

Supporting Information

Systematic dismantling of a carefully designed PC_{carbene}P pincer ligand via C-C bond activations at an iridium centre

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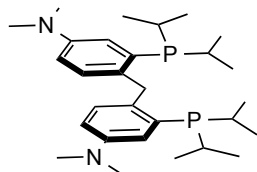
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Experimental Details

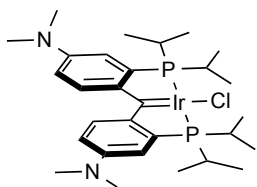
General Considerations. Storage and manipulation of all compounds were performed under an argon atmosphere either in a VAC glove box or using a double manifold high vacuum line using standard techniques. Passage of argon through a OxisorBW scrubber (Matheson Gas Products) removed any residual oxygen and moisture. Toluene and tetrahydrofuran were dried and purified using a Grubbs/Dow solvent purification system and stored in 500 mL thick-walled vessels over sodium/benzophenone ketal. *n*-Pentane was purified using a M-Braun solvent purification system, dried over sodium/benzophenone ketal and stored in a 100 mL thick-walled vessel. Benzene C₆D₆ was dried over sodium/benzophenone ketal and stored in a 100 mL thick-walled vessel. All dried solvents were degassed and vacuum distilled prior to use. ¹H and ¹³C NMR chemical shifts were referenced to residual solvent protons and naturally abundant ¹³C resonances for all deuterated solvents. Chemical shift assignments are based on ¹H, ¹H{³¹H}, ¹³C{¹³P}, ³¹P{¹H}, ¹H-¹H-COSY, ¹H-¹³C-HSQC and ¹H-¹³C- HMBC NMR experiments performed on Ascend-500 or Avance-600 MHz spectrometers. X-ray crystallographic analyses were performed on a Nonius system equipped with a Bruker Apex-II CCD using samples coated in Paratone 8277 oil (Exxon) and mounted on a glass fibre. Full crystallography details can be found in independently uploaded .cif files (CCDC numbers 1403689-1403692). Hydrogen gas (99.999%) was purchased from Praxair and used after passing through a OxisorBW scrubber (Matheson Gas Products) to remove any residual oxygen and moisture. Nitrous oxide (99%), 3-Bromo-*N,N*-dimethylaniline (97%), and ¹Pr₂PCl (96%) were purchased from Sigma-Aldrich and used as received. Iridium (III) chloride hydrate was purchased from Pressure Chemicals Inc. and used as received. 4,4'-methylenebis(3-bromo-*N,N*-dimethylaniline)¹ and [Ir(COE)₂(Cl)]₂² were prepared by literature methods. All other reagents were purchased from Sigma-Aldrich and used as received. Elemental and mass spectrometric analyses were performed by staff at the Instrumentation Facility in the Department of Chemistry, University of Calgary.



Synthesis of Proligand (1) – THF (50mL) was vacuum transferred at -78°C to a 150mL two-neck round bottom flask charged with 4,4'-methylenebis(3-bromo-*N,N*-dimethylaniline) (2.000 g, 4.847 mmol) and a teflon stirbar. ^tBuLi (11.4 mL, 1.7 M, 19.39 mmol)

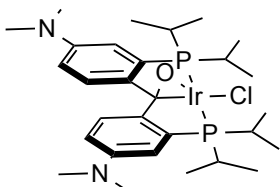
was added dropwise to the solution *via* a syringe over the course of 20 minutes. A slight colour change from colourless to pale yellow was observed. After two hours of stirring at -78°C , ⁱPr₂PCl (1.54 mL, 9.693 mmol) was added *via* syringe. The mixture was stirred for 18 hours while slowly warming to room temperature. Solvent was removed *in vacuo* and replaced with 35mL of *n*-pentane. Filtration using a PTFE 0.2 μm syringe filter was performed on the resulting mixture and a viscous solution was isolated after rotary evaporation under atmospheric conditions. Sonication was performed on the resulting liquid with approximately 3 mL of MeOH until a white precipitate formed. The product was isolated using vacuum filtration and a white solid obtained with a 75% yield (1.769 g, 3.635 mmol).

¹H NMR (500 MHz, C₆D₆) δ 7.22 (dd, $J_{\text{HH}} = 8.6$ Hz, $J_{\text{HP}} = 4.4$ Hz, 2H, ArH), 6.99 (dd, $J_{\text{HH}} = J_{\text{HP}} = 2.7$ Hz, 2H, ArH), 6.63 (dd, $J_{\text{HH}} = 2.7$ Hz, $J_{\text{HH}} = 8.6$ Hz, 2H, ArH), 5.16 (t, $J_{\text{HP}} = 2.7$ Hz, 2H, CH₂), 2.60 (s, 12H, N(CH₃)₂), 2.13 (sept, $J = 6.9$ Hz, 4H, CH(CH₃)₂), 1.21 (dd, $J_{\text{HH}} = 6.9$, $J_{\text{HP}} = 14.5$ Hz, 12H, CH(CH₃)₂), 1.10 (dd, $J_{\text{HH}} = 6.9$ Hz, $J_{\text{HP}} = 11.4$ Hz, 12H, CH(CH₃)₂). ¹³C{¹H} NMR (126 MHz, C₆D₆) 148.7 (s, aryl C), 138.7 (d, $J_{\text{CP}} = 27.5$ Hz, aryl C), 135.0 (d, $J_{\text{CP}} = 20.0$ Hz, aryl C), 131.4 (d, $J_{\text{CP}} = 7.1$ Hz, aryl CH), 117.0 (d, $J_{\text{CP}} = 2.5$ Hz, aryl CH), 114.6 (s, aryl CH), 40.7 (s, N(CH₃)₂), 37.5 (t, $J_{\text{CP}} = 25.6$ Hz, Ar-CH₂-Ar), 24.9 (d, $J_{\text{CP}} = 14.7$ Hz, CH(CH₃)₂), 20.7 (d, $J_{\text{CP}} = 20.0$ Hz, CH(CH₃)₂), 19.9 (d, $J_{\text{CP}} = 11.1$ Hz, CH(CH₃)₂). ³¹P{¹H} NMR (203 MHz, C₆D₆) δ -5.42 (s). Elemental Anal. Calcd. (%) for C₂₉H₄₈N₂P₂: C 71.57; H 9.94; N 5.76. Found C 71.74; H 10.17; N 5.77.



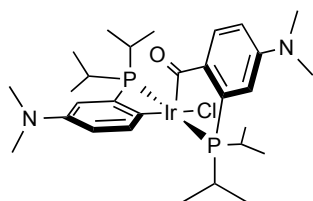
Synthesis of PCPNMe=IrCl (2) - Under an atmosphere of argon, toluene (15 mL) was added to a 50 mL round bottom flask equipped with **1** (0.217 g, 0.446 mmol), [Ir(COE)₂Cl]₂ (0.200 g, 0.223 mmol) and a teflon stir bar. The mixture was heated to 80 °C and stirred for 4 hours. Solvent was removed *in vacuo* and the resulting dark green solid was washed with pentane (3 x 5 mL) and dried under high vacuum at 150°C for 2 hours. A dark green solid (0.258 g, 0.362 mmol) was obtained with an 81% yield. X-ray quality crystals were grown by slow evaporation of a concentrated solution of **2** dissolved in pentane at room temperature.

