)	23(2)	24(2)	-3(2)	-5(2)	3(2)
C23	47(3)	30(3)	48(3)	-11(2)	12(3)	0(3)
C24	61(4)	24(3)	35(3)	4(2)	-8(2)	-2(2)
C25	23(2)	20(2)	30(2)	-1(1)	-4(2)	2(2)
C26	27(4)	19(4)	23(4)	2(3)	2(4)	-1(3)
C27	34(4)	20(4)	31(3)	-4(3)	1(3)	2(3)
C28	40(4)	32(4)	46(4)	-12(4)	15(4)	8(4)
C29	28(4)	36(4)	45(4)	-3(4)	5(3)	-1(3)
C30	16(4)	25(4)	35(5)	4(4)	-2(4)	4(4)
C31	45(5)	29(4)	34(4)	-9(3)	4(3)	2(3)
C32	48(4)	64(4)	65(4)	1(4)	21(4)	-6(4)
C101	28(6)	28(6)	35(8)	0(6)	0(6)	0(8)
C102	30(6)	23(6)	61(6)	-9(6)	10(6)	-13(5)
C103	34(7)	29(7)	82(8)	-8(7)	18(7)	-12(6)
C105	27(7)	26(6)	47(6)	-6(6)	7(6)	-9(5)
C106	43(9)	57(9)	35(8)	-6(7)	-10(7)	9(7)
C107	56(6)	59(6)	41(5)	-3(5)	-3(5)	0(5)
C108	56(6)	59(6)	41(5)	-3(5)	-3(5)	0(5)
C109	56(6)	59(6)	41(5)	-3(5)	-3(5)	0(5)
C110	34(8)	31(8)	76(9)	-11(8)	3(8)	1(7)
C111	52(10)	66(10)	44(9)	-22(8)	12(8)	15(8)
C112	52(11)	60(10)	98(10)	-3(9)	-14(10)	7(9)
C113	46(9)	62(9)	76(9)	-7(9)	0(8)	2(8)
C114	40(8)	45(8)	55(9)	10(8)	-11(8)	-10(8)
C115	65(9)	63(7)	69(8)	-7(7)	-16(9)	-22(7)
C126	23(6)	25(6)	35(7)	1(6)	-2(5)	4(5)
C127	36(6)	22(6)	34(6)	-1(6)	8(6)	2(6)
C128	39(6)	29(6)	39(6)	-9(6)	13(6)	3(6)
C129	26(6)	34(7)	37(6)	6(6)	9(5)	-7(6)
C130	13(7)	25(8)	31(8)	-2(8)	-9(6)	5(6)
C131	45(6)	26(6)	43(6)	-12(5)	6(6)	1(5)
C132	38(6)	49(7)	55(7)	-6(7)	18(6)	-16(6)
B1	18(2)	18(2)	25(2)	4(2)	4(2)	0(2)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for $\mathbf{3}^+$.

	x	y	z	U(eq)
H31	8741	6679	5113	74
H41	8331	8331	5000	80
H42	8331	8331	5000	80
H51	8143	4985	5321	56
H52	7826	4734	4902	56
H71	6797	5691	6230	67
H72	7440	5770	5860	67
H73	6330	6071	5848	67
H81	7273	3966	6316	72
H82	7932	3991	5949	72
H83	7114	3189	5991	72
H91	5530	4434	6295	66
H92	5025	4776	5915	66
H93	5317	3673	5969	66
H111	7766	2001	5177	77
H112	7799	2703	5532	77
H113	8207	3058	5137	77
H121	6619	2307	4650	69
H122	7025	3373	4593	69
H123	5897	3202	4647	69
H131	5984	1732	5263	54
H132	5960	2424	5620	54
H133	5240	2608	5278	54
H141	4306	3759	4456	44
H151	3063	2556	4429	63
H161	2208	2208	5000	69
H162	2208	2208	5000	69
H181	5398	3387	6863	30
H201	5182	627	7313	37
H221	5071	3027	8010	28
H261	5729	6168	8016	28
H281	3208	6305	8646	48
H301	3546	4173	7834	33
H1031	3388	2273	5491	61
H1051	4797	3728	5818	43
H1052	5142	2755	5621	43
H1071	7303	3903	6312	63

H1072	6290	3453	6192	63
H1073	7252	3130	5981	63
H1081	6673	5575	6219	63
H1082	5640	5177	6096	63
H1083	6199	5923	5834	63
H1091	8199	5064	5901	63
H1092	7771	5396	5506	63
H1093	8174	4327	5557	63
H1111	6295	1969	4717	64
H1112	5531	2121	5046	64
H1113	5547	2842	4697	64
H1121	7631	1925	5189	86
H1122	7798	2792	5476	86
H1123	6910	2076	5533	86
H1131	7727	3053	4643	69
H1132	7894	3955	4912	69
H1133	7022	3960	4620	69
H1141	5714	7305	5355	56
H1151	6930	8531	5388	82
H1261	5574	6329	7919	33
H1281	3262	6296	8668	44
H1301	3691	4001	7931	31

Table S6. Torsion angles [°] for $\mathbf{3}^{+}$.

C1-Ir1-P1-C5	-24.6(2)	C1-Ir1-P1-C6	87.86(16)
C1-Ir1-P1-C10	-137.10(16)	P1-Ir1-N1-C14	-103.1(3)
P1-Ir1-C1-C2	17.5(3)	N1-Ir1-P1-C10	42.90(16)
N1-Ir1-P1-C5	155.4(2)	N1-Ir1-P1-C6	-92.14(16)
C6-P1-C5-C2	-87.8(5)	Ir1-P1-C6-C8	173.6(3)
C10-P1-C5-C2	151.2(4)	Ir1-P1-C6-C7	-66.4(4)
Ir1-P1-C5-C2	31.0(5)	C5-P1-C6-C9	163.2(4)
C10-P1-C6-C7	158.0(4)	C10-P1-C6-C8	38.0(4)
C10-P1-C6-C9	-82.0(4)	Ir1-P1-C10-C11	159.0(3)
Ir1-P1-C10-C12	39.0(4)	Ir1-P1-C10-C13	-81.0(3)
C5-P1-C10-C11	49.0(4)	C5-P1-C10-C12	-71.0(4)
C5-P1-C10-C13	169.1(4)	C6-P1-C10-C11	-66.1(4)
C6-P1-C10-C12	173.9(3)	Ir1-P1-C6-C9	53.6(4)
C5-P1-C6-C7	43.2(5)	C5-P1-C6-C8	-76.8(4)
C6-P1-C10-C13	54.0(4)	B1-C17-C18-C19	174.5(4)
C18-C17-C22-C21	0.4(6)	C22-C17-C18-C19	1.2(7)
C18-C17-B1-C25	151.7(4)	B1-C17-C22-C21	-172.7(4)
C22-C17-B1-C25	-35.6(5)	C17-C18-C19-C23	176.7(4)
C17-C18-C19-C20	-2.2(7)	C18-C19-C20-C21	1.6(7)
C18-C19-C23-F34	67.8(5)	C18-C19-C23-F36	-52.1(5)
C18-C19-C23-F37	-172.0(4)	C20-C19-C23-F34	-113.3(4)
C20-C19-C23-F36	126.9(4)	C20-C19-C23-F37	7.0(5)
C23-C19-C20-C21	-177.4(4)	C19-C20-C21-C22	0.0(7)
C19-C20-C21-C24	-179.4(4)	C24-C21-C22-C17	178.5(4)
C20-C21-C24-F45	100.6(4)	C20-C21-C22-C17	-1.0(7)
C20-C21-C24-F47	-19.4(5)	C22-C21-C24-F45	-78.8(4)
C20-C21-C24-F46	-139.5(4)	C22-C21-C24-F47	161.2(4)
C22-C21-C24-F46	41.1(5)	C26-C25-C30-C29	-0.4(14)
B1-C25-C30-C29	-172.7(7)	C26-C25-B1-C17	150.2(6)
C30-C25-B1-C17	-37.9(7)	B1-C25-C26-C27	173.9(7)
C30-C25-C26-C27	1.5(13)	C25-C26-C27-C31	178.9(7)
C25-C26-C27-C28	-2.3(15)	C26-C27-C31-F56	-55.7(8)
C26-C27-C28-C29	1.9(17)	C31-C27-C28-C29	-179.4(8)
C28-C27-C31-F56	125.6(9)	C28-C27-C31-F57	-114.4(9)
C28-C27-C31-F58	5.6(10)	C26-C27-C31-F57	64.3(8)
C26-C27-C31-F58	-175.7(7)	C27-C28-C29-C30	-0.8(18)
C27-C28-C29-C32	176.5(9)	C28-C29-C30-C25	0.1(16)
C28-C29-C32-F61	126.6(10)	C28-C29-C32-F62	6.6(11)
C30-C29-C32-F60	63.9(10)	C30-C29-C32-F61	-56.0(10)
C30-C29-C32-F62	-176.0(8)	C32-C29-C30-C25	-177.3(8)
C28-C29-C32-F60	-113.4(11)	Ir1-N1-C14-C15	-178.9(4)

Ir1-C1-C2-C3	179.7(6)	Ir1-C1-C2-C5	-0.4(7)
C1-C2-C3-C4	0.6(12)	C5-C2-C3-C4	-179.3(7)
C1-C2-C5-P1	-22.8(7)	C3-C2-C5-P1	157.1(7)
N1-C14-C15-C16	-2.2(8)		

Symmetry transformations used to generate equivalent atoms:
#1 y,x,-z+1 #2 -y+1,-x+1,-z+3/2

[(^{tBu4}PCP)Ir(H)(lut)][BAr$^{F}_{4}$] (4^{+}). The sample was submitted by Andrew Walden (research group of Miller, Department of Chemistry, the University of North Carolina at Chapel Hill). An orange crystal (approximate dimensions 0.178 x 0.128 x 0.104 mm^3) was placed onto the tip of MiTeGen and mounted on a Bruker SMART Apex II diffractometer and measured at 100 K.

Data collection

A preliminary set of cell constants was calculated from reflections harvested from three sets of 12 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 681 reflections. The data collection was carried out using Cu Kα radiation (graphite monochromator) with a frame time of 20 seconds and a detector distance of 4.0 cm. A randomly oriented region of reciprocal space was surveyed to achieve complete data with a redundancy of 4. Sections of frames were collected with 0.50º steps in ω and ϕ scans. Data to a resolution of 0.84 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 4075 strong reflections from the actual data collection after integration (SAINT).[13] The intensity data were corrected for absorption (SADABS).[14] Please refer to Table S7 for additional crystal and refinement information.

Structure solution and refinement

The space group P4$_1$2$_1$2 was determined based on intensity statistics and systematic absences. The structure was solved using Superflip[15] and refined (full-matrix-least squares) using the Oxford University Crystals for Windows system.[16] The charge-flipping solution provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms.

4^{+}exhibits significant disorder on the 2,6-lutidine ligand, and was resolved successfully. The two-part disorder was modeled that the major and minor components of the disorder summed to 1. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydride was obtained from Fourier difference map and its position was refined with distance restraint of 1.6 Å to its parent iridium, the rest of the hydrogen atoms were placed in ideal positions and refined as riding atoms. The final full matrix least squares refinement converged to R1 = 0.0564 and wR2 = 0.1381 (F^2, all data).

