Getting the Sterics Just Right: A Five-Coordinate Iridium Trisboryl Complex that Reacts with C–H Bonds at Room Temperature

Ghayoor A. Chotana, Britt A. Vanchura, Man Kin Tse, Richard J. Staples,

Robert E. Maleczka, Jr., and Milton R. Smith, III*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824-1322

E-mail: smithmil@msu.edu

Supporting Information

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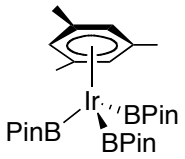
General Methods:

All commercially available chemicals were used as received unless otherwise indicated. Pinacolborane (HBPin containing 1% NEt_3) was generously supplied by BASF. (η^5-Indenyl)(cyclooctadiene)iridium (I) {(Ind)Ir(COD)} and bis-(di-*iso*-propylphosphino)-ethane (dippe) were prepared per the literature procedure.[1,2] We are thankful to Prof. Gregory L. Hillhouse (University of Chicago) for a generous gift of bis-(di-*tert*-butylphosphino)-ethane (dtbpe). Mesitylene was refluxed over sodium, distilled, and degassed. Tetrahydrofuran was obtained from a dry still packed with activated alumina and degassed before use. All the experiments were carried out in a glove box under a nitrogen atmosphere or by using standard Schlenk techniques.

^1H and ^{13}C NMR spectra were recorded on a Varian Inova-300 (300.11 and 75.47 MHz respectively), Varian VXR-500 or Varian Unity-500-Plus spectrometer (499.74 and 125.67 MHz respectively) and referenced to residual solvent signals (7.24 ppm and 77.0 ppm for $CDCl_3$, respectively). ^{11}B spectra were recorded on Varian VXR-500 or Varian Inova-300 operating at 160.41 and 96.29 MHz respectively, and were referenced to neat $BF_3{\cdot}Et_2O$ as the external standard. ^{31}P spectra were recorded on Varian Unity-500-Plus or Varian Inova-300 operating at 202.29 and 121.36 MHz respectively, and were referenced to neat 85% H_3PO_4 as the external standard. All coupling constants are apparent *J* values measured at the indicated field strengths. Elemental analyses were performed at Michigan State University using a Perkin Elmer Series II 2400 CHNS/O Analyzer. Melting points were measured on a MEL-TEMP® capillary melting apparatus and are uncorrected.

Synthesis of (η^6-MesH)Ir(BPin)$_3$ (3)



The literature prep[3] for the BCat analogue was modified to synthesize the (η^6-MesH)Ir(BPin)$_3$ (**3**). (Ind)Ir(COD) (1 g, 2.4 mmol, 1 equiv) and HBPin (3.5 mL, 3.1 g, 24 mmol, 10 equiv) were dissolved in 10 mL mesitylene in a Schlenk flask in a glove box. The flask was stoppered, brought out of the glove box, and heated in a 75 °C oil bath for 12 h. Mesitylene was removed under high vacuum overnight to give a viscous dark brown oil. The crude mixture was then triturated with 2 mL of cold hexamethyldisiloxane and filtered to give a white solid (680 mg). Additional material (45 mg) was obtained upon filtering the concentrated filtrate. Combined yield (725 mg, 44%, mp 164-166 °Ç dec). ^{1}H NMR (C_6D_6, 500 MHz): δ 5.62 (s, 3 H), 2.24 (s, 9 H, 3 CH_3), 1.33 (s, 36 H, 3 BPin); ^{13}C NMR {^{1}H} (C_6D_6, 500 MHz): δ 118.1 (C), 96.9 (CH), 81.0 (C), 25.7 (CH_3 of BPin), 19.7 (CH_3 of mesitylene); ^{11}B NMR (C_6D_6, 96 MHz): δ 33.2; Anal. Calcd for $C_{27}H_{48}IrB_3O_6$: C, 46.77; H, 6.98. Found: C, 47.13; H, 7.18.