¹H{³¹P} NMR (500 MHz, C₆D₆) δ 8.22 (d, *J* = 8.7 Hz, 2H, ArH), 6.68 (d, *J* = 2.4 Hz, 2H, ArH), 5.92 (dd, *J* = 2.4, 8.7 Hz, 2H, ArH), 3.13 (sept, *J* = 7.1 Hz, 4H, -CH(CH₃)₂), 2.18 (s, 12H, N(CH₃)₂), 1.67 (d, *J* = 7.1 Hz, -CH(CH₃)₂), 1.40 (d, *J* = 7.1 Hz, -CH(CH₃)₂). ¹³C {¹H} NMR (126 MHz, C₆D₆) δ 204.0 (t, *J*_{CP} = 3.2 Hz, Ir=C), 165.6 (vt, *J*_{CP} = 17.7 Hz, aryl C), 150.0 (vt, *J*_{CP} = 3.4 Hz, aryl C), 140.6 (vt *J*_{CP} = 18.0 Hz, aryl C), 124.7 (vt, *J*_{CP} = 7.7 Hz, aryl CH), 116.8 (s, aryl CH), 114.9 (s, aryl CH), 40.0 (s, N(CH₃)₂), 25.0 (vt, *J*_{CP} = 12.9 Hz, CH(CH₃)₂), 20.1 (vt, *J*_{CP} = 2.5 Hz, CH(CH₃)₂), 19.4 (s, CH(CH₃)₂). ³¹P {¹H} NMR (203 MHz, C₂D₂) δ 48.6 (s). Elemental Anal. Calcd. (%) for C₂₉H₄₆ClIrN₂P₂: C 48.90; H 6.51; N 3.93. Found: C 48.79; H, 6.65; N 3.99.



Synthesis of PCPNMe(O)Ir(Cl) (3) – Toluene (5 mL) was vacuum transferred into a round bottom flask (25 mL) loaded with **2** (0.100 g, 0.140 mmol) and a teflon stir bar. The argon atmosphere was evacuated at -78 °C and replaced with 1 atm. of N₂O. The mixture was stirred for 15 minutes at room temperature. Toluene was removed *in vacuo* until approximately 1 mL remained. *n*-pentane (5 mL) was added and the mixture was stirred until a precipitate formed. The toluene and *n*-pentane were removed *in vacuo* and the remaining bright red solid was washed with *n*-pentane (3 x 1 mL). The isolated solid was dried under high vacuum at 40 °C and 0.083 g (82%, 0.113 mmol) of a red crystalline solid were obtained. X-ray quality crystals were obtained by slow evaporation of toluene at room temperature.

$^1\text{H}\{^{31}\text{P}\}$ NMR (500 MHz, C_6D_6) δ 7.99 (d, $J = 8.7$ Hz, 2H, ArH), 6.68 (d, $J = 2.4$ Hz, 2H, ArH), 6.63 (dd, $J = 2.4, 8.7$ Hz, 2H, ArH), 3.10 (sept, 6.9 Hz, 2H, CH(CH₃)), 2.82 (sept, 6.9 Hz, 2H, CH(CH₃)), 2.50 (s, 12H, N(CH₃)₂), 1.54 (d, $J = 6.9$ Hz, 6H, CH(CH₃)₂), 1.51 (d, $J = 6.9$ Hz, 6H, CH(CH₃)₂), 1.41 (d, $J = 6.9$ Hz, 6H, CH(CH₃)₂), 1.28 (d, $J = 6.9$ Hz, 6H, CH(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6) 148.1 (vt, $J = 3.8$ Hz, aryl C), 140.2 (vt, $J_{\text{CP}} = 7.9$ Hz, aryl C), 132.4 (vt, $J_{\text{CP}} = 18.9$ Hz, aryl C), 125.9 (vt, $J_{\text{CP}} = 6.0$ Hz, aryl CH), 114.7 (s, aryl CH), 111.9 (s, aryl CH), 82.4 (t, $J_{\text{CP}} = 2.8$ Hz, C(O)Ir), 39.2 (s, N(CH₃)₂), 23.5 (vt, $J_{\text{CP}} = 13.1$ Hz, CH(CH₃)₂), 22.5 (vt, $J_{\text{CP}} = 14.9$ Hz, CH(CH₃)₂), 19.6 (vt, $J = 2.7$ Hz, CH(CH₃)₂), 18.3 (vt, $J_{\text{CP}} = 1.7$ Hz, CH(CH₃)₂), 17.6 (vt, $J_{\text{CP}} = 2.2$ Hz, CH(CH₃)₂), 16.5 (s, CH(CH₃)₂). $^{31}\text{P}\{^1\text{H}\}$ NMR (203 MHz, C_6D_6) δ 28.6(s). Elemental Anal. Calcd. (%) for $\text{C}_{29}\text{H}_{48}\text{N}_2\text{ClIrOP}_2$: C 47.83; H 6.37; N 3.85. Found C 48.18; H 6.42; N 3.77.

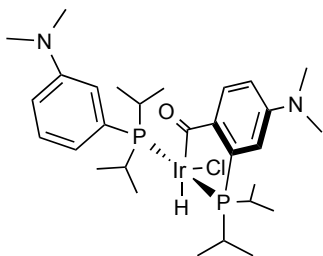


Synthesis of C-C Cleaved PCPNMe(O)IrCl (4) – Toluene (5 mL) was vacuum transferred into a round bottom flask (25 mL) loaded with **2** (0.100 g, 0.140 mmol) and a teflon stir bar. The argon atmosphere was evacuated at -78 °C and replaced

with 1 atm. of N_2O . The mixture was heated to 70 °C and stirred for 18 hours. Toluene was removed *in vacuo* until approximately 1 mL remained. *n*-pentane (5 mL) was added and the mixture was stirred until a precipitate formed. The remaining toluene and *n*-pentane were removed *in vacuo* and an air stable orange crystalline solid was obtained with >98% yield (0.100 g, 0.137 mmol). The product was also obtained in quantitative yield by stirring **4** (0.050 g, 0.069 mmol) at room temperature in toluene (5 mL) under an atmosphere of H_2 for 5 minutes and then removing the solvent *in vacuo*. X-ray quality crystals were grown at room temperature from a solution of **4** dissolved in toluene and layered with pentane

$^1\text{H}\{^{31}\text{P}\}$ NMR (500 MHz, C_6D_6) δ 7.73 (d, $J = 8.7$ Hz, 1H, ArH), 6.70 (s, ArH), 6.37 (s, 1H, ArH), 6.32 (d, $J = 8.6$ Hz, 1H, ArH), 6.16 (dd, $J = 2.5, 8.6$ Hz, 1H, ArH), 6.11 (d, $J = 8.7$ Hz, 1H, ArH), 3.31 (sept, $J = 7.0$ Hz, 1H, CH(CH₃)₃), 3.14 (sept, $J = 7.0$ Hz, 1H,

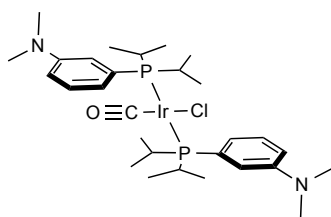
CH(CH₃)₃), 2.88 – 2.74 (m, 2H, CH(CH₃)₃), 2.41 (s, 6H, N(CH₃)₂), 2.37 (s, 6H, N(CH₃)₂), 1.79 (d, *J* = 7.1 Hz, 3H, CH(CH₃)₂), 1.57 (d, *J* = 7.1 Hz, CH(CH₃)₂), 1.53 – 1.47 (m, 9H, CH(CH₃)₂), 1.32 (d, *J* = 7.1 Hz, CH(CH₃)₂), 1.20 (d, *J* = 7.1 Hz, CH(CH₃)₂), 1.07 (d, *J* = 7.1 Hz, CH(CH₃)₂). ¹³C{¹H} NMR (126 MHz, C₆D₆) δ 180.9 (s, acyl CO), 151.2 (d, *J*_{CP} = 6.5 Hz, aryl C), 149.0 (d, *J*_{CP} = 41.8 Hz, aryl C), 147.7 (d, *J*_{CP} = 8.2 Hz, aryl C), 143.8 (d, *J*_{CP} = 31.7, aryl C) 139.4, (dd, *J*_{CP} = 2.7, 37.8 Hz, aryl C), 134.2 (dd, *J*_{CP} = 2.4, 15.5 Hz, aryl CH), 126.2 (d, *J*_{CP} = 16.4 Hz, aryl CH), 116.2 (d, *J*_{CP} = 2.8 Hz, aryl CH), 114.8 (s, aryl CH), 113.8 (s, aryl CH), 112.9 (dd, *J*_{CP} = 1.9, 11.0 Hz, aryl C), 110.3 (d, *J*_{CP} = 3.2 Hz, aryl CH), 40.6 (s, N(CH₃)₂), 39.7 (s, N(CH₃)₂), 24.8 (dd, *J*_{CP} = 4.3, 17.5 Hz, CH(CH₃)₂), 24.4 (dd, *J*_{CP} = 4.5, 16.8 Hz, CH(CH₃)₂), 23.0 (overlapping vt, *J*_{CP} = 27.3 Hz, CH(CH₃)₂), 20.6 (d, *J*_{CP} = 3.9 Hz, CH(CH₃)₂), 20.4 (s, CH(CH₃)₂), 20.0 (d, *J*_{CP} = 3.6 Hz, CH(CH₃)₂), 19.9 (d, *J*_{CP} = 3.3 Hz, CH(CH₃)₂), 19.5 (d, *J*_{CP} = 1.6 Hz, CH(CH₃)₂), 19.0 (vt, *J*_{CP} = 2.8, CH(CH₃)₂), 18.6 (s, CH(CH₃)₂), 16.9 -16.8 (m, CH(CH₃)₂). ³¹P{¹H} NMR (203 MHz, C₆D₆) 50.8 (d, *J*_{CP} = 344), -30.1 (d, *J*_{CP} = 344). IR (NaCl) 1622cm⁻¹ (acyl CO). Elemental Anal. Calcd. (%) for C₂₉H₄₈N₂ClIrOP₂: C 47.83; H 6.37; N 3.85. Found C 47.93; H 6.08; N 3.73.