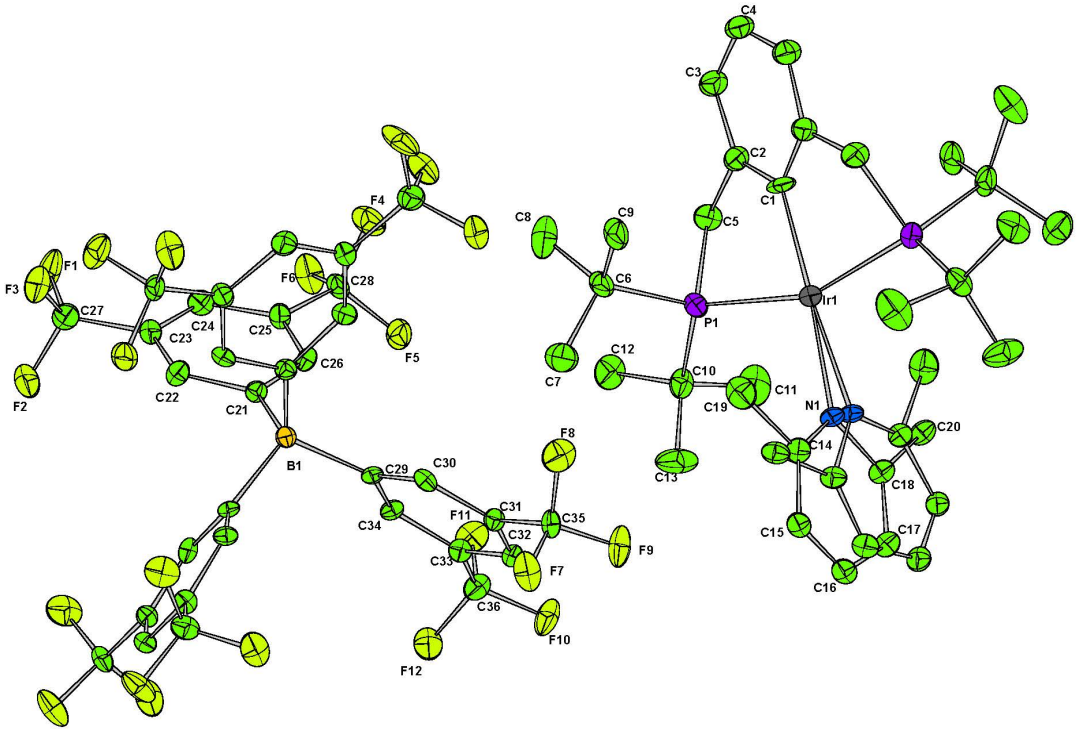


Figure S40. Molecular structure with labels on the asymmetric unit

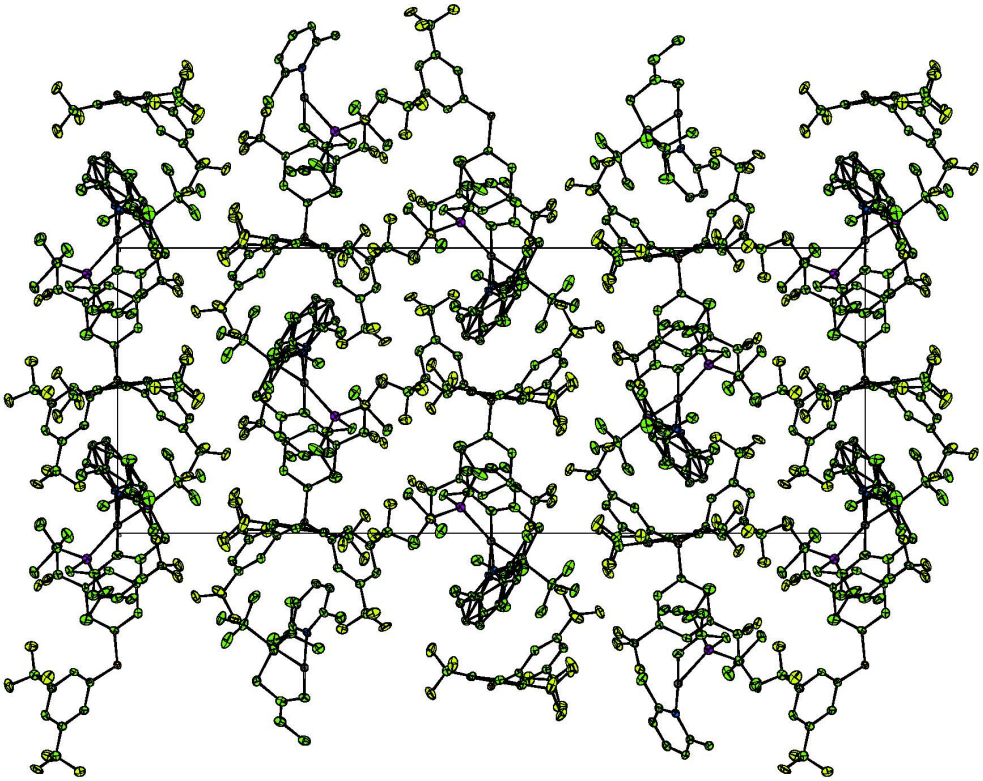


Figure S41. Cell plot, viewed along a- axis

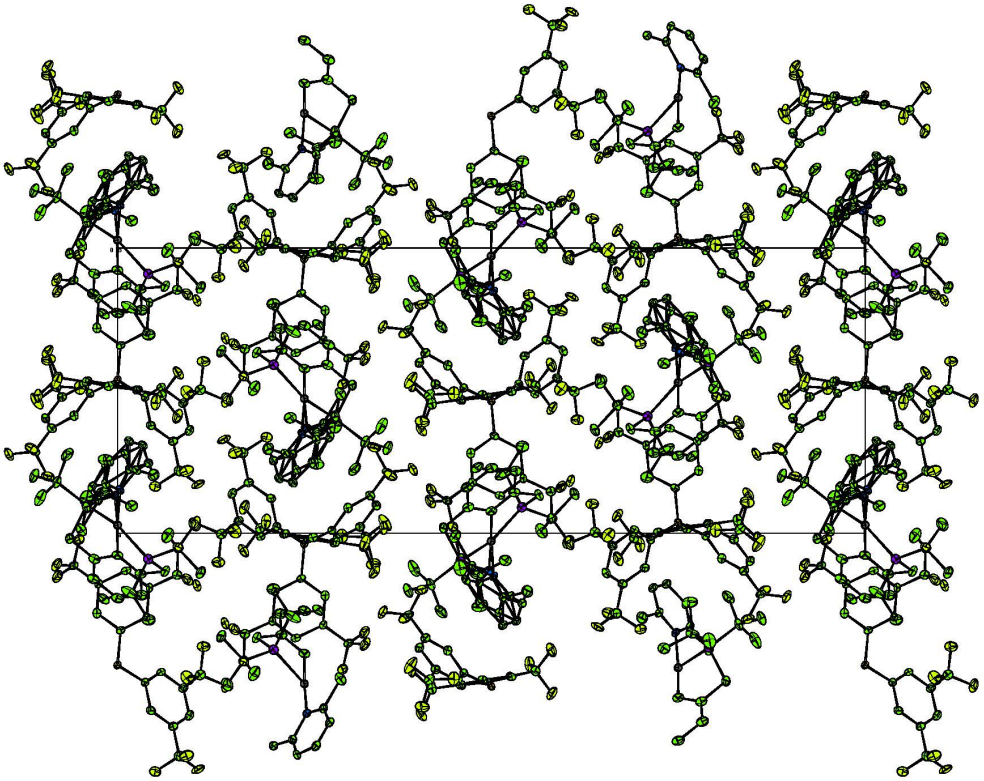


Figure S42. Cell plot, viewed along b- axis

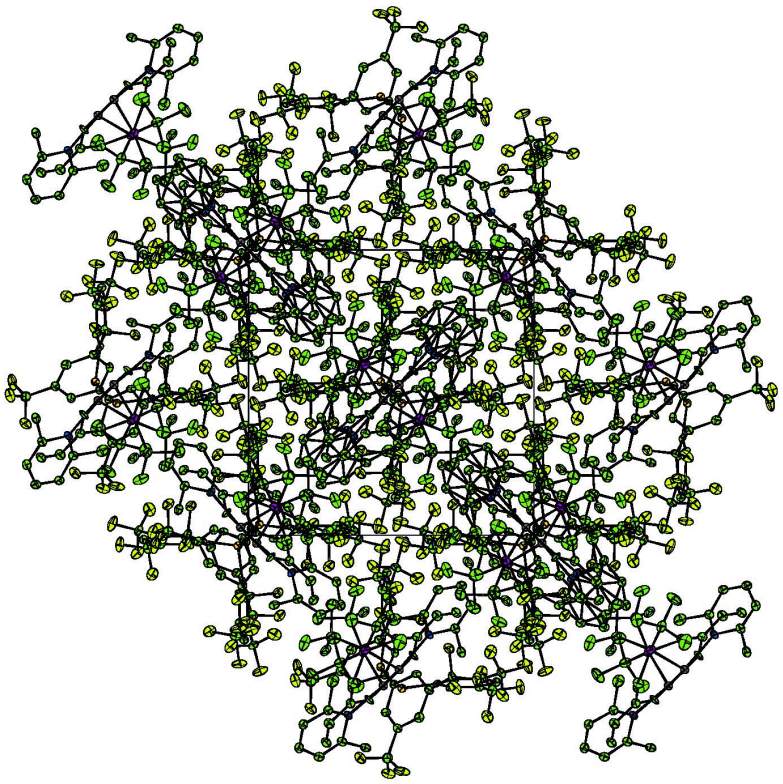


Figure S43. Cell plot, viewed along c- axis

Table S7. Crystal data and structure refinement for *[(^{tBu4}PCP)Ir(H)(lut)][BAr$^{F}_{4}$] (**4**$^{+}$)*.

Empirical formula	C63 H65 B1 F24 Ir1 N1 P2	
Formula weight	1557.15	
Crystal color, shape, size	orange block, 0.178 x 0.128 x 0.104 mm^3	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system, space group	Tetragonal, $P4_12_12$	
Unit cell dimensions	a = 13.4206(9) Å	α= 90°.
	b = 13.4206(9) Å	β= 90°.
	c = 35.170(3) Å	γ = 90°.
Volume	6334.6(10) Å^3	
Z	4	
Density (calculated)	1.633 Mg/m^3	
Absorption coefficient	5.559 mm^{-1}	
F(000)	3112	
Data collection		
Diffractometer	Bruker Apex Kappa Duo, Bruker	
Theta range for data collection	3.525 to 70.089°.	
Index ranges	-13<=h<=15, -14<=k<=15, -39<=l<=41	
Reflections collected	39025	
Independent reflections	5762 [R(int) = 0.108]	

Observed Reflections	4350
Completeness to theta = 34.344°	99.5 %
Solution and Refinement	
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.56 and 0.49
Solution	Charge-Flip
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = [\sigma^2 Fo^2 + AP^2 + BP]^{-1}$, with
	$P = (Fo^2 + 2\,Fc^2)/3$, A = 0.074, B = 0.000
Data / restraints / parameters	5737 / 107 / 458
Goodness-of-fit on F^2	0.9610
Final R indices [I>2sigma(I)]	R1 = 0.0565, wR2 = 0.1320
R indices (all data)	R1 = 0.0728, wR2 = 0.1382
Largest diff. peak and hole	1.82 and -1.81 e.$Å^{-3}$

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for $\mathbf{4}^+$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir1	281(1)	10281(1)	5000	34
P1	979(2)	9093(2)	4590(1)	44
F1	4632(7)	1715(4)	3922(2)	89
F2	6086(5)	2182(5)	4077(2)	79
F3	5102(5)	1635(4)	4497(2)	72
F4	1990(4)	4931(6)	4068(2)	78
F5	2976(5)	6025(4)	3849(2)	65
F6	2767(5)	4649(6)	3548(2)	75
F7	5620(5)	8894(5)	5812(2)	75
F8	4098(6)	8481(5)	5803(2)	76
F9	4596(5)	9776(5)	5512(2)	75
F10	5328(6)	9517(4)	4189(2)	72
F11	4819(6)	8166(4)	3939(2)	66
F12	6368(5)	8372(5)	4064(2)	70
N1	1488(9)	11309(10)	5033(4)	37
C1	-777(6)	9223(6)	5000	49
C2	-904(8)	8570(7)	4692(3)	52
C3	-1607(8)	7825(8)	4677(3)	61
C4	-2279(7)	7721(7)	5000(1)	59
C5	-188(8)	8662(7)	4361(3)	50
C6	1464(8)	7890(9)	4810(3)	62
C7	2575(9)	7927(9)	4844(3)	89
C8	1222(12)	6960(9)	4584(3)	95
C9	956(8)	7698(8)	5189(3)	66
C10	1792(8)	9472(7)	4190(3)	52
C11	1241(10)	10305(11)	3968(3)	102
C12	2015(9)	8619(9)	3887(3)	73
C13	2755(9)	9921(10)	4329(3)	90
C14	2211(13)	11158(15)	5254(5)	42
C15	3083(11)	11636(13)	5339(4)	43
C16	3231(10)	12460(12)	5154(4)	46
C17	2533(12)	12776(11)	4900(4)	43
C18	1723(13)	12240(13)	4843(4)	42
C19	2040(16)	10124(15)	5484(4)	70
C20	901(13)	12454(14)	4589(4)	46
C21	4905(5)	4767(6)	4631(2)	34

C22	5189(8)	3779(6)	4553(2)	42
C23	4780(8)	3223(6)	4256(3)	42
C24	4023(7)	3603(7)	4037(3)	45
C25	3680(7)	4566(7)	4120(3)	42
C26	4116(6)	5128(6)	4418(2)	37
C27	5138(9)	2180(8)	4173(3)	53
C28	2861(7)	5029(7)	3892(3)	46
C29	5210(6)	6590(5)	4957(2)	33
C30	5048(6)	7193(7)	5276(3)	38
C31	5025(6)	8221(6)	5251(3)	35
C32	5155(7)	8682(6)	4886(2)	40
C33	5315(8)	8085(6)	4572(2)	36
C34	5330(7)	7056(6)	4611(2)	33
C35	4831(8)	8859(7)	5590(3)	45
C36	5459(9)	8535(8)	4203(3)	52
B1	5373(6)	5373(6)	5000	32

Table S9. Bond lengths [Å] and angles [°] for $\mathbf{4}^{+}$.

Ir1-N1#1	2.131(9)	Ir1-H1#1	1.62(2)
Ir1-P1#1	2.345(2)	Ir1-P1	2.345(2)
Ir1-N1	2.131(9)	Ir1-C1	2.008(11)
Ir1-H1	1.62(2)	P1-C5	1.855(10)
P1-C6	1.904(10)	P1-C10	1.853(10)
F1-C27	1.275(11)	F2-C27	1.316(14)
F3-C27	1.356(11)	F4-C28	1.328(11)
F5-C28	1.354(11)	F6-C28	1.318(11)
F7-C35	1.315(11)	F8-C35	1.336(12)
F9-C35	1.300(10)	F10-C36	1.330(11)
F11-C36	1.357(12)	F12-C36	1.333(13)
N1-C14#1	1.64(3)	N1-C18#1	1.23(2)
N1-C14	1.26(3)	N1-C18	1.45(2)
C1-C2#1	1.405(10)	C1-C2	1.405(10)
C2-C3	1.375(12)	C2-C5	1.515(13)
C3-C4	1.458(12)	C3-H31	0.950
C4-H41	0.950	C5-H51	0.950
C5-H52	0.950	C6-C7	1.496(14)
C6-C8	1.515(16)	C6-C9	1.520(13)
C7-H71	0.950	C7-H72	0.950
C7-H73	0.950	C8-H81	0.950
C8-H82	0.950	C8-H83	0.950
C9-H91	0.950	C9-H92	0.950
C9-H93	0.950	C10-C11	1.552(15)
C10-C12	1.592(12)	C10-C13	1.507(14)
C11-H111	0.950	C11-H112	0.950
C11-H113	0.950	C12-H121	0.950
C12-H122	0.950	C12-H123	0.950
C13-H131	0.950	C13-H132	0.950
C13-H133	0.950	C14-C15	1.37(2)
C14-C19	1.62(3)	C15-C16	1.30(2)
C15-H151	0.950	C16-C17	1.363(19)
C16-H161	0.950	C17-C18#1	1.72(2)
C17-C18	1.32(2)	C17-H171	0.950
C18-C20	1.45(2)	C19-H191	0.950
C19-H192	0.950	C19-H193	0.950
C20-H201	0.950	C20-H202	0.950
C20-H203	0.950	C21-C22	1.407(11)
C21-C26	1.386(10)	C21-B1	1.654(10)
C22-C23	1.396(11)	C22-H221	0.950
C23-C24	1.374(12)	C23-C27	1.508(12)