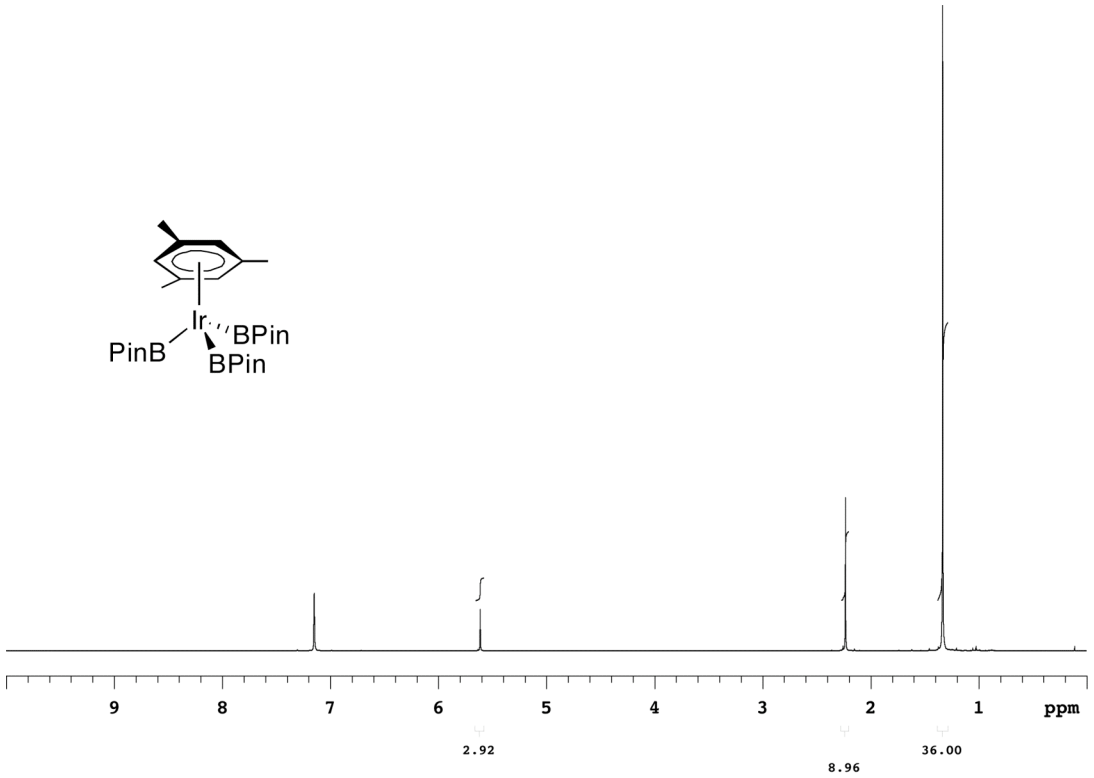


Figure S1. ^{1}H spectrum of **3** (η^6-MesH)Ir(BPin)$_3$

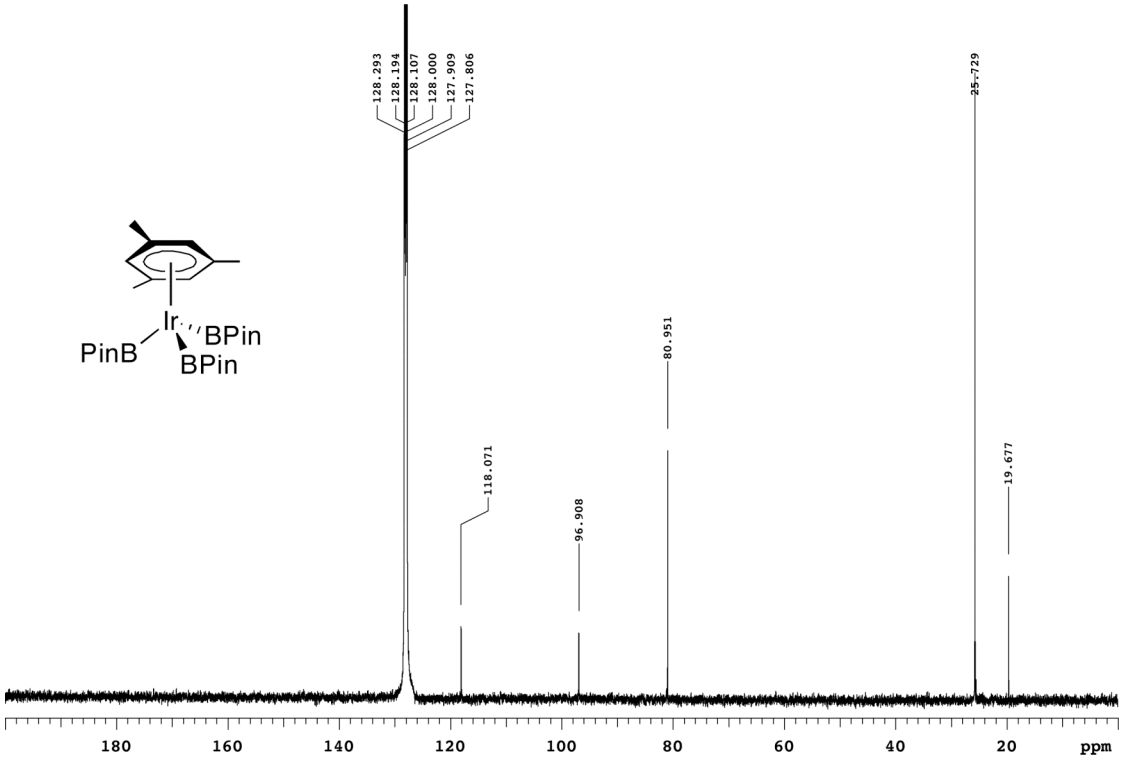
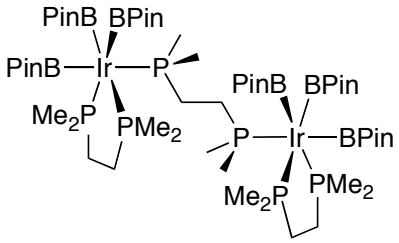


Figure S2. ^{13}C spectrum of **3** (η^6-MesH)Ir(BPin)$_3$.

Synthesis of $(dmpe)_3Ir_2(BPin)_6$ (4)



In a 20 mL vial, equipped with a magnetic stirring bar, (η^6-MesH)Ir(BPin)$_3$ (**3**) (174 mg, 0.25 mmol, 1 equiv) was dissolved in THF (1 mL). Bis-(di-methylphosphino)-ethane (dmpe) (57 mg, 0.37 mmol, 1.5 equiv) was weighed out in a test tube and was transferred to the reaction vial by dissolving in THF (1 mL × 2). The reaction was stirred at room temperature for 0.25 h. The crude reaction mixture was pumped down under high vacuum and