Synthesis of C-C Cleaved PCPNMe(O)IrCl hydrido complex (5) – Compound **4** (0.030 g, 0.041 mmol) was loaded into a 25 mL thick walled round bottom pressure vessel equipped with a teflon stir bar. The red solid was dissolved in toluene (2 mL). The solution was cooled to -78

°C and the atmosphere was evacuated using high vacuum. H₂ (1 atm) was then added to the flask. The vessel was sealed, heated to 60°C and stirred for 30 hours. Toluene was removed *in vacuo*. The remaining yellow oil was re-dissolved in benzene (0.5 mL) and layered with *n*-pentane. The solution was cooled to -20 °C for 18 hours. A yellow solid was isolated by decanting the supernatant and dried under high vacuum for 3 hours at room temperature. Compound **5** was obtained as a yellow-orange solid in 67% yield (0.020 g, 0.027 mmol).

$^1\text{H}\{^{31}\text{P}\}$ NMR (500 MHz, C_6D_6) δ 7.97-7.97 (br m, 1H, ArH), 7.86 (d, J = 8.7 Hz, 1H, ArH) 7.24 (t, J = 7.8 Hz, 1H, ArH), 7.10 (d, J = 7.5 Hz, 1H, ArH), 6.60 (dd, J = 8.3, 2.3 Hz, 1H, ArH), 6.53 (d, J = 2.4 Hz, 1H, ArH), 6.19 (dd, J = 8.7, 2.4 Hz, 1H, ArH), 3.42 (sept, J = 7.1 Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 3.19 (sept, J = 7.1 Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 3.13 (sept, J = 7.1 Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 2.66 (s, 6H, $\text{N}(\text{CH}_3)_2$), 2.56 (sept, J = 7.1 Hz, $\text{CH}(\text{CH}_3)_2$), 2.35 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.51 (d, J = 7.1 Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.41-1.35 (m, 9H, $\text{CH}(\text{CH}_3)_2$), 1.33 (d, J = 7.1 Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.20 (d, J = 7.1 Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.14 (overlapping d, J = 7.1, 7.1 Hz, 6H, $\text{CH}(\text{CH}_3)_2$), -22.7 (s, 1H, Ir-H) or (^1H NMR dd, $^2J_{\text{HP}}$ = 10.1 and 15.8 Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6) δ 182.1 (s, acyl CO), 151.4 (d, J_{CP} = 6.7 Hz, aryl C), 150.4 (d, J_{CP} = 12.7 Hz, aryl C), 145.8 (d, J_{CP} = 30.1 Hz, aryl C), 139.0 (dd, J_{CP} = 2.2, 41.3 Hz, aryl C), 132.4 (dd, J_{CP} = 2.7, 38.6 Hz, aryl C), 128.4 (m, aryl CH) 125.0 (d, J_{CP} = 16.1 Hz, aryl CH), 122.5 (d, J_{CP} = 18.2 Hz, aryl CH), 120.7 (dd, dd, J_{CP} = 2.2, 3.9 Hz aryl CH), 113.9 (dd, J_{CP} = 1.9, 3.3 Hz, aryl CH), 110.3 (d, J_{CP} = 3.4 Hz, aryl CH), 40.4 (s, $\text{N}(\text{CH}_3)_2$), 39.8 (s, $\text{N}(\text{CH}_3)_2$), 26.4 (dd, J_{CP} = 2.3, 25.4 Hz, $\text{CH}(\text{CH}_3)_2$), 25.0 (dd, J_{CP} = 2.0, 25.9 Hz, $\text{CH}(\text{CH}_3)_2$), 22.6 (d, J_{CP} = 32.1 Hz, $\text{CH}(\text{CH}_3)_2$), 21.5 (dd, J_{CP} = 3.2, 25.0 Hz, $\text{CH}(\text{CH}_3)_2$), 20.3 (s, $\text{CH}(\text{CH}_3)_2$), 20.2 (d, J_{CP} = 2.9 Hz, $\text{CH}(\text{CH}_3)_2$), 20.0 (d, J = 2.7 Hz, $\text{CH}(\text{CH}_3)_2$), 19.7 (d, J = 2.9 Hz, $\text{CH}(\text{CH}_3)_2$), 19.6 (s, $\text{CH}(\text{CH}_3)_2$), 18.9 (d, J_{CP} = 2.5 Hz, $\text{CH}(\text{CH}_3)_2$), 18.2 (d, J_{CP} = 5.3 Hz, $\text{CH}(\text{CH}_3)_2$), 16.7 (dd, J_{CP} = 2.9, 5.7 Hz $\text{CH}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (203 MHz, C_6D_6) δ 58.5 (d, J = 334 Hz), 42.9 (d, J = 334 Hz). IR (NaCl) 2199 cm^{-1} (Ir-H), 1615 cm^{-1} (acyl CO). MS (ESI+) for $\text{C}_{29}\text{H}_{48}\text{ClIrN}_2\text{OP}_2$; m/z calcd $\text{C}_{29}\text{H}_{48}\text{ClIrN}_2\text{OP}_2$ m/z [M+1]: 731.2632 (100%); found m/z [M+1]: 731.2604 (100%).



Synthesis of Vaska's Analog (6) – 4 (0.050 g, 0.069 mmol) was dissolved with toluene (4 mL) in a 25 mL round bottom thick walled pressure vessel equipped with a teflon stir bar. The vessel was cooled to -78 °C and placed under static high

vacuum. After allowing the mixture to warm to room temperature 1 atm. of H_2 was introduced. The flask was sealed and stirred for 48 hrs at 120 °C. The mixture was cooled to room temperature and the toluene was removed *in vacuo* until ~0.5 mL remained. *n*-pentane was added to induce precipitation. All liquid was then removed *in vacuo* and the

product was left to dry at room temperature under high vacuum. **6** was obtained as a yellow solid with >99% yield (0.050 g, 0.068 mmol). **6** was also obtained in quantitative yield by heating a mixture of **5** in toluene to 120°C for 30 hours. X-ray quality crystals were grown from a solution of **6** dissolved in toluene layered with *n*-pentane.