C24-C25	1.403(12)	C24-H241	0.950
C25-C26	1.418(11)	C25-C28	1.496(11)
C26-H261	0.950	C29-C30	1.400(10)
C29-C34	1.378(10)	C29-B1	1.656(10)
C30-C31	1.383(12)	C30-H301	0.950
C31-C32	1.437(11)	C31-C35	1.490(11)
C32-C33	1.380(11)	C32-H321	0.950
C33-C34	1.387(11)	C33-C36	1.445(13)
C34-H341	0.950		

N1#1-Ir1-H1#1	101(6)	N1#1-Ir1-P1#1	99.8(3)
H1#1-Ir1-P1#1	81(5)	N1#1-Ir1-P1	102.9(3)
H1#1-Ir1-P1	97(5)	P1#1-Ir1-P1	157.11(15)
N1#1-Ir1-N1	11.1(11)	H1#1-Ir1-N1	91(6)
P1#1-Ir1-N1	102.9(3)	P1-Ir1-N1	99.8(3)
N1#1-Ir1-C1	174.5(5)	H1#1-Ir1-C1	84(5)
P1#1-Ir1-C1	78.56(7)	P1-Ir1-C1	78.56(7)
N1-Ir1-C1	174.5(5)	N1#1-Ir1-H1	91(6)
H1#1-Ir1-H1	168(11)	P1#1-Ir1-H1	97(5)
P1-Ir1-H1	81(5)	N1-Ir1-H1	101(6)
C1-Ir1-H1	84(5)	Ir1-P1-C5	98.2(3)
Ir1-P1-C6	117.6(4)	C5-P1-C6	101.6(5)
Ir1-P1-C10	121.0(3)	C5-P1-C10	104.6(5)
C6-P1-C10	109.9(5)	Ir1-N1-C14#1	103.8(11)
Ir1-N1-C18#1	159.2(17)	C14#1-N1-C18#1	96.1(16)
Ir1-N1-C14	121.0(15)	C14#1-N1-C14	135.1(19)
C18#1-N1-C14	39.1(12)	Ir1-N1-C18	134.2(13)
C14#1-N1-C18	30.5(9)	C18#1-N1-C18	66.2(16)
C14-N1-C18	104.8(16)	C2#1-C1-Ir1	121.8(6)
C2#1-C1-C2	116.3(12)	Ir1-C1-C2	121.8(6)
C1-C2-C3	124.5(11)	C1-C2-C5	117.7(8)
C3-C2-C5	117.7(9)	C2-C3-C4	117.6(11)
C2-C3-H31	120.8	C4-C3-H31	121.6
C3-C4-C3#1	119.4(12)	C3-C4-H41	120.3
C3#1-C4-H41	120.3	C2-C5-P1	103.1(6)
C2-C5-H51	110.2	P1-C5-H51	110.4
C2-C5-H52	111.3	P1-C5-H52	112.3
H51-C5-H52	109.5	P1-C6-C7	110.2(8)
P1-C6-C8	114.4(8)	C7-C6-C8	106.4(10)
P1-C6-C9	110.3(7)	C7-C6-C9	112.5(10)
C8-C6-C9	102.9(9)	C6-C7-H71	109.4

C6-C7-H72	107.8	H71-C7-H72	109.5
C6-C7-H73	111.2	H71-C7-H73	109.5
H72-C7-H73	109.5	C6-C8-H81	109.8
C6-C8-H82	109.6	H81-C8-H82	109.5
C6-C8-H83	109.0	H81-C8-H83	109.5
H82-C8-H83	109.5	C6-C9-H91	109.9
C6-C9-H92	108.6	H91-C9-H92	109.5
C6-C9-H93	109.9	H91-C9-H93	109.5
H92-C9-H93	109.5	P1-C10-C11	107.4(7)
P1-C10-C12	114.9(7)	C11-C10-C12	105.8(9)
P1-C10-C13	111.6(8)	C11-C10-C13	106.5(10)
C12-C10-C13	110.1(9)	C10-C11-H111	109.1
C10-C11-H112	109.5	H111-C11-H112	109.5
C10-C11-H113	109.9	H111-C11-H113	109.5
H112-C11-H113	109.5	C10-C12-H121	109.4
C10-C12-H122	109.0	H121-C12-H122	109.5
C10-C12-H123	110.0	H121-C12-H123	109.5
H122-C12-H123	109.5	C10-C13-H131	110.2
C10-C13-H132	109.0	H131-C13-H132	109.5
C10-C13-H133	109.2	H131-C13-H133	109.5
H132-C13-H133	109.5	N1#1-C14-N1	6.5(7)
N1#1-C14-C15	129.7(19)	N1-C14-C15	136(2)
N1#1-C14-C19	115.7(15)	N1-C14-C19	109.7(17)
C15-C14-C19	114.5(20)	C14-C15-C16	115.0(16)
C14-C15-H151	123.0	C16-C15-H151	122.0
C15-C16-C17	119.2(9)	C15-C16-H161	120.4
C17-C16-H161	120.4	C16-C17-C18#1	63.7(9)
C16-C17-C18	119.8(15)	C18#1-C17-C18	56.2(15)
C16-C17-H171	120.7	C18#1-C17-H171	173.9
C18-C17-H171	119.6	N1-C18-C17#1	97.6(13)
N1-C18-C17	125.4(16)	C17#1-C18-C17	28.4(11)
N1-C18-N1#1	15.0(15)	C17#1-C18-N1#1	111.8(17)
C17-C18-N1#1	140.0(20)	N1-C18-C20	106.8(16)
C17#1-C18-C20	154.6(16)	C17-C18-C20	127.8(18)
N1#1-C18-C20	92.1(17)	C14-C19-H191	110.3
C14-C19-H192	108.4	H191-C19-H192	109.5
C14-C19-H193	109.7	H191-C19-H193	109.5
H192-C19-H193	109.5	C18-C20-H201	109.3
C18-C20-H202	109.5	H201-C20-H202	109.5
C18-C20-H203	109.6	H201-C20-H203	109.5
H202-C20-H203	109.5	C22-C21-C26	115.6(7)
C22-C21-B1	120.9(6)	C26-C21-B1	122.9(7)
C21-C22-C23	122.9(8)	C21-C22-H221	117.9

C23-C22-H221	119.2	C22-C23-C24	120.8(9)
C22-C23-C27	121.1(9)	C24-C23-C27	118.0(9)
C23-C24-C25	117.9(8)	C23-C24-H241	121.3
C25-C24-H241	120.8	C24-C25-C26	120.6(8)
C24-C25-C28	120.8(8)	C26-C25-C28	118.6(8)
C25-C26-C21	122.0(8)	C25-C26-H261	119.2
C21-C26-H261	118.9	C23-C27-F3	109.0(9)
C23-C27-F2	110.9(9)	F3-C27-F2	104.5(9)
C23-C27-F1	114.8(9)	F3-C27-F1	107.3(9)
F2-C27-F1	109.8(10)	C25-C28-F5	112.7(8)
C25-C28-F4	110.9(8)	F5-C28-F4	104.4(8)
C25-C28-F6	113.7(8)	F5-C28-F6	106.9(9)
F4-C28-F6	107.7(8)	C30-C29-C34	117.6(7)
C30-C29-B1	121.2(7)	C34-C29-B1	120.9(6)
C29-C30-C31	122.0(8)	C29-C30-H301	118.8
C31-C30-H301	119.1	C30-C31-C32	118.8(8)
C30-C31-C35	121.8(9)	C32-C31-C35	119.4(7)
C31-C32-C33	119.0(8)	C31-C32-H321	120.1
C33-C32-H321	120.8	C32-C33-C34	120.0(8)
C32-C33-C36	119.8(8)	C34-C33-C36	120.2(8)
C33-C34-C29	122.5(8)	C33-C34-H341	118.8
C29-C34-H341	118.6	C31-C35-F8	111.0(8)
C31-C35-F7	110.8(8)	F8-C35-F7	105.9(9)
C31-C35-F9	114.7(8)	F8-C35-F9	107.3(9)
F7-C35-F9	106.6(9)	C33-C36-F11	112.1(9)
C33-C36-F12	112.5(10)	F11-C36-F12	105.7(9)
C33-C36-F10	115.5(9)	F11-C36-F10	104.7(9)
F12-C36-F10	105.7(9)	C29#2-B1-C29	105.5(9)
C29#2-B1-C21#2	111.3(4)	C29-B1-C21#2	112.4(4)
C29#2-B1-C21	112.4(4)	C29-B1-C21	111.3(4)
C21#2-B1-C21	104.0(8)		

Symmetry transformations used to generate equivalent atoms:

#1 y-1,x+1,-z+1 #2 y,x,-z+1

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $\mathbf{4}^+$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir1	35(1)	35(1)	33(1)	1(1)	-1(1)	-3(1)
P1	38(2)	48(2)	46(2)	2(1)	3(1)	6(1)
F1	140(7)	43(4)	85(5)	-30(3)	-62(5)	20(4)
F2	64(5)	70(5)	104(5)	-16(4)	9(4)	21(4)
F3	99(6)	51(4)	68(5)	4(3)	-4(4)	17(4)
F4	45(4)	101(7)	88(5)	19(4)	-11(3)	8(4)
F5	58(4)	52(4)	87(5)	2(3)	-23(3)	11(3)
F6	83(5)	97(5)	45(4)	-18(4)	-29(3)	34(5)
F7	83(5)	86(5)	55(4)	-30(4)	-32(4)	32(4)
F8	100(6)	76(5)	54(5)	-22(4)	24(4)	-9(4)
F9	121(6)	52(3)	51(4)	-6(3)	9(4)	36(5)
F10	123(6)	36(3)	55(4)	9(2)	31(4)	12(4)
F11	92(5)	70(4)	34(4)	15(3)	1(4)	-6(4)
F12	82(5)	68(5)	61(5)	21(3)	32(4)	12(4)
N1	37(4)	38(4)	35(4)	-12(5)	-16(4)	-15(4)
C1	42(3)	42(3)	63(7)	7(4)	-7(4)	-24(4)
C2	48(4)	41(4)	67(6)	2(4)	-10(4)	-2(3)
C3	54(5)	52(4)	76(6)	1(4)	-10(4)	-7(4)
C4	49(4)	49(4)	79(8)	10(5)	-10(5)	-12(5)
C5	53(6)	61(6)	38(6)	-18(5)	2(5)	-6(5)
C6	39(5)	55(5)	94(7)	32(5)	14(5)	14(4)
C7	59(6)	79(7)	130(8)	53(6)	-6(6)	4(6)
C8	134(14)	62(9)	90(11)	0(8)	14(10)	34(9)
C9	61(6)	59(6)	77(7)	27(5)	4(5)	22(5)
C10	70(7)	46(7)	39(7)	-2(4)	17(5)	9(5)
C11	142(14)	91(10)	72(10)	17(9)	51(9)	23(11)
C12	98(10)	73(9)	48(8)	-19(6)	27(7)	4(7)
C13	84(9)	111(13)	76(10)	-28(8)	35(7)	-47(9)
C14	43(5)	46(5)	36(5)	-8(5)	-14(4)	-2(5)
C15	39(6)	49(5)	40(5)	-15(5)	-11(5)	1(6)
C16	41(6)	54(7)	44(6)	-14(6)	-9(6)	-1(7)
C17	55(7)	42(7)	32(8)	6(6)	-4(6)	-4(7)
C18	49(5)	43(5)	35(5)	-4(4)	-11(4)	-8(5)
C19	69(10)	82(19)	60(11)	19(13)	4(10)	12(11)
C20	58(7)	40(6)	39(6)	-3(6)	-9(7)	-10(6)
C21	35(5)	34(4)	32(5)	-1(4)	-2(3)	-1(4)
C22	47(5)	36(5)	43(6)	3(4)	-21(5)	1(4)

C23	41(5)	38(5)	45(6)	-3(4)	2(5)	4(4)
C24	45(6)	52(6)	39(6)	-12(4)	-6(4)	-2(4)
C25	43(5)	39(6)	44(6)	-7(4)	-6(4)	7(4)
C26	48(5)	27(5)	37(6)	-6(4)	-1(4)	-1(4)
C27	52(7)	51(6)	56(8)	1(5)	-14(6)	-1(5)
C28	32(5)	51(7)	54(8)	-4(4)	-9(4)	9(4)
C29	27(4)	31(4)	41(5)	-7(4)	-5(5)	-9(3)
C30	28(5)	50(5)	35(6)	1(4)	-2(3)	7(4)
C31	38(5)	35(5)	30(6)	-7(4)	2(3)	1(3)
C32	41(5)	31(4)	48(7)	-7(4)	3(4)	0(4)
C33	43(5)	41(5)	23(5)	0(3)	5(5)	0(4)
C34	39(5)	33(4)	27(5)	-2(3)	0(4)	-8(4)
C35	51(6)	37(5)	47(7)	-10(4)	2(5)	14(5)
C36	64(8)	43(6)	49(8)	1(5)	5(6)	-5(5)
B1	33(4)	33(4)	29(7)	-4(5)	4(5)	2(6)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $\mathbf{4}^+$.

	x	y	z	U(eq)
H31	-1655	7401	4461	75
H51	-422	9147	4185	63
H52	-106	8042	4234	63
H71	2778	7537	5056	102
H72	2761	8601	4884	102
H73	2887	7683	4620	102
H81	1488	6391	4710	101
H82	520	6892	4562	101
H83	1509	7015	4338	101
H91	1201	7098	5298	76
H92	1097	8239	5355	76
H93	256	7646	5153	76
H111	1639	10506	3758	110
H112	1133	10859	4131	110
H113	619	10063	3878	110
H121	2422	8878	3690	87
H122	2353	8087	4010	87
H123	1408	8380	3782	87
H131	3158	10113	4119	117
H132	2609	10490	4480	117
H133	3102	9444	4478	117
H151	3556	11382	5514	51
H161	3816	12842	5198	55
H171	2623	13379	4763	51
H191	1349	10016	5526	77
H192	2302	9593	5336	77
H193	2377	10152	5721	77
H201	826	13155	4566	56
H202	306	12175	4690	56
H203	1032	12173	4346	56
H221	5680	3482	4712	51
H241	3737	3227	3836	57
H261	3864	5774	4472	43
H301	4948	6885	5516	45
H321	5140	9387	4863	45
H341	5428	6657	4391	44
H41	-2779	7221	5000	71

H1	-240(110)	10620(110)	4610(20)	50

Table S12. Torsion angles [°] for $\mathbf{4}^{+}$.