then recrystallized from 1,3-bis-(trifluoromethyl)-benzene/hexamethyldisiloxane at -35 °C to give the complex **4** as a white solid. ^{1}H NMR (C_6D_6, 500 MHz): δ 2.10 (s, 4 H), 1.82 (d, J = 9.2 Hz, 12 H), 1.68 (d, J = 6.7 Hz, 12 H), 1.38 (s, 24 H), 1.34 (d, overlapped with the BPin singlet, 12 H), 1.33 (s, 24 H), 1.29 (s, 24 H), 1.2-1.02 (br, 8 H); ^{13}C NMR {^{1}H} (C_6D_6, 125 MHz): δ 80.5 (4 C), 80.3 (8 C), 33.1 (m), 27.1 (8 CH_3 of BPin), 26.2 (8 CH_3 of BPin), 25.3 (8 CH_3 of BPin), 24.6 (s), 20.4 (m), 19.7 (m), 18.9 (m); ^{11}B NMR (C_6D_6, 160 MHz): δ 37.3; ^{31}P NMR (C_6D_6, 202 MHz): δ -11.1 (s, 4 P), -50.9 (s, 2 P); Anal. Calcd for $C_{54}H_{120}Ir_2B_6O_{12}P_6$: C, 40.62; H, 7.58. Found: C, 40.81; H, 7.56.