$^1\text{H} \{^{31}\text{P}\}$ NMR (500 MHz, C_6D_6) δ 7.63 -7.60 (br m, 1H), 7.19 (t, $J = 7.8$ Hz, 1H), 7.10 (d, $J = 7.5$ Hz, 1H), 6.55 (dd, $J = 8.2, 2.6$ Hz), 3.09 (sept, $J = 6.9$ Hz, 2H), 2.62 (s, 6H), 1.46 (d, $J = 6.9$, 12H), 1.18 (d, $J = 6.9$ Hz, 6H). $^{13}\text{C} \{^1\text{H}\}$ NMR (151 MHz, C_6D_6) δ 172.1 (t, $J_{\text{CP}} = 11.44$ Hz Ir(CO)), 149.9 (vt, $J_{\text{CP}} = 5.7$ Hz, aryl C), 129.1 (vt, $J_{\text{CP}} = 22.2$ Hz, aryl C), 122.0 (vt, $J_{\text{CP}} = 3.7$ Hz, aryl CH), 121.7 (vt, $J_{\text{CP}} = 7.9$ Hz, aryl CH), 40.2 (s, $\text{N}(\text{CH}_3)_2$), 22.2 (vt, $J_{\text{CP}} = 15.1$ Hz, $\text{CH}(\text{CH}_3)_2$), 19.1 (vt, $J_{\text{CP}} = 2.2$ Hz, $\text{CH}(\text{CH}_3)_2$), 18.2 (s, $\text{CH}(\text{CH}_3)_2$). $^{31}\text{P} \{^1\text{H}\}$ NMR (243 MHz, C_6D_6) δ 42.5 (s). IR (NaCl) 1952 cm^{-1} . MS (ESI+) for $\text{C}_{29}\text{H}_{48}\text{ClIrN}_2\text{OP}_2$; m/z calcd $\text{C}_{29}\text{H}_{48}\text{ClIrN}_2\text{OP}_2$ m/z [M+1]: 731.2632 (100%); found m/z [M+1]: 731.2597 (100%).