C1-Ir1-P1-C5	35.5(4)	C1-Ir1-P1-C6	-72.2(4)
C1-Ir1-P1-C10	148.1(4)	P1#1-Ir1-P1-C5	35.5(4)
P1#1-Ir1-P1-C6	-72.2(5)	P1#1-Ir1-P1-C10	148.1(4)
N1#1-Ir1-P1-C5	-139.1(5)	N1#1-Ir1-P1-C6	113.3(5)
N1#1-Ir1-P1-C10	-26.5(6)	P1-Ir1-N1-C14	-81.5(14)
P1-Ir1-N1-C18	97.9(14)	P1#1-Ir1-N1-C14	96.4(13)
P1#1-Ir1-N1-C18	-84.2(14)	N1#1-Ir1-N1-C14	171(4)
N1#1-Ir1-N1-C18	-10(2)	P1-Ir1-C1-C2	-26.4(7)
P1-Ir1-C1-C2#1	153.6(7)	P1#1-Ir1-C1-C2	153.6(7)
N1-Ir1-P1-C10	-37.3(6)	N1-Ir1-P1-C5	-149.9(5)
N1-Ir1-P1-C6	102.5(5)	Ir1-P1-C5-C2	-43.2(6)
C6-P1-C5-C2	77.3(7)	C10-P1-C5-C2	-168.4(6)
Ir1-P1-C6-C7	-101.6(7)	C5-P1-C6-C8	33.0(10)
C5-P1-C6-C9	-82.5(8)	C10-P1-C6-C7	42.4(9)
C10-P1-C6-C8	-77.4(10)	Ir1-P1-C6-C8	138.6(8)
Ir1-P1-C6-C9	23.2(9)	C5-P1-C6-C7	152.8(8)
Ir1-P1-C10-C13	66.5(8)	C5-P1-C10-C11	59.2(8)
C5-P1-C10-C12	-58.2(8)	C5-P1-C10-C13	175.6(8)
C6-P1-C10-C11	167.6(7)	C6-P1-C10-C12	50.2(9)
C6-P1-C10-C13	-76.1(9)	Ir1-P1-C10-C11	-49.9(8)
Ir1-P1-C10-C12	-167.3(6)	C10-P1-C6-C9	167.1(7)
C26-C21-B1-C29#2	-146.0(7)	C22-C21-C26-C25	-5.0(11)
B1-C21-C26-C25	-175.4(7)	B1-C21-C22-C23	176.9(8)
C26-C21-B1-C29	-27.7(9)	C26-C21-B1-C21#2	93.5(8)
C26-C21-C22-C23	6.3(12)	C22-C21-B1-C29	162.4(7)
C22-C21-B1-C21#2	-76.4(8)	C22-C21-B1-C29#2	44.1(9)
C21-C22-C23-C24	-4.1(15)	C21-C22-C23-C27	177.5(9)
C22-C23-C24-C25	0.4(15)	C22-C23-C27-F2	-62.3(13)
C22-C23-C27-F3	52.3(13)	C24-C23-C27-F1	-5.7(14)
C24-C23-C27-F2	119.3(10)	C24-C23-C27-F3	-126.2(10)
C27-C23-C24-C25	178.8(9)	C22-C23-C27-F1	172.7(9)
C23-C24-C25-C28	179.7(9)	C23-C24-C25-C26	0.8(14)
C24-C25-C28-F4	98.0(11)	C28-C25-C26-C21	-177.2(8)
C26-C25-C28-F4	-83.1(11)	C24-C25-C28-F5	-145.3(9)
C24-C25-C28-F6	-23.5(13)	C24-C25-C26-C21	1.7(13)
C26-C25-C28-F6	155.4(8)	C26-C25-C28-F5	33.6(12)
C34-C29-B1-C21#2	-156.3(7)	B1-C29-C30-C31	172.4(7)
B1-C29-C34-C33	-172.3(8)	C30-C29-B1-C21	146.6(7)
C30-C29-C34-C33	1.3(13)	C34-C29-B1-C29#2	82.2(8)
C34-C29-C30-C31	-1.2(12)	C34-C29-B1-C21	-40.1(10)
C30-C29-B1-C21#2	30.4(10)	C30-C29-B1-C29#2	-91.2(7)

C29-C30-C31-C35	178.7(8)	C29-C30-C31-C32	1.0(12)
C35-C31-C32-C33	-178.7(9)	C30-C31-C35-F7	75.0(11)
C30-C31-C32-C33	-1.0(13)	C32-C31-C35-F8	135.3(9)
C32-C31-C35-F9	13.4(13)	C30-C31-C35-F9	-164.3(8)
C32-C31-C35-F7	-107.4(9)	C30-C31-C35-F8	-42.4(12)
C31-C32-C33-C34	1.2(14)	C31-C32-C33-C36	-179.3(9)
C32-C33-C36-F12	115.1(11)	C34-C33-C36-F10	173.2(10)
C34-C33-C36-F11	53.6(14)	C34-C33-C36-F12	-65.3(13)
C32-C33-C34-C29	-1.4(15)	C36-C33-C34-C29	179.1(10)
C32-C33-C36-F10	-6.3(15)	C32-C33-C36-F11	-126.0(10)
Ir1-N1-C14-C15	178.7(17)	Ir1-N1-C14-C19	-0.2(19)
C18-N1-C14-C15	-1(3)	C18-N1-C14-C19	-179.7(13)
Ir1-N1-C18-C17	-179.1(12)	Ir1-N1-C18-C20	2(2)
C14-N1-C18-C17	0(2)	C14-N1-C18-C20	-179.1(14)
Ir1-C1-C2-C3	179.3(8)	Ir1-C1-C2-C5	2.2(12)
C2#1-C1-C2-C3	-0.7(14)	C2#1-C1-C2-C5	-177.8(8)
C1-C2-C3-C4	1.3(15)	C5-C2-C3-C4	178.5(9)
C1-C2-C5-P1	31.1(10)	C3-C2-C5-P1	-146.3(8)
C2-C3-C4-C3#1	-0.6(14)	N1-C14-C15-C16	1(3)
C19-C14-C15-C16	179.4(14)	C14-C15-C16-C17	0(2)
C15-C16-C17-C18	-1(2)	C16-C17-C18-N1	0(2)
C16-C17-C18-C20	179.6(15)		

Symmetry transformations used to generate equivalent atoms:

#1 y-1,x+1,-z+1 #2 y,x,-z+1

[(^{tBu4}PCP)Ir(H)(2-Phpy)][BAr$^{F}_{4}$] (5^{+}). The sample was submitted by Andrew Walden (research group of Miller, Department of Chemistry, the University of North Carolina at Chapel Hill). A yellow crystal (approximate dimensions 0.124 x 0.080 x 0.064 mm^3) was placed onto the tip of MiTeGen and mounted on a Bruker SMART Apex II diffractometer and measured at 150 K.

Data collection

A preliminary set of cell constants was calculated from reflections harvested from three sets of 12 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 120 reflections. The data collection was carried out using Cu Kα radiation (graphite monochromator) with a frame time of 10 seconds and a detector distance of 4.0 cm. A randomly oriented region of reciprocal space was surveyed to achieve complete data with a redundancy of 4. Sections of frames were collected with 0.50º steps in ω and ϕ scans. Data to a resolution of 0.81 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 9074 strong reflections from the actual data collection after integration (SAINT).[13] The intensity data were corrected for absorption (SADABS).[14] Please refer to Table S13 for additional crystal and refinement information.

Structure solution and refinement

The space group $P2_12_12_1$ was determined based on intensity statistics and systematic absences. The structure was solved using Superflip[15] and refined (full-matrix-least squares) using the Oxford University Crystals for Windows system.[16] The charge-flipping solution provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms.

Structure $\mathbf{5}^{+}$ exhibits significant disorder, which was modeled successfully. The two-part disorder on the CF_3's were modeled that the occupancies of the major and minor compoments summed to 1. All non-hydrogen atoms were refined with anisotropic displacement parameters. The iridium hydride was obtained from the Fourier difference map and refined its position. The rest of the hydrogen atoms were placed in ideal positions and refined as riding atoms. The final full matrix least squares refinement converged to R1 = 0.0424 and wR2 = 0.1021 (F^2, all data).

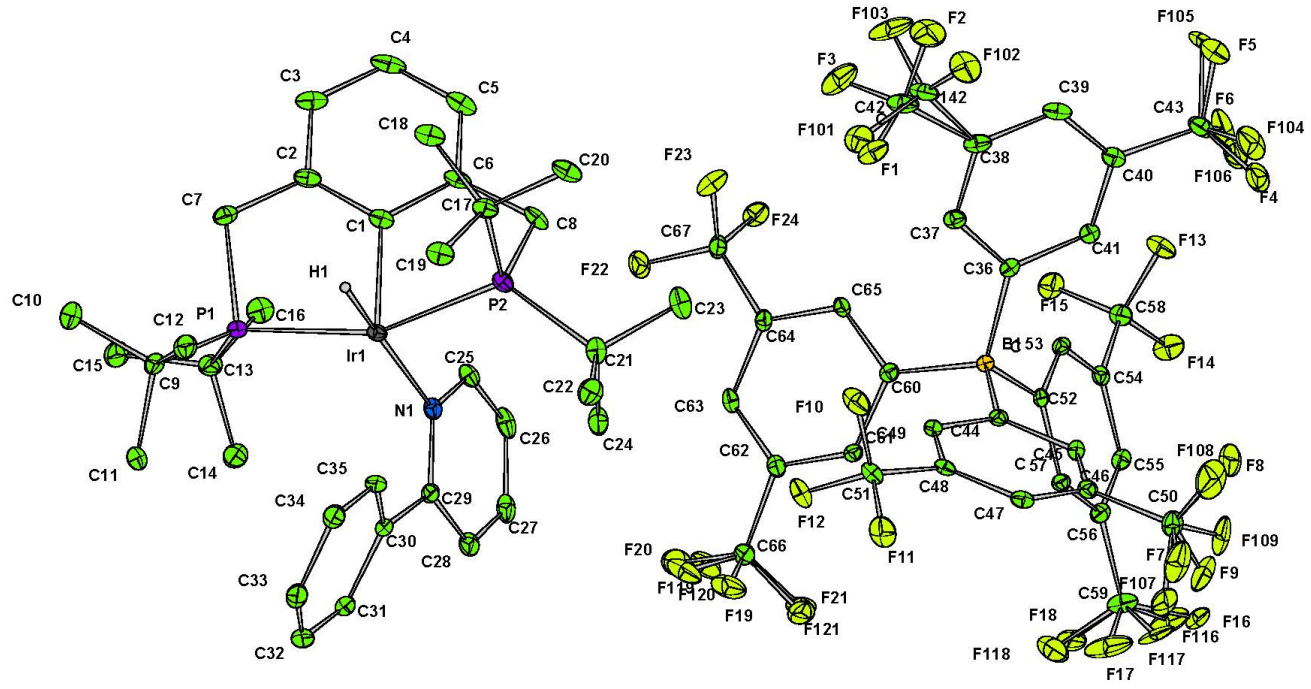


Figure S44. Molecular structure with labels on the asymmetric unit

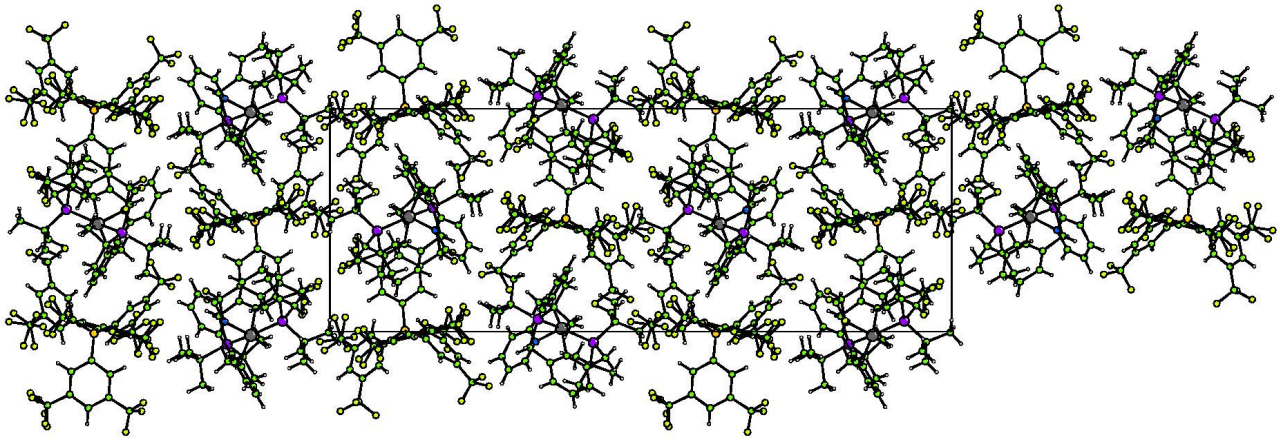


Figure S45. Cell plot, viewed along a- axis

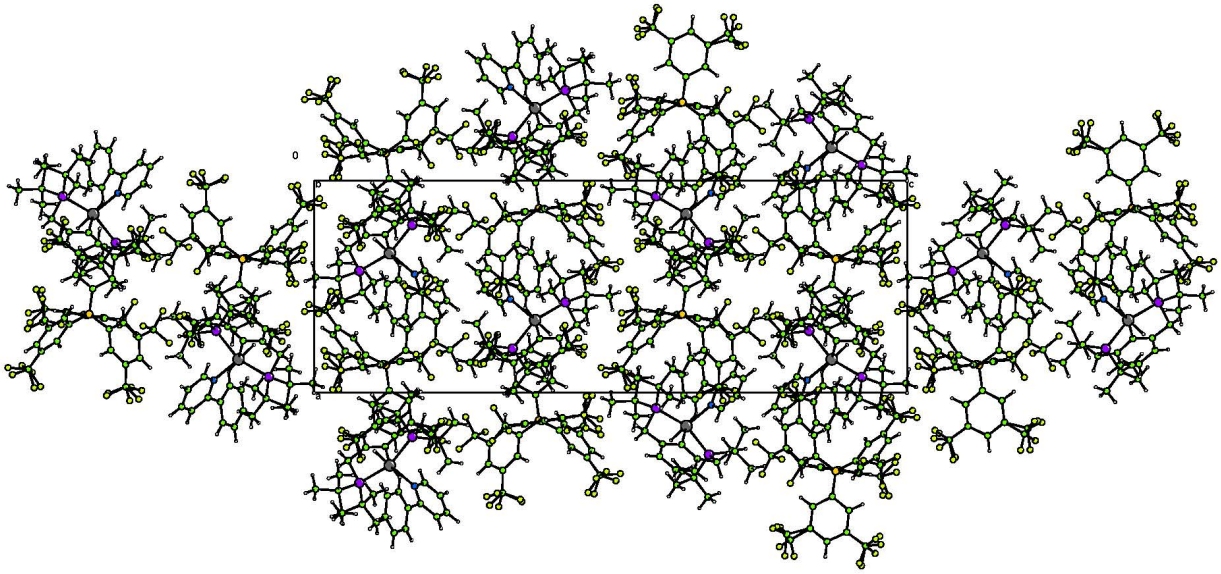


Figure S46. Cell plot, viewed along b- axis

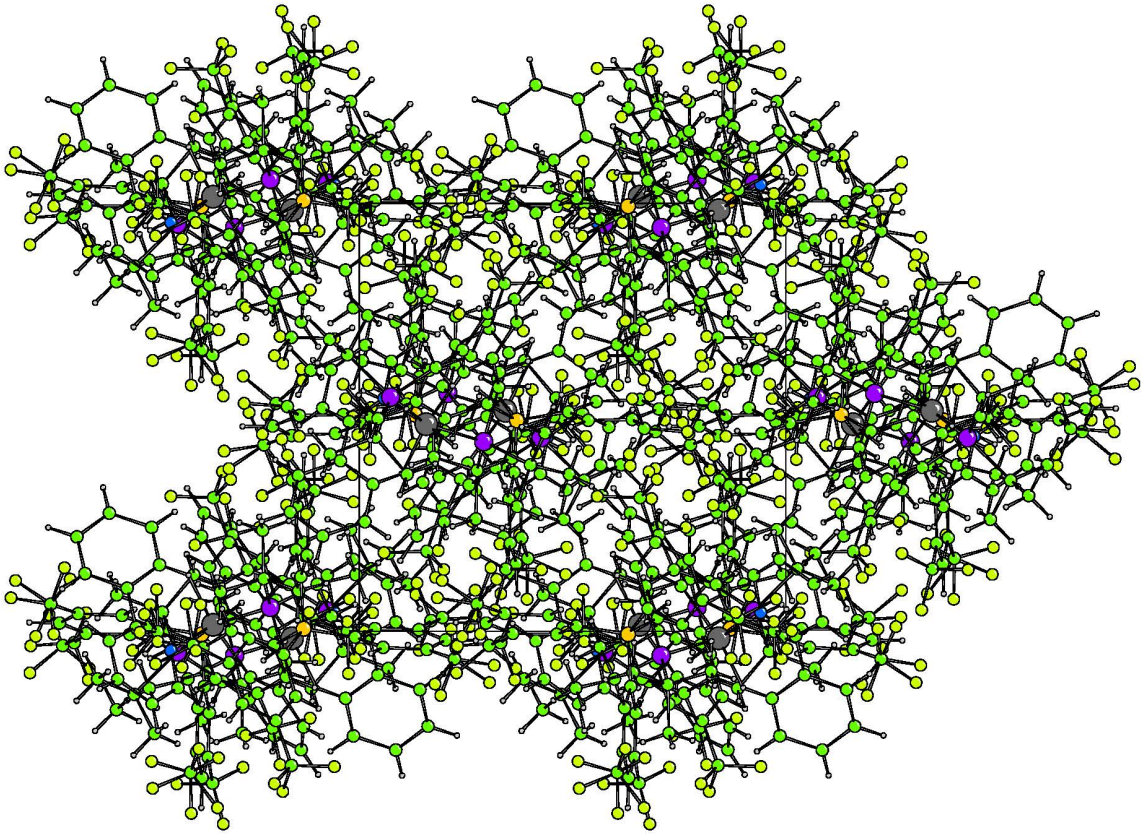


Figure S47. Cell plot, viewed along c- axis

Table S13. Crystal data and structure refinement for [(^{tBu4}PCP)Ir(H)(2-Phpy)][BAr$^{F}_{4}$] (**5**$^{+}$)

Empirical formula	C67 H65 B1 F24 Ir1 N1 P2	
Formula weight	1605.19	
Crystal color, shape, size	yellow plate, 0.124 x 0.080 x 0.064 mm^3	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system, space group	Orthorhombic, $P2_12_12_1$	
Unit cell dimensions	a = 13.3252(3) Å	α= 90°.
	b = 13.3891(3) Å	β= 90°.
	c = 37.2399(9) Å	γ = 90°.
Volume	6644.1(3) Å^3	
Z	4	
Density (calculated)	1.605 Mg/m^3	
Absorption coefficient	5.322 mm^{-1}	
F(000)	3208.000	
Data collection		
Diffractometer	Bruker Apex Kappa Duo, Bruker	
Theta range for data collection	2.373 to 70.130°.	
Index ranges	-16<=h<=16, -16<=k<=13, -45<=l<=45	
Reflections collected	61902	
Independent reflections	12538 [R(int) = 0.044]	
Observed Reflections	11813	
Completeness to theta = 70.130°	99.7 %	
Solution and Refinement		
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.71 and 0.65	
Solution	Charge Flip	
Refinement method	Full-matrix least-squares on F^2	
Weighting scheme	w = [σ^{2}Fo^2+ AP^2+ BP]$^{-1}$, with	
	P = (Fo^2+ 2 Fc^2)/3, A = 0.05, B = 23.63	
Data / restraints / parameters	12482 / 244 / 1017	
Goodness-of-fit on F^2	0.9984	
Final R indices [I>2sigma(I)]	R1 = 0.0424, wR2 = 0.1003	
R indices (all data)	R1 = 0.0451, wR2 = 0.1021	
Largest diff. peak and hole	0.72 and -0.57 e.Å^{-3}	

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $\mathbf{5}^+$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir1	1573(1)	5157(1)	6276(1)	20
P1	739(1)	4521(1)	5764(1)	25
P2	2919(1)	5562(1)	6654(1)	24
F1	6326(11)	6132(9)	7857(3)	43
F2	7706(8)	5372(13)	7941(3)	66
F3	6435(12)	4570(8)	7739(2)	72
F4	7142(10)	5056(6)	9555(2)	49
F5	8169(5)	4238(10)	9231(2)	66
F6	6918(6)	3498(7)	9461(2)	60
F7	3926(8)	9248(5)	9550(1)	65
F8	4868(6)	8030(8)	9687(2)	65
F9	3295(6)	7954(6)	9792(2)	58
F10	4276(3)	8561(4)	8027(1)	52
F11	3187(4)	9497(3)	8284(1)	48
F12	2724(3)	8175(3)	8005(1)	41
F13	4416(3)	1843(3)	9582(1)	41
F14	3015(3)	1445(3)	9831(1)	45
F15	3210(3)	1265(3)	9262(1)	40
F16	1183(4)	4569(7)	10163(1)	46
F17	940(6)	5653(5)	9751(2)	73
F18	227(4)	4232(7)	9724(2)	60
F19	240(5)	5965(11)	8068(8)	59
F20	-327(7)	4519(15)	7970(6)	53
F21	-130(8)	5010(20)	8507(3)	43
F22	2343(4)	2570(4)	7443(1)	56
F23	3851(4)	2976(3)	7552(1)	48
F24	3148(3)	1891(3)	7884(1)	39
F101	6338(7)	5870(7)	7804(2)	53
F102	7723(5)	5966(6)	8092(2)	54
F103	7283(8)	4618(6)	7841(2)	74
F104	7546(16)	5117(6)	9469(4)	59
F105	8072(10)	3836(18)	9195(2)	55
F106	6775(7)	3748(15)	9531(3)	54
F107	3341(12)	9121(9)	9580(2)	54
F108	4865(8)	8648(12)	9588(2)	78
F109	3756(12)	7736(6)	9818(2)	54

F116	880(11)	4188(10)	10101(4)	60
F117	1261(9)	5638(8)	9915(6)	59
F118	259(8)	4719(17)	9619(3)	71
F119	97(3)	5624(6)	7905(2)	53
F120	-378(3)	4216(4)	8114(2)	45
F121	-28(3)	5414(6)	8473(2)	58
N1	588(4)	4556(4)	6695(1)	25
C1	2451(4)	3931(4)	6196(2)	27
C2	2419(5)	3425(5)	5869(2)	32
C3	3009(5)	2558(5)	5825(2)	41
C4	3642(5)	2234(5)	6096(2)	42
C5	3698(5)	2769(5)	6415(2)	37
C6	3125(4)	3621(5)	6461(2)	29
C7	1797(5)	3830(5)	5572(2)	32
C8	3278(5)	4289(4)	6787(2)	29
C9	386(5)	5456(5)	5409(2)	34
C10	439(6)	5027(7)	5024(2)	47
C11	-683(6)	5856(6)	5473(2)	41
C12	1122(6)	6329(6)	5424(2)	38
C13	-274(5)	3531(6)	5811(2)	34
C14	-1136(5)	3895(6)	6045(2)	40
C15	-692(6)	3178(7)	5447(2)	46
C16	201(6)	2623(5)	5995(2)	38
C17	4013(5)	6105(5)	6400(2)	32
C18	4350(5)	5358(5)	6112(2)	38
C19	3699(5)	7080(5)	6212(2)	36
C20	4925(5)	6328(6)	6639(2)	40
C21	2762(6)	6237(6)	7095(2)	35
C22	2738(6)	7369(6)	7044(2)	41
C23	3577(6)	5954(6)	7373(2)	47
C24	1752(5)	5927(6)	7258(2)	40
C25	748(5)	3684(5)	6860(2)	28
C26	144(5)	3310(6)	7128(2)	38
C27	-662(5)	3885(6)	7234(2)	38
C28	-858(4)	4781(6)	7068(2)	34
C29	-234(4)	5099(5)	6790(1)	28
C30	-439(5)	6012(5)	6583(2)	27
C31	-1430(5)	6353(6)	6539(2)	35
C32	-1617(6)	7211(6)	6348(2)	43
C33	-854(6)	7766(6)	6196(2)	41
C34	135(5)	7434(5)	6231(2)	34
C35	321(5)	6556(5)	6420(2)	30
C36	4907(4)	4868(4)	8734(2)	21

C37	5370(5)	5068(5)	8406(2)	27
C38	6403(4)	5049(4)	8362(1)	32
C39	7024(4)	4802(5)	8646(2)	33
C40	6588(4)	4581(4)	8978(1)	28
C41	5558(4)	4628(4)	9016(2)	24
C42	6690(6)	5262(5)	7972(2)	41
C43	7231(3)	4358(3)	9297(1)	43
C44	3630(4)	6286(4)	8835(2)	21
C45	3779(5)	6783(5)	9162(2)	22
C46	3806(4)	7810(4)	9187(1)	26
C47	3683(4)	8411(5)	8887(2)	24
C48	3541(5)	7938(4)	8558(2)	23
C49	3510(5)	6904(4)	8533(2)	23
C50	3953(3)	8290(3)	9547(1)	34
C51	3439(5)	8540(4)	8220(2)	28
C52	3229(4)	4466(4)	9134(2)	21
C53	3512(5)	3483(4)	9212(1)	22
C54	3051(4)	2918(5)	9476(2)	23
C55	2264(5)	3308(5)	9678(2)	25
C56	1953(4)	4270(4)	9602(1)	26
C57	2424(4)	4836(5)	9337(1)	22
C58	3413(6)	1871(5)	9541(2)	30
C59	1104(2)	4682(3)	9819(1)	42
C60	3004(4)	4683(5)	8456(2)	23
C61	2006(4)	5020(4)	8429(1)	22
C62	1338(4)	4622(4)	8178(1)	28
C63	1634(5)	3900(4)	7940(2)	27
C64	2615(5)	3558(5)	7958(2)	25
C65	3288(5)	3943(4)	8214(1)	22
C66	273(2)	4992(3)	8176(1)	35
C67	2974(5)	2745(5)	7713(2)	31
C142	6953(4)	5337(4)	8026(1)	42
B1	3698(4)	5066(5)	8793(2)	21

Table S15. Bond lengths [Å] and angles [°] for $\mathbf{5}^{+}$.