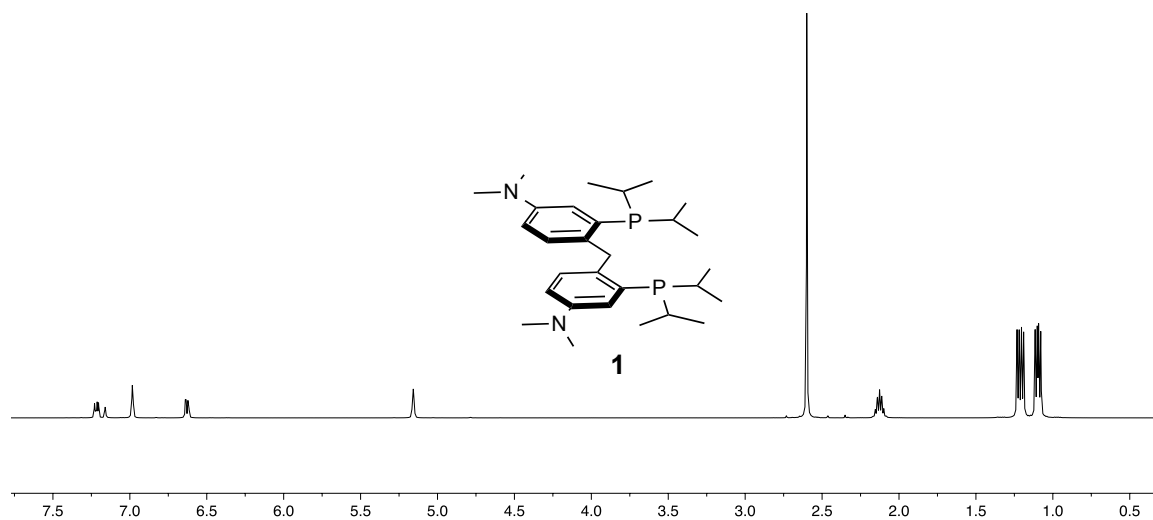


Figure S1. ^1H NMR spectrum of **1** in C_6D_6

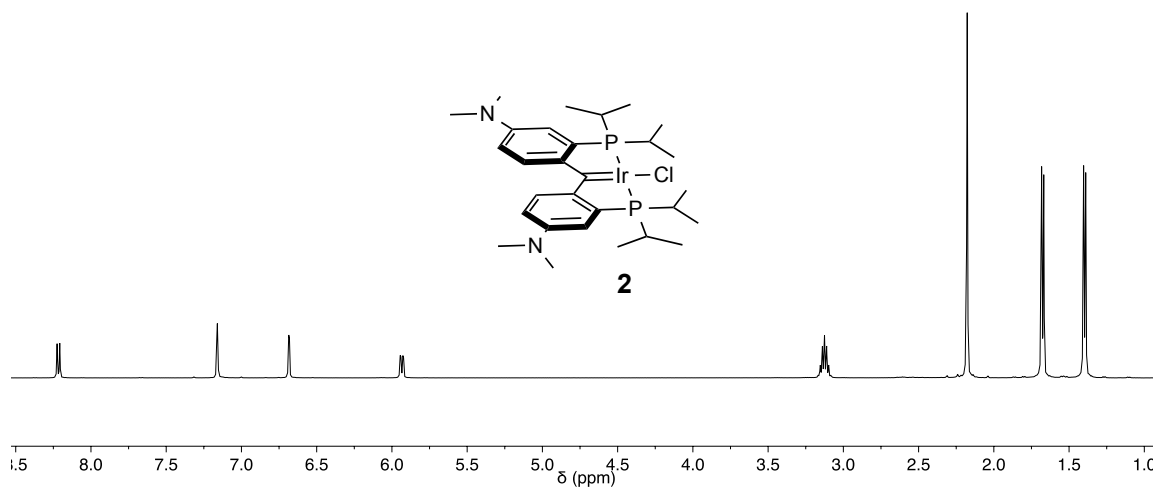


Figure S2. ^1H $\{^{31}\text{P}\}$ NMR spectrum of **2** in C_6D_6

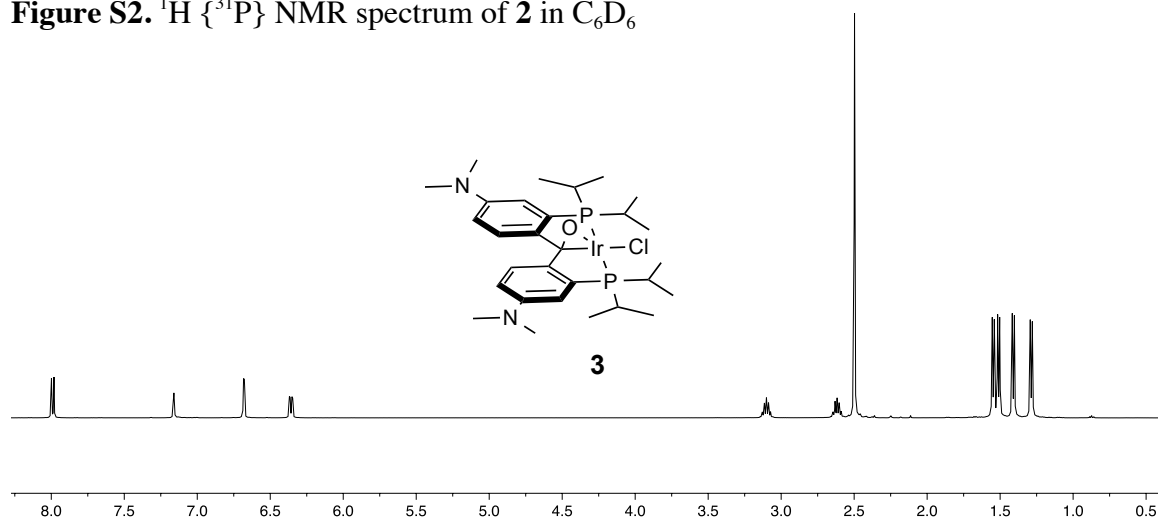


Figure S3. ^1H $\{^{31}\text{P}\}$ NMR spectrum of **3** in C_6D_6

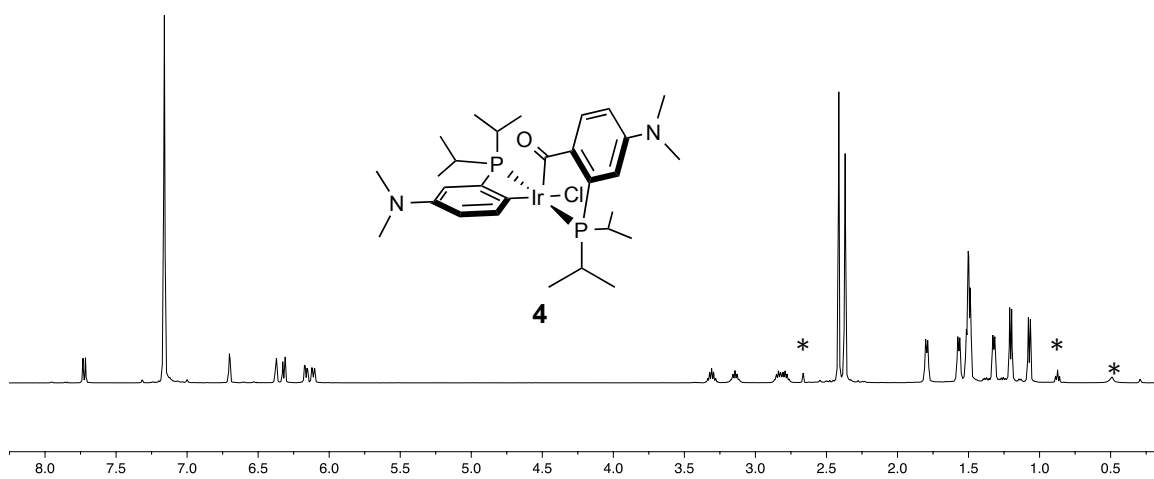


Figure S4. ^1H $\{^{31}\text{P}\}$ NMR spectrum of **4** in C_6D_6 . * impurities

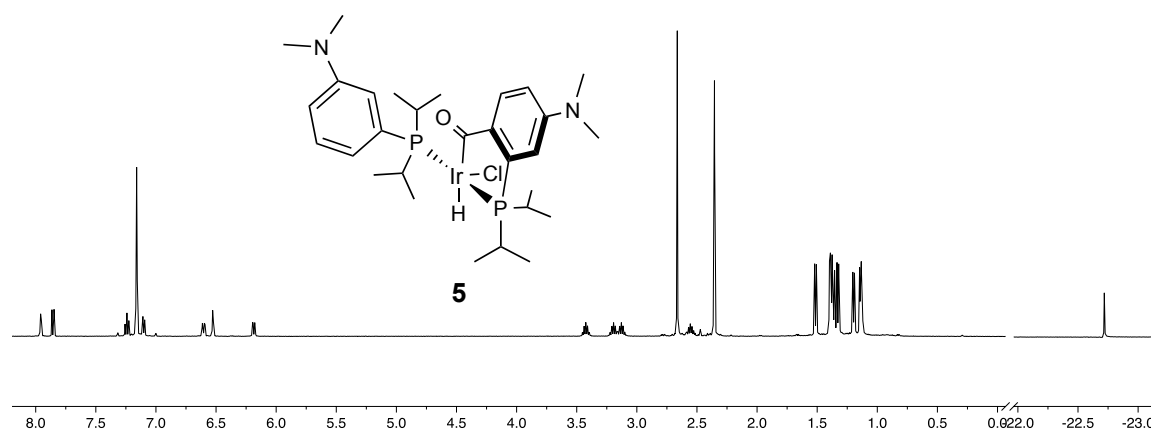


Figure S5. ^1H $\{^{31}\text{P}\}$ NMR spectrum of **5** in C_6D_6

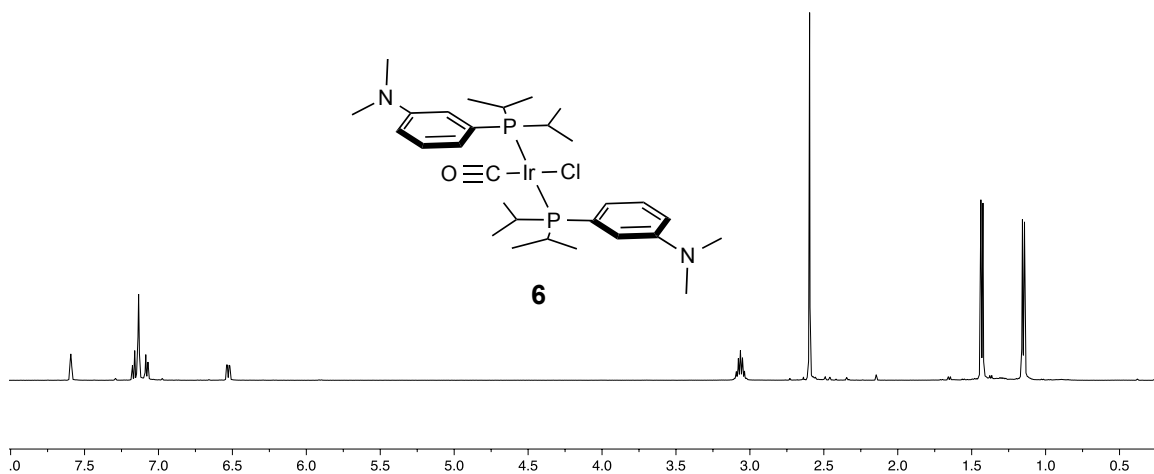
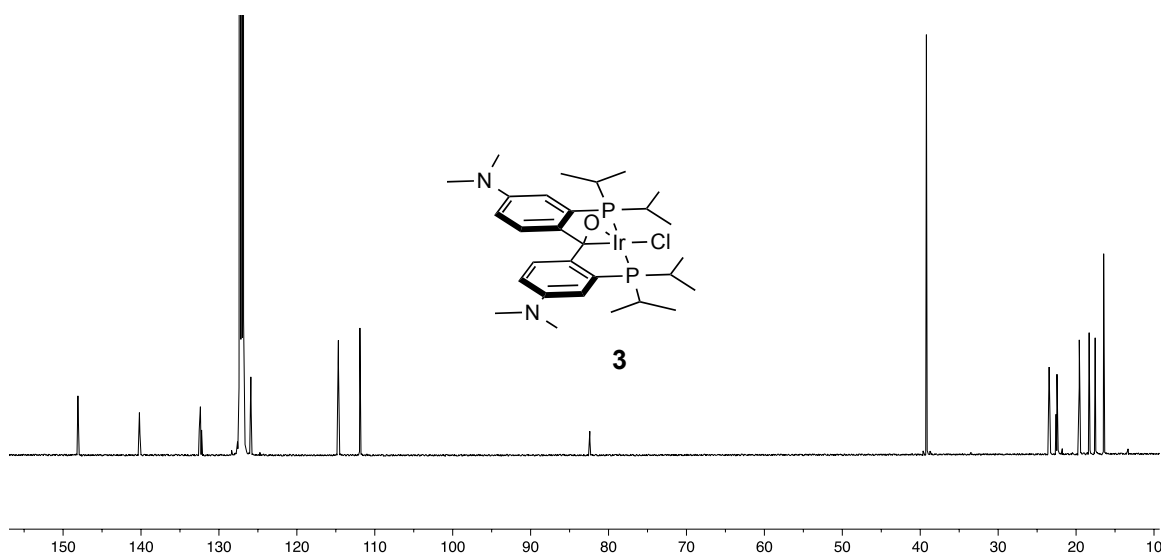
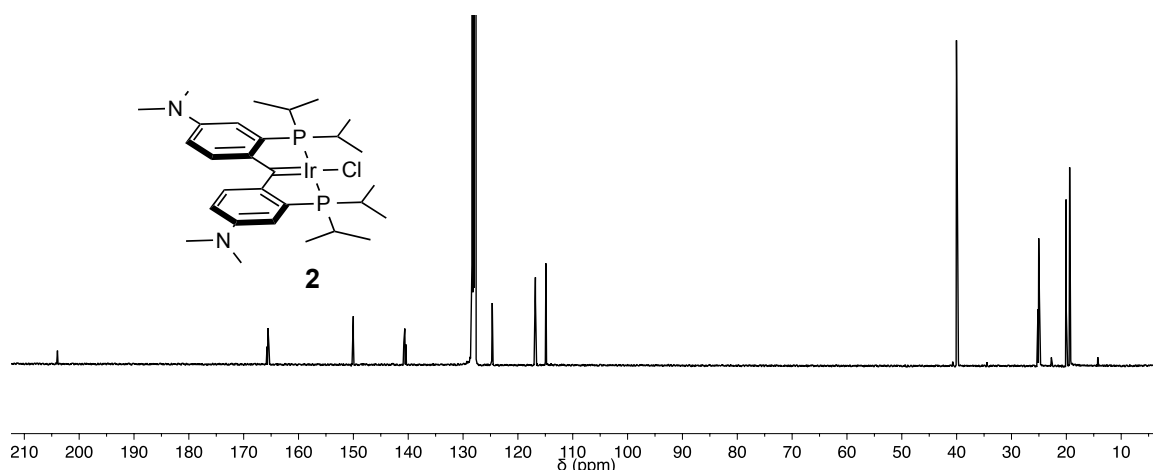
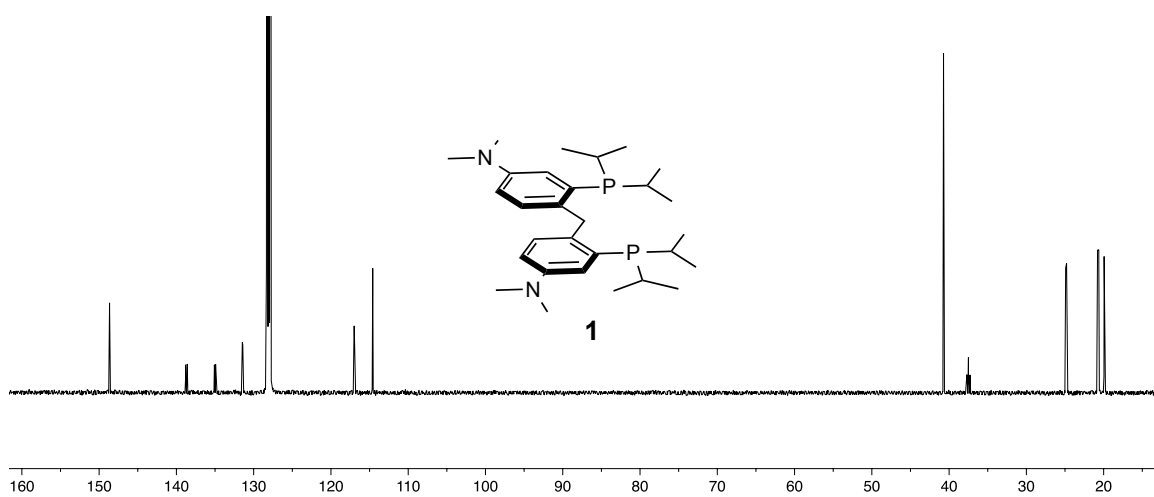