Ir1-P1	2.3652(16)	Ir1-P2	2.3449(16)
Ir1-N1	2.192(5)	Ir1-C1	2.038(6)
Ir1-C35	2.565(6)	Ir1-H351	1.837
Ir1-H1	1.52(8)	P1-C7	1.833(6)
P1-C9	1.879(7)	P1-C13	1.901(7)
P2-C8	1.838(6)	P2-C17	1.884(7)
P2-C21	1.885(7)	F1-C42	1.332(9)
F2-C42	1.367(8)	F3-C42	1.313(9)
F4-C43	1.344(7)	F5-C43	1.284(8)
F6-C43	1.369(8)	F7-C50	1.283(7)
F8-C50	1.370(7)	F9-C50	1.342(7)
F10-C51	1.328(8)	F11-C51	1.346(7)
F12-C51	1.338(8)	F13-C58	1.345(9)
F14-C58	1.332(7)	F15-C58	1.346(7)
F16-C59	1.295(6)	F17-C59	1.342(7)
F18-C59	1.362(6)	F19-C66	1.364(10)
F20-C66	1.277(10)	F21-C66	1.343(10)
F22-C67	1.332(8)	F23-C67	1.350(8)
F24-C67	1.329(8)	F101-C142	1.365(8)
F102-C142	1.351(7)	F103-C142	1.263(7)
F104-C43	1.272(9)	F105-C43	1.374(9)
F106-C43	1.340(9)	F107-C50	1.386(9)
F108-C50	1.315(9)	F109-C50	1.278(9)
F116-C59	1.277(9)	F117-C59	1.345(9)
F118-C59	1.350(9)	F119-C66	1.337(6)
F120-C66	1.374(6)	F121-C66	1.303(6)
N1-C25	1.338(8)	N1-C29	1.361(8)
C1-C2	1.395(10)	C1-C6	1.397(9)
C2-C3	1.412(10)	C2-C7	1.486(10)
C3-C4	1.387(11)	C3-H31	0.950
C4-C5	1.389(11)	C4-H41	0.950
C5-C6	1.383(9)	C5-H51	0.950
C6-C8	1.521(9)	C7-H71	0.950
C7-H72	0.950	C8-H81	0.950
C8-H82	0.950	C9-C10	1.547(9)
C9-C11	1.540(10)	C9-C12	1.526(10)
C10-H101	0.950	C10-H102	0.950
C10-H103	0.950	C11-H111	0.950
C11-H112	0.950	C11-H113	0.950
C12-H121	0.950	C12-H122	0.950
C12-H123	0.950	C13-C14	1.521(9)

C13-C15	1.540(10)	C13-C16	1.531(10)
C14-H141	0.950	C14-H142	0.950
C14-H143	0.950	C15-H151	0.950
C15-H152	0.950	C15-H153	0.950
C16-H161	0.950	C16-H162	0.950
C16-H163	0.950	C17-C18	1.534(10)
C17-C19	1.539(9)	C17-C20	1.536(9)
C18-H181	0.950	C18-H182	0.950
C18-H183	0.950	C19-H191	0.950
C19-H192	0.950	C19-H193	0.950
C20-H201	0.950	C20-H202	0.950
C20-H203	0.950	C21-C22	1.527(10)
C21-C23	1.549(10)	C21-C24	1.534(10)
C22-H221	0.950	C22-H222	0.950
C22-H223	0.950	C23-H231	0.950
C23-H232	0.950	C23-H233	0.950
C24-H241	0.950	C24-H242	0.950
C24-H243	0.950	C25-C26	1.377(9)
C25-H251	0.950	C26-C27	1.379(11)
C26-H261	0.950	C27-C28	1.373(11)
C27-H271	0.950	C28-C29	1.397(8)
C28-H281	0.950	C29-C30	1.470(9)
C30-C31	1.407(9)	C30-C35	1.386(10)
C31-C32	1.375(10)	C31-H311	0.950
C32-C33	1.380(12)	C32-H321	0.950
C33-C34	1.397(10)	C33-H331	0.950
C34-C35	1.393(9)	C34-H341	0.950
C35-H351	0.964	C36-C37	1.395(8)
C36-C41	1.399(8)	C36-B1	1.647(7)
C37-C38	1.387(8)	C37-H371	0.950
C38-C39	1.382(8)	C38-C42	1.529(7)
C38-C39	1.382(8)	C38-C142	1.500(6)
C39-C40	1.398(8)	C39-H391	0.950
C40-C41	1.381(8)	C40-C43	1.497(5)
C41-H411	0.950	C44-C45	1.401(8)
C44-C49	1.405(8)	C44-B1	1.644(8)
C45-C46	1.379(8)	C45-H451	0.950
C46-C47	1.386(8)	C46-C50	1.501(5)
C47-C48	1.391(8)	C47-H471	0.950
C48-C49	1.389(8)	C48-C51	1.500(8)
C49-H491	0.950	C52-C53	1.400(8)
C52-C57	1.403(8)	C52-B1	1.626(8)
C53-C54	1.384(8)	C53-H531	0.950

C54-C55	1.391(8)	C54-C58	1.502(9)
C55-C56	1.382(8)	C55-H551	0.950
C56-C57	1.394(8)	C56-C59	1.496(5)
C57-H571	0.950	C60-C61	1.409(8)
C60-C65	1.394(8)	C60-B1	1.639(8)
C61-C62	1.396(7)	C61-H611	0.950
C62-C63	1.370(8)	C62-C66	1.503(5)
C63-C64	1.388(9)	C63-H631	0.950
C64-C65	1.405(8)	C64-C67	1.498(9)
C65-H651	0.950		

P1-Ir1-P2	158.02(6)	P1-Ir1-N1	99.20(13)
P2-Ir1-N1	96.61(13)	P1-Ir1-C1	82.15(18)
P2-Ir1-C1	80.43(18)	N1-Ir1-C1	98.7(2)
P1-Ir1-C35	97.25(15)	P2-Ir1-C35	101.68(16)
N1-Ir1-C35	74.3(2)	C1-Ir1-C35	172.8(2)
P1-Ir1-H351	112.4	P2-Ir1-H351	85.4
N1-Ir1-H351	79.6	C1-Ir1-H351	165.4
C35-Ir1-H351	16.7	P1-Ir1-H1	87(3)
P2-Ir1-H1	78(3)	N1-Ir1-H1	172(3)
C1-Ir1-H1	86(3)	C35-Ir1-H1	101(3)
H351-Ir1-H1	93.8	Ir1-P1-C7	97.7(2)
Ir1-P1-C9	116.4(2)	C7-P1-C9	104.7(3)
Ir1-P1-C13	120.7(2)	C7-P1-C13	103.3(3)
C9-P1-C13	110.7(3)	Ir1-P2-C8	98.4(2)
Ir1-P2-C17	112.3(2)	C8-P2-C17	107.0(3)
Ir1-P2-C21	123.3(2)	C8-P2-C21	103.8(3)
C17-P2-C21	109.8(3)	Ir1-N1-C25	123.5(4)
Ir1-N1-C29	118.1(4)	C25-N1-C29	118.4(6)
Ir1-C1-C2	120.0(5)	Ir1-C1-C6	120.4(5)
C2-C1-C6	119.5(6)	C1-C2-C3	119.0(7)
C1-C2-C7	119.4(6)	C3-C2-C7	121.5(7)
C2-C3-C4	120.7(7)	C2-C3-H31	119.1
C4-C3-H31	120.2	C3-C4-C5	119.6(6)
C3-C4-H41	120.4	C5-C4-H41	119.9
C4-C5-C6	120.2(7)	C4-C5-H51	120.5
C6-C5-H51	119.3	C1-C6-C5	120.7(7)
C1-C6-C8	118.4(5)	C5-C6-C8	120.7(6)
C2-C7-P1	108.8(4)	C2-C7-H71	109.7
P1-C7-H71	109.9	C2-C7-H72	109.2
P1-C7-H72	109.6	H71-C7-H72	109.5

C6-C8-P2	107.2(4)	C6-C8-H81	109.8
P2-C8-H81	110.0	C6-C8-H82	110.3
P2-C8-H82	110.0	H81-C8-H82	109.5
P1-C9-C10	113.2(5)	P1-C9-C11	110.7(5)
C10-C9-C11	108.3(6)	P1-C9-C12	108.9(5)
C10-C9-C12	106.8(6)	C11-C9-C12	108.7(6)
C9-C10-H101	109.5	C9-C10-H102	109.9
H101-C10-H102	109.5	C9-C10-H103	109.0
H101-C10-H103	109.5	H102-C10-H103	109.5
C9-C11-H111	109.8	C9-C11-H112	109.9
H111-C11-H112	109.5	C9-C11-H113	108.7
H111-C11-H113	109.5	H112-C11-H113	109.5
C9-C12-H121	109.7	C9-C12-H122	109.8
H121-C12-H122	109.5	C9-C12-H123	108.9
H121-C12-H123	109.5	H122-C12-H123	109.5
P1-C13-C14	111.4(5)	P1-C13-C15	112.8(5)
C14-C13-C15	109.3(6)	P1-C13-C16	107.6(5)
C14-C13-C16	108.2(6)	C15-C13-C16	107.4(6)
C13-C14-H141	109.7	C13-C14-H142	109.6
H141-C14-H142	109.5	C13-C14-H143	109.1
H141-C14-H143	109.5	H142-C14-H143	109.5
C13-C15-H151	109.9	C13-C15-H152	108.8
H151-C15-H152	109.5	C13-C15-H153	109.7
H151-C15-H153	109.5	H152-C15-H153	109.5
C13-C16-H161	109.3	C13-C16-H162	109.9
H161-C16-H162	109.5	C13-C16-H163	109.1
H161-C16-H163	109.5	H162-C16-H163	109.5
P2-C17-C18	109.0(5)	P2-C17-C19	110.1(5)
C18-C17-C19	108.4(6)	P2-C17-C20	113.3(5)
C18-C17-C20	107.6(6)	C19-C17-C20	108.3(6)
C17-C18-H181	110.0	C17-C18-H182	108.5
H181-C18-H182	109.5	C17-C18-H183	109.8
H181-C18-H183	109.5	H182-C18-H183	109.5
C17-C19-H191	109.6	C17-C19-H192	109.6
H191-C19-H192	109.5	C17-C19-H193	109.2
H191-C19-H193	109.5	H192-C19-H193	109.5
C17-C20-H201	109.6	C17-C20-H202	110.3
H201-C20-H202	109.5	C17-C20-H203	108.5
H201-C20-H203	109.5	H202-C20-H203	109.5
P2-C21-C22	111.7(5)	P2-C21-C23	112.8(5)
C22-C21-C23	110.0(6)	P2-C21-C24	108.1(5)
C22-C21-C24	107.4(6)	C23-C21-C24	106.5(6)
C21-C22-H221	109.3	C21-C22-H222	109.4

H221-C22-H222	109.5	C21-C22-H223	109.7
H221-C22-H223	109.5	H222-C22-H223	109.5
C21-C23-H231	109.2	C21-C23-H232	110.0
H231-C23-H232	109.5	C21-C23-H233	109.3
H231-C23-H233	109.5	H232-C23-H233	109.5
C21-C24-H241	109.2	C21-C24-H242	109.5
H241-C24-H242	109.5	C21-C24-H243	109.7
H241-C24-H243	109.5	H242-C24-H243	109.5
N1-C25-C26	123.9(7)	N1-C25-H251	117.7
C26-C25-H251	118.5	C25-C26-C27	117.4(7)
C25-C26-H261	120.9	C27-C26-H261	121.7
C26-C27-C28	120.5(6)	C26-C27-H271	119.7
C28-C27-H271	119.7	C27-C28-C29	119.1(7)
C27-C28-H281	120.9	C29-C28-H281	120.0
C28-C29-N1	120.6(6)	C28-C29-C30	122.2(6)
N1-C29-C30	117.2(5)	C29-C30-C31	120.3(6)
C29-C30-C35	122.0(6)	C31-C30-C35	117.7(6)
C30-C31-C32	120.0(7)	C30-C31-H311	120.0
C32-C31-H311	120.0	C31-C32-C33	122.0(7)
C31-C32-H321	119.0	C33-C32-H321	119.0
C32-C33-C34	118.9(7)	C32-C33-H331	120.4
C34-C33-H331	120.7	C33-C34-C35	119.0(7)
C33-C34-H341	120.6	C35-C34-H341	120.4
C34-C35-C30	122.2(6)	C34-C35-Ir1	128.7(5)
C30-C35-Ir1	100.6(4)	C34-C35-H351	119.6
C30-C35-H351	118.2	Ir1-C35-H351	33.3
C37-C36-C41	115.2(5)	C37-C36-B1	121.2(5)
C41-C36-B1	123.0(5)	C36-C37-C38	122.7(5)
C36-C37-H371	118.5	C38-C37-H371	118.8
C37-C38-C39	120.5(5)	C37-C38-C42	110.9(4)
C39-C38-C42	128.4(5)	C37-C38-C39	120.5(5)
C37-C38-C142	125.4(4)	C39-C38-C142	114.0(4)
C38-C39-C40	118.5(5)	C38-C39-H391	120.6
C40-C39-H391	120.9	C39-C40-C41	119.7(5)
C39-C40-C43	120.5(4)	C41-C40-C43	119.7(4)
C36-C41-C40	123.3(5)	C36-C41-H411	118.2
C40-C41-H411	118.5	C38-C42-F2	110.29(9)
C38-C42-F1	112.22(9)	F2-C42-F1	103.91(9)
C38-C42-F3	115.50(9)	F2-C42-F3	106.04(9)
F1-C42-F3	108.08(9)	C40-C43-F6	110.34(9)
C40-C43-F4	112.23(9)	F6-C43-F4	103.91(9)
C40-C43-F5	115.43(9)	F6-C43-F5	106.06(9)
F4-C43-F5	108.08(9)	C40-C43-F105	110.30(9)

C40-C43-F106	112.24(9)	F105-C43-F106	103.90(9)
C40-C43-F104	115.45(9)	F105-C43-F104	106.08(9)
F106-C43-F104	108.08(9)	C45-C44-C49	115.5(5)
C45-C44-B1	123.2(5)	C49-C44-B1	121.0(5)
C44-C45-C46	122.4(5)	C44-C45-H451	119.0
C46-C45-H451	118.6	C45-C46-C47	121.4(5)
C45-C46-C50	119.3(4)	C47-C46-C50	119.2(4)
C46-C47-C48	117.5(5)	C46-C47-H471	121.2
C48-C47-H471	121.3	C47-C48-C49	121.1(5)
C47-C48-C51	120.4(5)	C49-C48-C51	118.5(5)
C44-C49-C48	122.0(5)	C44-C49-H491	118.8
C48-C49-H491	119.1	C46-C50-F8	110.27(9)
C46-C50-F9	112.25(9)	F8-C50-F9	103.85(9)
C46-C50-F7	115.49(9)	F8-C50-F7	106.00(9)
F9-C50-F7	108.17(9)	C46-C50-F107	110.24(9)
C46-C50-F108	112.28(9)	F107-C50-F108	103.92(9)
C46-C50-F109	115.45(9)	F107-C50-F109	106.02(9)
F108-C50-F109	108.13(9)	C48-C51-F11	112.6(5)
C48-C51-F12	111.9(5)	F11-C51-F12	106.1(5)
C48-C51-F10	112.9(5)	F11-C51-F10	106.6(5)
F12-C51-F10	106.3(5)	C53-C52-C57	115.2(6)
C53-C52-B1	121.6(5)	C57-C52-B1	122.7(5)
C52-C53-C54	122.8(6)	C52-C53-H531	118.2
C54-C53-H531	118.9	C53-C54-C55	120.9(6)
C53-C54-C58	118.7(6)	C55-C54-C58	120.4(6)
C54-C55-C56	117.7(5)	C54-C55-H551	121.3
C56-C55-H551	121.0	C55-C56-C57	121.2(5)
C55-C56-C59	117.4(4)	C57-C56-C59	121.5(4)
C52-C57-C56	122.3(6)	C52-C57-H571	118.8
C56-C57-H571	119.0	C54-C58-F15	112.0(5)
C54-C58-F13	111.3(5)	F15-C58-F13	105.7(6)
C54-C58-F14	113.6(6)	F15-C58-F14	106.7(5)
F13-C58-F14	106.9(5)	C56-C59-F18	110.24(9)
C56-C59-F17	112.31(9)	F18-C59-F17	103.92(9)
C56-C59-F16	115.45(9)	F18-C59-F16	105.94(9)
F17-C59-F16	108.18(9)	C56-C59-F118	110.34(9)
C56-C59-F117	112.15(9)	F118-C59-F117	103.91(9)
C56-C59-F116	115.49(9)	F118-C59-F116	106.10(9)
F117-C59-F116	108.06(9)	C61-C60-C65	116.0(5)
C61-C60-B1	119.2(5)	C65-C60-B1	124.4(5)
C60-C61-C62	121.9(5)	C60-C61-H611	118.7
C62-C61-H611	119.4	C61-C62-C63	121.3(5)
C61-C62-C66	118.6(4)	C63-C62-C66	120.1(4)

C62-C63-C64	118.2(5)	C62-C63-H631	121.0
C64-C63-H631	120.8	C63-C64-C65	120.9(6)
C63-C64-C67	120.7(6)	C65-C64-C67	118.4(6)
C64-C65-C60	121.8(6)	C64-C65-H651	119.2
C60-C65-H651	119.0	C62-C66-F19	110.31(9)
C62-C66-F21	112.21(9)	F19-C66-F21	103.90(9)
C62-C66-F20	115.47(9)	F19-C66-F20	106.06(9)
F21-C66-F20	108.09(9)	C62-C66-F120	110.34(9)
C62-C66-F119	112.21(9)	F120-C66-F119	103.89(9)
C62-C66-F121	115.42(9)	F120-C66-F121	106.06(9)
F119-C66-F121	108.13(9)	C64-C67-F23	112.3(6)
C64-C67-F22	112.7(6)	F23-C67-F22	104.5(5)
C64-C67-F24	112.9(5)	F23-C67-F24	105.0(6)
F22-C67-F24	108.7(6)	C38-C142-F101	110.28(9)
C38-C142-F102	112.30(9)	F101-C142-F102	103.92(9)
C38-C142-F103	115.43(9)	F101-C142-F103	106.08(9)
F102-C142-F103	108.04(9)	C36-B1-C44	103.0(4)
C36-B1-C60	113.6(4)	C44-B1-C60	110.7(5)
C36-B1-C52	113.6(5)	C44-B1-C52	113.2(4)
C60-B1-C52	103.1(4)	Ir1-H351-C35	130.0

Symmetry transformations used to generate equivalent atoms:

Table S16. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $\mathbf{5}^+$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir1	18(1)	18(1)	22(1)	4(1)	2(1)	2(1)
P1	21(1)	29(1)	24(1)	-1(1)	2(1)	4(1)
P2	22(1)	21(1)	30(1)	6(1)	-3(1)	-1(1)
F1	57(6)	34(7)	37(6)	9(5)	23(5)	10(5)
F2	42(5)	92(7)	64(8)	20(6)	22(5)	-3(7)
F3	105(9)	58(6)	54(6)	12(5)	47(7)	16(8)
F4	43(5)	50(4)	54(4)	-12(4)	-21(4)	6(4)
F5	41(4)	89(5)	68(4)	-15(4)	-13(3)	18(4)
F6	75(5)	47(5)	57(5)	8(4)	-39(4)	-4(4)
F7	113(6)	40(4)	43(4)	-9(3)	-9(4)	-2(4)
F8	65(5)	78(7)	52(5)	-27(4)	-26(4)	1(5)
F9	66(7)	78(5)	28(4)	-18(4)	8(4)	-27(5)
F10	32(2)	78(4)	45(3)	34(3)	2(2)	-1(2)
F11	66(3)	25(2)	52(2)	9(2)	-13(2)	4(2)
F12	38(2)	39(2)	46(2)	10(2)	-19(2)	-4(2)
F13	27(2)	41(3)	56(3)	14(2)	-3(2)	7(2)
F14	56(3)	33(2)	46(2)	16(2)	19(2)	3(2)
F15	57(3)	22(2)	42(2)	-4(2)	-1(2)	4(2)
F16	37(3)	74(6)	27(3)	-17(3)	9(2)	4(3)
F17	86(4)	60(3)	74(4)	34(4)	54(4)	36(4)
F18	20(3)	105(7)	55(5)	-16(5)	8(3)	9(4)
F19	48(7)	61(10)	67(8)	26(7)	10(7)	19(8)
F20	37(7)	48(7)	73(10)	-15(8)	-12(8)	0(8)
F21	26(7)	54(10)	48(8)	-6(8)	9(7)	8(8)
F22	60(3)	56(3)	52(3)	-31(2)	-30(2)	24(2)
F23	63(3)	41(3)	40(2)	-10(2)	22(2)	-3(2)
F24	57(3)	25(2)	35(2)	3(2)	6(2)	11(2)
F101	56(5)	61(7)	40(4)	21(5)	20(4)	11(5)
F102	32(4)	69(6)	61(5)	20(4)	9(4)	-19(4)
F103	89(5)	63(5)	70(4)	26(4)	60(5)	33(6)
F104	51(7)	48(5)	77(6)	-20(5)	-28(6)	0(6)
F105	32(6)	70(9)	64(7)	-20(6)	-19(5)	31(6)
F106	56(7)	62(8)	45(6)	13(6)	-16(6)	1(6)
F107	73(7)	43(5)	46(6)	-18(4)	-7(7)	15(6)
F108	73(7)	92(8)	69(8)	-32(6)	-13(6)	-29(9)
F109	95(11)	49(6)	19(5)	3(5)	-14(6)	-8(7)
F116	57(8)	77(10)	46(8)	-2(7)	35(7)	-1(8)

F117	82(9)	45(7)	50(8)	14(7)	41(7)	36(7)
F118	59(10)	82(11)	72(14)	0(9)	-24(10)	25(9)
F119	30(3)	58(4)	72(5)	31(4)	0(3)	11(3)
F120	22(2)	45(4)	69(4)	9(3)	-9(3)	-10(2)
F121	41(3)	76(5)	57(3)	-33(3)	-5(3)	4(3)
N1	22(3)	30(3)	23(2)	4(2)	-2(2)	-5(2)
C1	22(3)	18(3)	42(4)	3(2)	1(3)	-5(2)
C2	19(3)	30(4)	48(4)	2(3)	7(3)	-2(3)
C3	30(4)	29(4)	63(5)	-7(3)	13(4)	1(3)
C4	21(4)	21(3)	83(6)	1(3)	5(3)	1(3)
C5	24(3)	20(3)	66(5)	13(3)	-4(3)	-4(3)
C6	18(3)	17(3)	51(4)	9(3)	2(3)	2(2)
C7	28(4)	35(4)	34(3)	-8(3)	10(3)	0(3)
C8	20(3)	22(3)	45(4)	11(3)	-10(3)	-1(3)
C9	37(4)	41(4)	22(3)	3(3)	3(3)	8(3)
C10	53(4)	59(6)	28(3)	0(3)	1(3)	5(4)
C11	41(4)	53(5)	29(4)	0(3)	-7(3)	16(4)
C12	46(4)	40(4)	29(4)	9(3)	3(3)	8(4)
C13	24(3)	39(4)	39(4)	-5(3)	3(3)	-4(3)
C14	28(3)	54(5)	40(4)	-10(3)	2(3)	-10(3)
C15	38(4)	52(5)	46(5)	-18(4)	-3(4)	-6(4)
C16	35(4)	29(4)	50(4)	-3(3)	4(4)	-12(3)
C17	24(3)	30(4)	42(4)	6(3)	4(3)	-1(3)
C18	30(3)	25(4)	57(4)	7(3)	6(3)	1(3)
C19	34(4)	26(3)	47(4)	8(3)	7(3)	-4(3)
C20	23(3)	32(4)	64(5)	5(3)	-5(3)	0(3)
C21	38(4)	36(4)	30(4)	4(3)	-5(3)	-7(3)
C22	46(4)	38(4)	39(4)	-2(3)	1(3)	-5(3)
C23	50(5)	47(4)	44(4)	5(3)	-19(4)	-9(4)
C24	37(4)	54(5)	28(3)	3(3)	-5(3)	-10(3)
C25	23(3)	29(4)	32(3)	7(3)	-5(3)	-6(3)
C26	33(4)	44(4)	36(4)	13(3)	-14(3)	-20(3)
C27	30(4)	62(5)	23(3)	7(3)	-2(3)	-17(4)
C28	22(3)	53(4)	28(3)	0(3)	-2(2)	-7(3)
C29	19(3)	42(4)	23(3)	-7(3)	0(2)	-4(3)
C30	25(3)	36(4)	20(3)	-5(2)	-1(2)	8(3)
C31	31(4)	48(4)	27(3)	-10(3)	0(3)	7(3)
C32	41(4)	49(4)	39(4)	-13(3)	-5(4)	21(4)
C33	59(5)	34(4)	31(4)	-6(3)	-8(3)	22(4)
C34	45(4)	27(3)	30(4)	1(3)	-2(3)	8(3)
C35	27(3)	32(4)	31(3)	-3(3)	0(3)	11(3)
C36	24(2)	17(2)	23(2)	-3(3)	4(2)	-3(2)
C37	30(3)	21(3)	30(3)	4(2)	4(2)	4(3)

C38	33(3)	22(3)	41(3)	7(2)	13(3)	6(3)
C39	21(3)	27(3)	52(4)	1(3)	8(3)	2(3)
C40	21(3)	21(3)	42(3)	-3(2)	-2(3)	-4(3)
C41	23(3)	23(4)	25(3)	-2(2)	1(2)	-3(2)
C42	35(5)	40(5)	48(5)	17(5)	18(5)	13(6)
C43	27(3)	44(4)	59(4)	-14(3)	-13(3)	10(3)
C44	17(3)	23(3)	24(3)	-2(2)	3(2)	-1(2)
C45	25(3)	22(3)	19(3)	0(2)	-2(2)	-1(2)
C46	20(3)	29(3)	29(3)	-4(3)	-3(2)	1(3)
C47	17(3)	18(3)	38(3)	-3(2)	0(2)	-2(2)
C48	15(3)	24(3)	31(3)	4(2)	0(2)	2(3)
C49	19(3)	29(3)	22(3)	-1(2)	0(3)	2(3)
C50	41(4)	28(4)	32(4)	-4(3)	-6(3)	-4(3)
C51	22(3)	27(3)	36(3)	7(2)	-6(3)	-1(3)
C52	19(3)	22(3)	20(3)	-4(2)	-3(2)	-2(2)
C53	21(3)	24(3)	20(3)	-2(2)	1(3)	-3(3)
C54	20(3)	25(3)	23(3)	-1(2)	-2(2)	-4(2)
C55	25(3)	25(3)	24(3)	-1(2)	3(2)	-6(3)
C56	24(3)	28(4)	26(3)	-5(2)	2(2)	-5(3)
C57	19(3)	24(3)	24(3)	-5(2)	1(2)	0(3)
C58	29(3)	28(3)	33(3)	5(2)	2(3)	2(3)
C59	42(4)	34(4)	49(4)	3(3)	21(3)	8(3)
C60	26(3)	22(3)	21(3)	5(2)	2(2)	-1(3)
C61	23(3)	21(4)	24(3)	-3(2)	1(2)	2(2)
C62	26(3)	35(4)	24(3)	3(2)	-4(2)	-3(3)
C63	30(3)	27(3)	25(3)	0(2)	-9(3)	-4(3)
C64	30(3)	25(3)	21(3)	0(2)	-5(3)	1(3)
C65	23(3)	23(3)	21(3)	1(2)	-5(2)	1(3)
C66	25(3)	48(5)	32(3)	-6(3)	0(3)	1(3)
C67	38(4)	33(4)	22(3)	-3(3)	-7(3)	3(3)
C142	32(4)	48(5)	48(5)	18(5)	13(5)	17(5)
B1	19(3)	23(3)	21(3)	-3(2)	1(2)	2(2)

Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $\mathbf{5}^+$.

	x	y	z	U(eq)
H31	2967	2197	5605	52
H41	4039	1651	6065	48
H51	4117	2547	6605	44
H71	2191	4261	5426	39
H72	1552	3292	5430	39
H81	2864	4067	6979	35
H82	3960	4277	6861	35
H101	256	5532	4856	58
H102	1101	4803	4974	58
H103	-15	4483	5004	58
H111	-849	6329	5292	46
H112	-721	6165	5702	46
H113	-1140	5313	5463	46
H121	952	6808	5246	47
H122	1096	6633	5654	47
H123	1780	6085	5381	47
H141	-1628	3385	6065	49
H142	-890	4061	6277	49
H143	-1427	4470	5938	49
H151	-1191	2682	5484	58
H152	-979	3734	5326	58
H153	-163	2909	5306	58
H161	-290	2114	6021	47
H162	453	2806	6224	47
H163	736	2382	5850	47
H181	4896	5625	5979	44
H182	4554	4759	6227	44
H183	3808	5220	5954	44
H191	4254	7349	6085	46
H192	3477	7549	6387	46
H193	3168	6943	6049	46
H201	5447	6608	6498	50
H202	4745	6783	6824	50
H203	5149	5720	6743	50
H221	2658	7683	7271	50
H222	3349	7582	6937	50
H223	2193	7545	6892	50

H231	3461	6313	7589	57
H232	3553	5257	7421	57
H233	4220	6124	7281	57
H241	1662	6260	7480	44
H242	1746	5225	7296	44
H243	1223	6104	7099	44
H251	1311	3300	6785	36
H261	280	2679	7234	44
H271	-1083	3661	7423	45
H281	-1410	5182	7141	40
H311	-1971	5990	6642	42
H321	-2291	7428	6318	50
H331	-1002	8365	6069	50
H341	672	7795	6125	40
H351	1000	6316	6443	36
H371	4959	5222	8205	33
H391	7732	4791	8616	40
H411	5276	4488	9245	29
H451	3866	6400	9374	29
H471	3704	9118	8905	31
H491	3405	6602	8305	29
H531	4050	3198	9080	27
H551	1953	2928	9862	31
H571	2187	5492	9290	27
H611	1781	5527	8589	28
H631	1180	3640	7767	33
H651	3955	3691	8222	26
H1	2280(60)	5700(60)	6020(20)	50

Table S18. Torsion angles [°] for $\mathbf{5}^{+}$.