Figure S6. ^1H $\{^{31}\text{P}\}$ NMR spectrum of **6** in C_6D_6



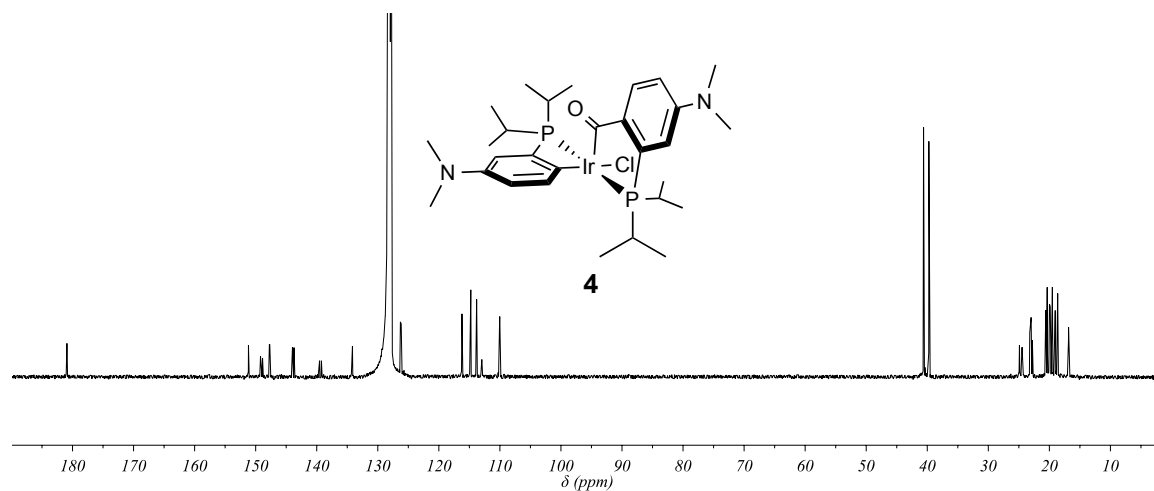


Figure S10. ^{13}C $\{^1\text{H}\}$ NMR spectrum of **4** in C_6D_6

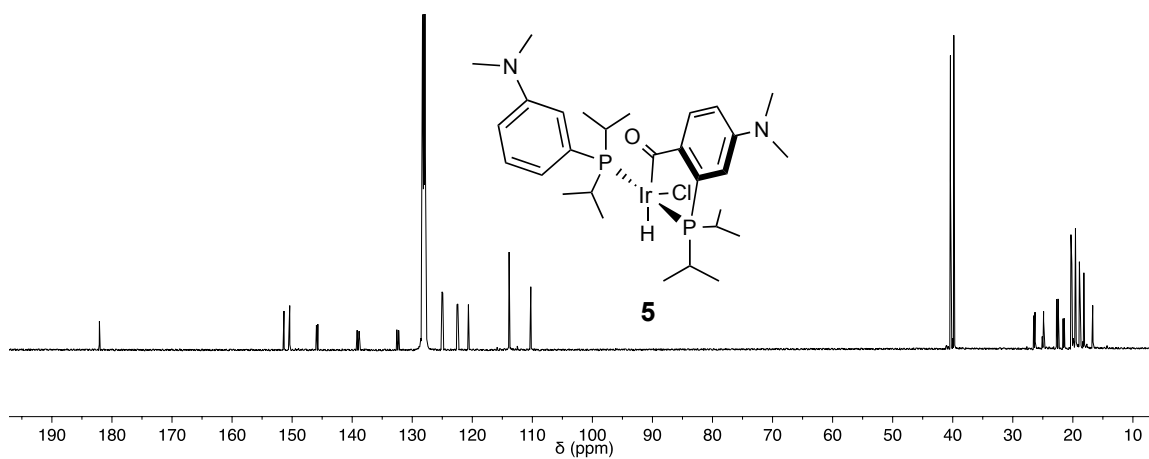


Figure S11. ^{13}C $\{^1\text{H}\}$ NMR spectrum of **5** in C_6D_6

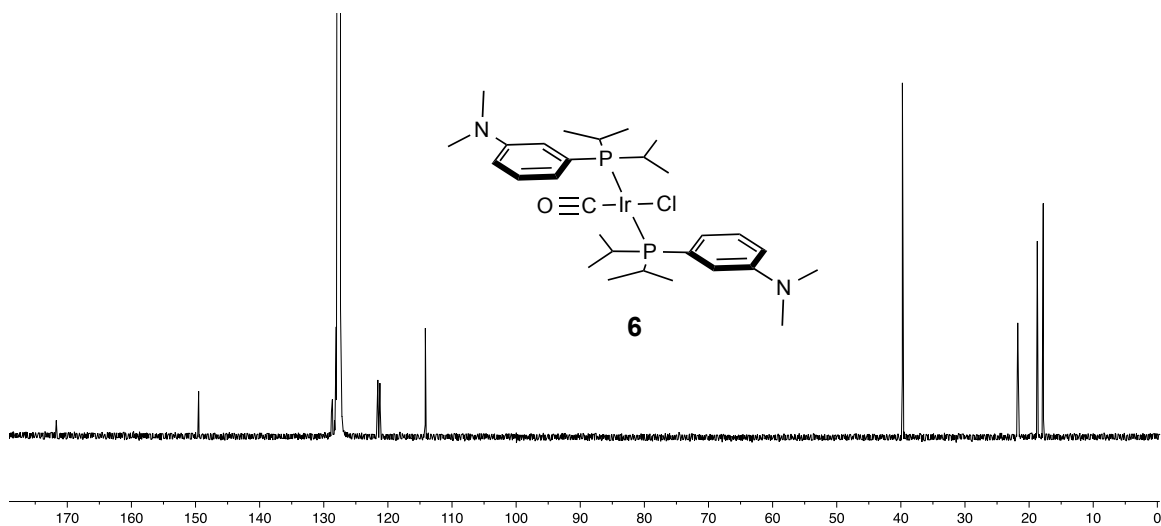


Figure S12. ^{13}C $\{^1\text{H}\}$ NMR spectrum of **6** in C_6D_6

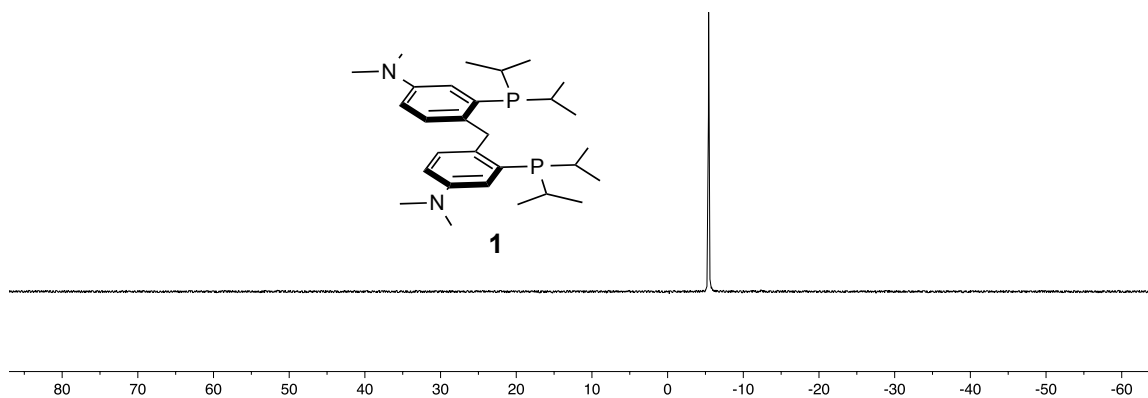


Figure S13. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** in C_6D_6

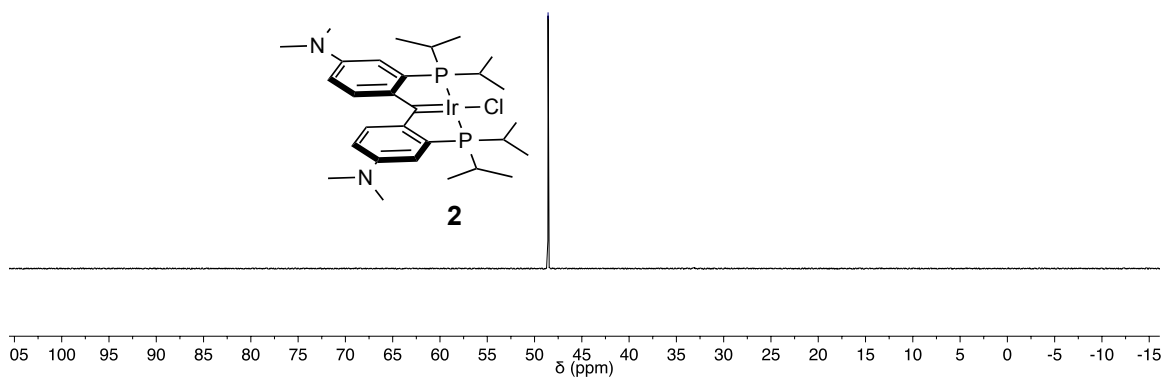


Figure S14. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** in C_6D_6

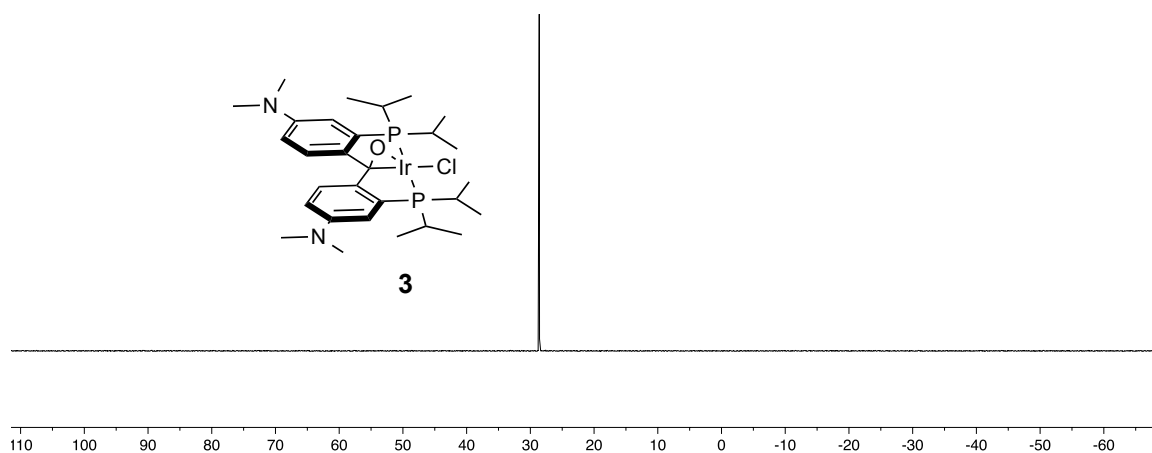
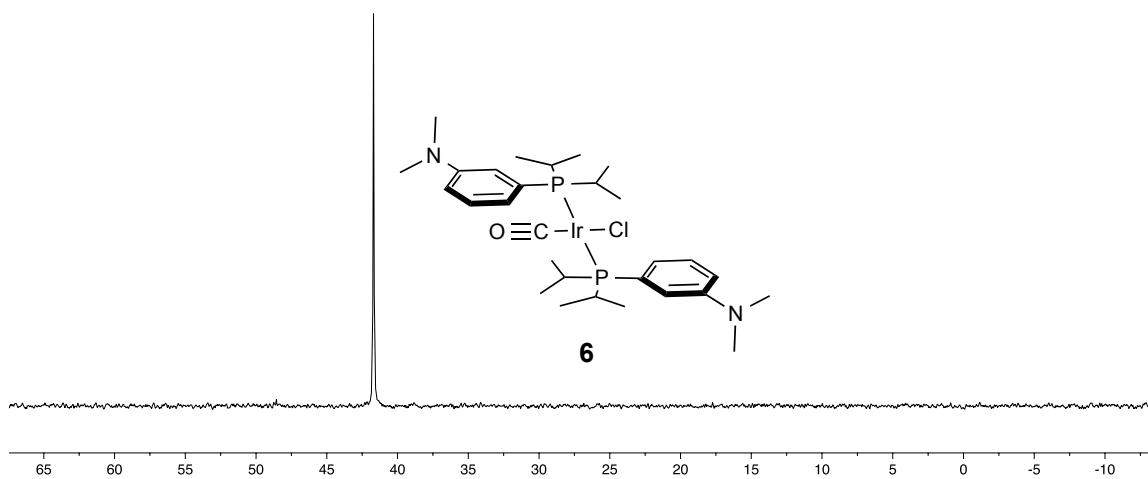
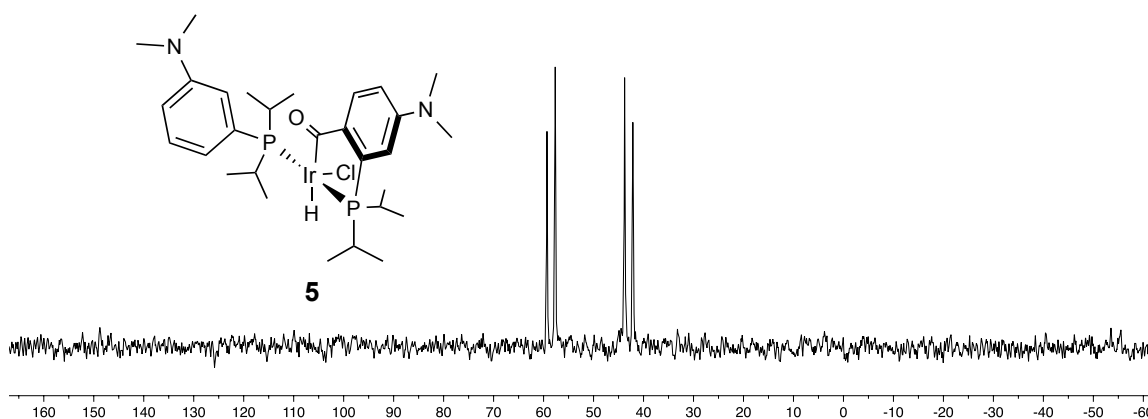
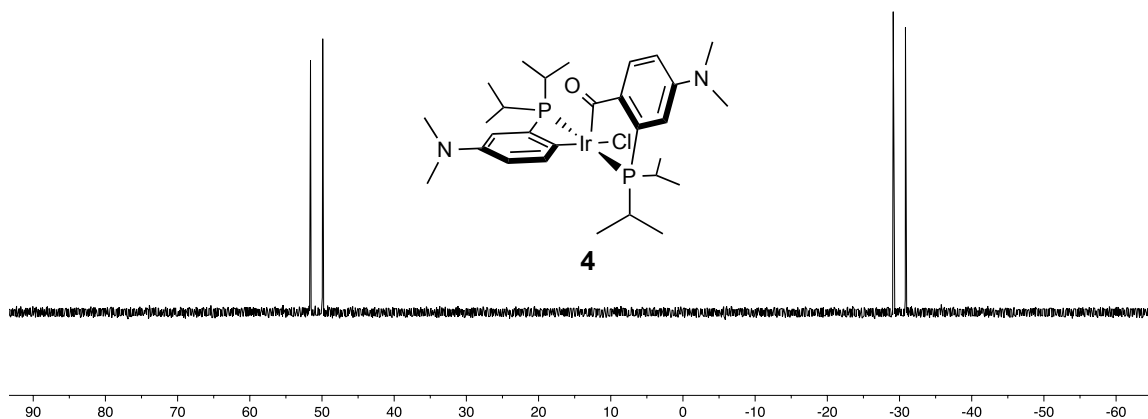