C1-Ir1-P1-C9	-136.1(3)	C1-Ir1-P1-C13	85.2(3)
P1-Ir1-P2-C8	-69.4(3)	P1-Ir1-P2-C17	42.9(3)
P1-Ir1-P2-C21	177.9(3)	N1-Ir1-P2-C8	66.4(3)
N1-Ir1-P2-C17	178.7(3)	N1-Ir1-P2-C21	-46.3(3)
C1-Ir1-P2-C8	-31.4(3)	C1-Ir1-P2-C17	81.0(3)
C1-Ir1-P2-C21	-144.1(3)	P1-Ir1-N1-C25	93.0(5)
P1-Ir1-N1-C29	-86.6(4)	P2-Ir1-N1-C25	-71.7(5)
P2-Ir1-N1-C29	108.8(4)	C1-Ir1-N1-C25	9.6(5)
C1-Ir1-N1-C29	-170.0(4)	P1-Ir1-C1-C2	15.9(5)
P1-Ir1-C1-C6	-167.3(5)	P2-Ir1-C1-C2	-150.6(5)
P2-Ir1-C1-C6	26.1(4)	N1-Ir1-C1-C2	114.1(5)
N1-Ir1-C1-C6	-69.2(5)	N1-Ir1-P1-C9	126.4(3)
N1-Ir1-P1-C13	-12.4(3)	C1-Ir1-P1-C7	-25.3(3)
P2-Ir1-P1-C7	12.5(3)	P2-Ir1-P1-C9	-98.2(3)
P2-Ir1-P1-C13	123.0(3)	N1-Ir1-P1-C7	-122.9(3)
Ir1-P1-C7-C2	34.3(5)	C9-P1-C7-C2	154.2(5)
C13-P1-C7-C2	-89.9(5)	C13-P1-C9-C11	50.8(5)
C13-P1-C9-C12	170.3(5)	Ir1-P1-C13-C14	59.4(6)
Ir1-P1-C13-C15	-177.3(4)	Ir1-P1-C13-C16	-59.0(5)
C7-P1-C13-C14	166.9(5)	C7-P1-C13-C15	-69.8(6)
C7-P1-C13-C16	48.5(5)	C9-P1-C13-C14	-81.5(5)
C9-P1-C13-C15	41.8(6)	C9-P1-C13-C16	160.2(5)
Ir1-P1-C9-C12	27.6(5)	C7-P1-C9-C10	39.6(6)
C7-P1-C9-C11	161.5(5)	C7-P1-C9-C12	-79.0(5)
C13-P1-C9-C10	-71.1(6)	Ir1-P1-C9-C10	146.2(4)
Ir1-P1-C9-C11	-91.9(5)	Ir1-P2-C17-C20	-177.1(4)
C8-P2-C17-C20	-70.2(6)	C21-P2-C17-C18	161.5(5)
C21-P2-C17-C19	-79.7(5)	C21-P2-C17-C20	41.9(6)
Ir1-P2-C21-C22	-85.2(6)	C8-P2-C17-C18	49.5(5)
C8-P2-C17-C19	168.3(5)	Ir1-P2-C8-C6	36.3(4)
C17-P2-C8-C6	-80.1(5)	C21-P2-C8-C6	163.8(4)
Ir1-P2-C17-C18	-57.5(5)	Ir1-P2-C17-C19	61.4(5)
C17-P2-C21-C24	168.7(5)	C17-P2-C21-C23	-73.8(6)
C8-P2-C21-C22	164.7(5)	Ir1-P2-C21-C23	150.4(4)
Ir1-P2-C21-C24	32.8(6)	C17-P2-C21-C22	50.6(6)
C8-P2-C21-C23	40.4(6)	C8-P2-C21-C24	-77.2(5)
C37-C36-C41-C40	-0.4(8)	C41-C36-B1-C60	-145.5(5)
B1-C36-C41-C40	-171.8(5)	C37-C36-B1-C44	-76.1(6)
C37-C36-B1-C52	160.9(5)	C37-C36-B1-C60	43.7(8)
C41-C36-B1-C44	94.8(6)	C41-C36-B1-C52	-28.2(7)
B1-C36-C37-C38	170.4(5)	C41-C36-C37-C38	-1.1(9)

C36-C37-C38-C39	1.6(9)	C36-C37-C38-C142	-174.7(5)
C37-C38-C39-C40	-0.5(9)	C142-C38-C39-C40	176.2(5)
C37-C38-C142-F101	16.4(8)	C37-C38-C142-F102	131.7(7)
C37-C38-C142-F103	-103.9(8)	C39-C38-C142-F102	-44.8(7)
C39-C38-C142-F103	79.6(8)	C39-C38-C142-F101	-160.2(6)
C38-C39-C40-C41	-0.9(9)	C38-C39-C40-C43	-177.0(5)
C43-C40-C41-C36	177.6(5)	C39-C40-C43-F4	114.3(7)
C39-C40-C41-C36	1.5(9)	C41-C40-C43-F4	-61.7(8)
C39-C40-C43-F5	-10.1(9)	C39-C40-C43-F6	-130.3(6)
C41-C40-C43-F5	173.9(8)	C41-C40-C43-F6	53.6(7)
B1-C44-C49-C48	-174.1(6)	C49-C44-B1-C60	-32.9(7)
B1-C44-C45-C46	174.2(5)	C45-C44-B1-C36	-85.0(6)
C45-C44-B1-C52	38.1(7)	C45-C44-B1-C60	153.2(5)
C49-C44-B1-C36	88.8(6)	C49-C44-B1-C52	-148.0(5)
C49-C44-C45-C46	0.0(9)	C45-C44-C49-C48	0.2(9)
C44-C45-C46-C47	0.2(9)	C44-C45-C46-C50	179.1(5)
C45-C46-C47-C48	-0.6(8)	C50-C46-C47-C48	-179.5(5)
C45-C46-C50-F7	-177.1(7)	C45-C46-C50-F8	62.8(7)
C45-C46-C50-F9	-52.5(7)	C47-C46-C50-F7	1.8(8)
C47-C46-C50-F9	126.4(6)	C47-C46-C50-F8	-118.4(6)
C46-C47-C48-C51	-177.8(5)	C46-C47-C48-C49	0.9(9)
C47-C48-C49-C44	-0.7(10)	C47-C48-C51-F10	101.3(7)
C47-C48-C51-F11	-19.5(9)	C51-C48-C49-C44	178.1(6)
C49-C48-C51-F10	-77.5(7)	C49-C48-C51-F11	161.7(6)
C47-C48-C51-F12	-138.9(6)	C49-C48-C51-F12	42.4(8)
C53-C52-B1-C44	-157.4(5)	C53-C52-B1-C60	83.1(6)
C57-C52-C53-C54	-1.4(8)	B1-C52-C53-C54	-173.0(5)
C53-C52-C57-C56	1.1(8)	C57-C52-B1-C36	148.9(5)
C57-C52-B1-C44	31.7(7)	C57-C52-B1-C60	-87.9(6)
B1-C52-C57-C56	172.5(5)	C53-C52-B1-C36	-40.2(7)
C52-C53-C54-C55	0.5(9)	C52-C53-C54-C58	-179.8(6)
C58-C54-C55-C56	-178.9(6)	C53-C54-C55-C56	0.9(9)
C53-C54-C58-F14	171.3(6)	C53-C54-C58-F15	-67.6(8)
C55-C54-C58-F13	-129.7(6)	C55-C54-C58-F14	-8.9(9)
C55-C54-C58-F15	112.2(7)	C53-C54-C58-F13	50.5(7)
C54-C55-C56-C57	-1.2(9)	C54-C55-C56-C59	179.7(5)
C55-C56-C59-F16	48.3(7)	C55-C56-C59-F17	172.9(5)
C59-C56-C57-C52	179.2(5)	C57-C56-C59-F16	-130.8(6)
C57-C56-C59-F17	-6.2(7)	C55-C56-C59-F18	-71.7(6)
C55-C56-C57-C52	0.2(8)	C57-C56-C59-F18	109.2(6)
C65-C60-B1-C52	-99.5(6)	B1-C60-C61-C62	-171.3(5)
C61-C60-C65-C64	-0.2(8)	B1-C60-C65-C64	171.9(5)
C61-C60-B1-C36	-164.4(5)	C61-C60-B1-C44	-49.0(7)

C65-C60-B1-C44	139.2(6)	C65-C60-C61-C62	1.2(8)
C65-C60-B1-C36	23.8(8)	C61-C60-B1-C52	72.4(6)
C60-C61-C62-C66	177.5(5)	C60-C61-C62-C63	-1.8(8)
C61-C62-C66-F119	103.8(6)	C61-C62-C63-C64	1.2(8)
C66-C62-C63-C64	-178.1(5)	C61-C62-C66-F121	-20.7(7)
C63-C62-C66-F119	-76.9(7)	C63-C62-C66-F120	38.5(6)
C63-C62-C66-F121	158.6(6)	C61-C62-C66-F120	-140.8(5)
C62-C63-C64-C65	-0.2(9)	C62-C63-C64-C67	177.9(5)
C63-C64-C67-F22	13.5(9)	C63-C64-C67-F23	131.2(6)
C63-C64-C67-F24	-110.2(7)	C65-C64-C67-F22	-168.4(6)
C65-C64-C67-F23	-50.7(8)	C65-C64-C67-F24	67.9(8)
C63-C64-C65-C60	-0.3(9)	C67-C64-C65-C60	-178.4(6)
Ir1-N1-C25-C26	178.7(5)	C29-N1-C25-C26	-1.7(9)
Ir1-N1-C29-C28	-176.4(4)	Ir1-N1-C29-C30	4.7(7)
C25-N1-C29-C28	4.0(9)	C25-N1-C29-C30	-174.9(6)
Ir1-C1-C2-C3	-177.9(5)	Ir1-C1-C2-C7	4.4(8)
C6-C1-C2-C3	5.4(9)	C6-C1-C2-C7	-172.4(6)
Ir1-C1-C6-C5	177.7(5)	Ir1-C1-C6-C8	-7.4(8)
C2-C1-C6-C5	-5.6(9)	C2-C1-C6-C8	169.3(6)
C1-C2-C3-C4	-2.6(10)	C7-C2-C3-C4	175.1(6)
C1-C2-C7-P1	-29.0(7)	C3-C2-C7-P1	153.3(6)
C2-C3-C4-C5	-0.1(10)	C3-C4-C5-C6	-0.1(10)
C4-C5-C6-C1	2.9(10)	C4-C5-C6-C8	-171.9(6)
C1-C6-C8-P2	-23.2(7)	C5-C6-C8-P2	151.7(5)
N1-C25-C26-C27	-1.1(10)	C25-C26-C27-C28	1.6(10)
C26-C27-C28-C29	0.6(10)	C27-C28-C29-N1	-3.4(9)
C27-C28-C29-C30	175.4(6)	N1-C29-C30-C31	150.5(6)
N1-C29-C30-C35	-28.5(9)	C28-C29-C30-C31	-28.4(9)
C28-C29-C30-C35	152.6(6)	C29-C30-C31-C32	179.6(6)
C35-C30-C31-C32	-1.4(10)	C29-C30-C35-C34	-178.5(6)
C31-C30-C35-C34	2.5(10)	C30-C31-C32-C33	-0.6(11)
C31-C32-C33-C34	1.5(11)	C32-C33-C34-C35	-0.4(10)
C33-C34-C35-C30	-1.6(10)		

Symmetry transformations used to generate equivalent atoms:

9. References

[1] M. Gupta, C. Hagen, R. J. Flesher, W. C. Kaska and C. M. Jensen, *Chem. Commun*. 1996, 2083–2084.
[2] C. J. Moulton and B. L. Shaw, *J. Chem. Soc. Dalton Trans.* 1976, 1020–1024.
[3] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics* 2010, **29**, 2176–2179.
[4] E. D. Becker, *High Resolution NMR, 2nd Edition*. Academic Press: New York, NY, 1980. Pgs. 163–166.
[5] X. Zhang, M. Kanzelberger, T. J. Emge and A. S. Goldman, *J. Am. Chem. Soc*., 2004, **126**, 13192–13193.
[6] D. A. Laviska, PhD Thesis, Rutgers University, 2013.
[7] A. Casuras, PhD Thesis, Rutgers University, 2019.
[8] Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
[9] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865-3868.
[10] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* 1997, **78**, 1396.
[11] C. Adamo and V. Barone, *J. Chem. Phys.* 1999, **110**, 6158–6169.
[12] P. J. Hay and W. R. Wadt, *J. Chem. Phys.* 1985, **82**, 270–283.
[13] P. J. Hay and W. R. Wadt, *J. Chem. Phys.* 1985, **82**, 299–310.
[14] W. R. Wadt and P. J. Hay, *J. Chem. Phys.* 1985, **82**, 284–298.
[15] A. D. McLean and G. S. Chandler, *J. Chem. Phys.* 1980, **72**, 5639–5648.
[16] K. Raghavachari, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.* 1980, **72**, 650–654.
[17] GaussView, Version 6, Roy Dennington, Todd A. Keith, and John M. Millam. Semichem Inc., Shawnee Mission, KS, 2016.
[18] SAINT, Bruker Analytical X-Ray Systems, Madison, WI.
[19] R. Blessing, *Acta Cryst. A*. 1995, **51**, 33–38.
[20] L. Palatinus and G. Chapuis, *J. Appl. Cryst*. 2007, **40**, 786–790.
[21] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Cryst*. 2003, **36**, 1487.