Figure S15. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** in C_6D_6



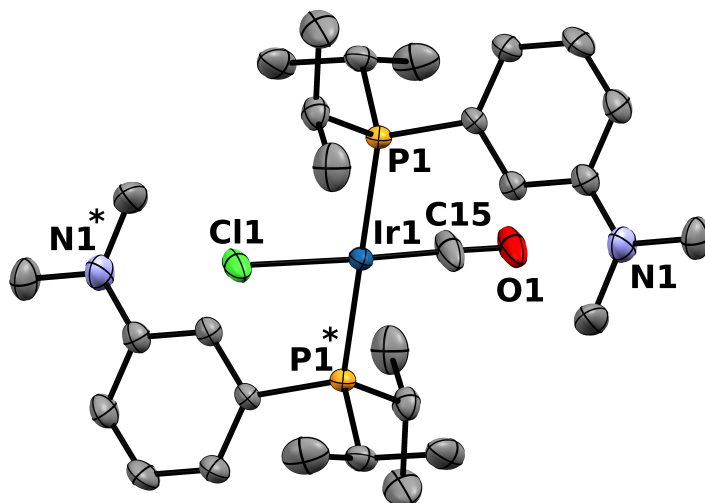


Figure S19. Thermal ellipsoid diagrams of **6** (50 % probability ellipsoids, all hydrogens are omitted for clarity). Selected metrical data for **6**: Bond Distances (Å); Ir(1)-P(1), 2.331(1); Ir(1)-Cl(1), 2.378(4); Ir(1)-C(15), 1.688(15); C(15)-O(1), 1.204(15). Bond angles (°); P(1)-Ir(1)-P*(1), 180.0; C(15)-Ir(1)-Cl(1), 178.1(4) C(15)-Ir(1)-P(1), 88.1(4), C(15)-Ir(1)-P*(1), 91.9(4), P(1)-Ir(1)-Cl(1), 90.03(8).

Table S1. Data collection and structure refinement details for **2 – 4**, and **6**.

	2	3	4	6
formula	C ₂₉ H ₄₆ ClIrN ₂ P ₂	C ₂₉ H ₄₆ ClIrN ₂ OP ₂ ,C ₇ H ₈	C ₂₉ H ₄₆ ClIrN ₂ OP ₂	C ₂₉ H ₄₈ ClIrN ₂ OP ₂
<i>fw</i>	714.28	820.40	728.27	730.28
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	C2/c	P21/c	P21/c	P-1
<i>a</i> (Å)	41.206(8)	11.1980(5)	9.673	8.6040(17)
<i>b</i> (Å)	11.786(2)	17.9220(8)	19.055	9.7140(19)
<i>c</i> (Å)	22.435(5)	18.1890(7)	18.068	11.476(2)
<i>α</i> (deg)	90	90	90	114.99(3)
<i>β</i> (deg)	121.41(3)	93.231(3)	115.36	98.12(3)
<i>γ</i> (deg)	90	90	90	104.36(3)
<i>V</i> (Å ³)	9299(4)	3644.6(3)	3009.4	808.5(3)
<i>Z</i>	12	4	4	1
<i>T</i> (K)	293(2)	153(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.7107	0.71073
<i>ρ</i> _{calcd} (g·cm ⁻³)	1.531	1.495	1.607	1.500
<i>F</i> (000)	4320	1664	1464	368
<i>μ</i> (mm ⁻¹)	4.517	3.854	4.656	4.333
crystal size, mm³	0.3×0.3×0.3	0.2×0.2×0.2	0.4×0.35×0.35	0.1×0.05×0.02
transmission factors	0.258 – 0.288	0.4321 – 0.4631	0.169 – 0.196	0.542 – 0.734
<i>θ</i> range (deg)	2.257 – 25.998	2.243 – 24.496	2.330 – 26.018	2.040 – 27.135
data/restraints/param	8890/0/493	5777/0/401	5903/0/337	3564/0/178
GOF	1.153	1.256	1.179	1.018
R₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0409	0.0748	0.0281	0.0202
wR₂ [all data]	0.1006	0.2268	0.0758	0.0856
residual density, e/Å³	1.680 and -1.054	1.929 and -1.658	1.634 and -0.798	0.919 and -1.942

References

- (1) Lukinavičius, G.; Umezawa, K.; Olivier, N.; Honigmann, A.; Yang, G.; Plass, T.; Mueller, V.; Reymond, L.; Corrêa Jr, I. R.; Luo, Z.; Schultz, C.; Lemke, E. A.; Heppenstall, P.; Eggeling, C.; Manley, S; Johnsson, K. *Nature Chem.* **2013**, 5, 132–139
- (2) Herde, J. L.; Lambert, J. C.; Senoff, C. V.; Cushing, M. A. *Inorg. Synth.*; John Wiley & Sons, Inc.: 2007, p 18.