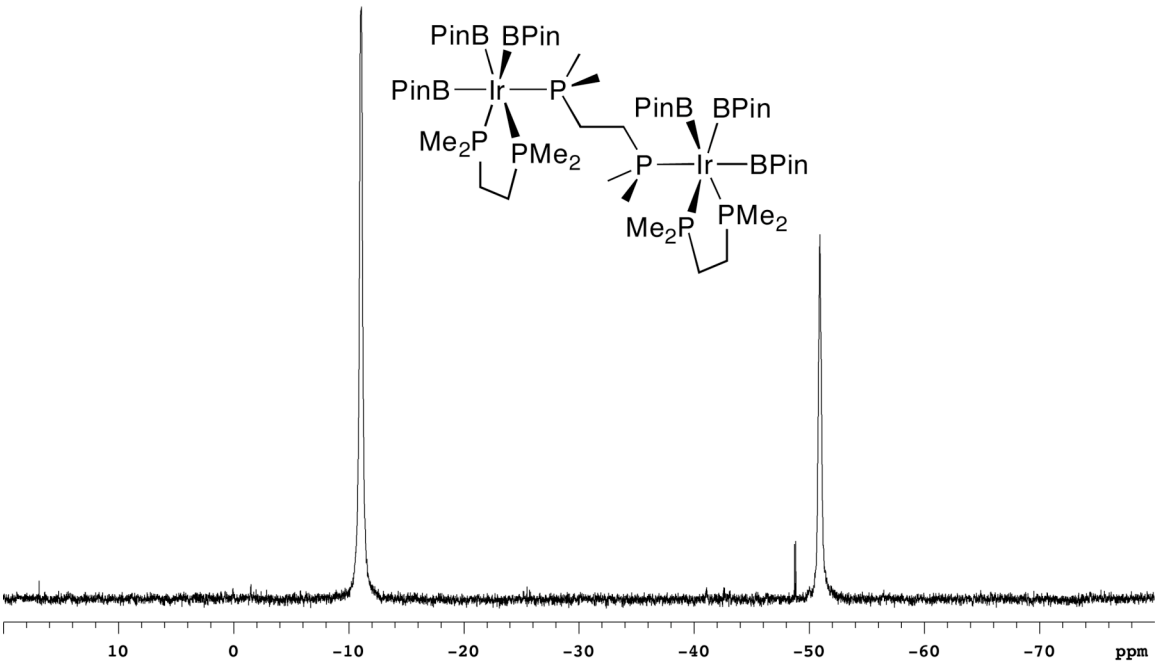
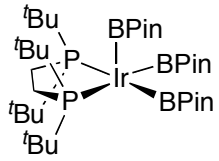


Figure S3. ^{31}P spectrum of $(dmpe)_3Ir_2(BPin)_6$ **(4).**

Synthesis of (dtbpe)Ir(BPin)$_3$ (5)



In a 20 mL vial, equipped with a magnetic stirring bar, (η^6-MesH)Ir(BPin)$_3$ (**3**) (174 mg, 0.25 mmol, 1 equiv) was dissolved in THF (1 mL). Bis-(di-*tert*-butylphosphino)-ethane (dtbpe) (80 mg, 0.25 mmol, 1 equiv) was weighed out in a test tube and was transferred to the reaction vial by dissolving in THF (1 mL × 2). The reaction was stirred at room temperature for 2 h. ^{31}P NMR showed full consumption of the starting phosphine ligand and the appearance of a single new peak. The crude reaction mixture was pumped down under high vacuum to give the desired complex **5** as a light yellow solid (yield 220 mg, quantitative, mp 108-110 °C dec). ^{1}H NMR (C_7D_8, 500 MHz): δ 1.60-1.54 (m, 4 H), 1.35 (s, 36 H, 3 BPin), 1.25 (d, $^3J_{H-P}$ = 11.9 Hz, 36 H, 12 CH_3), ^{1}H NMR (C_6D_{12}, 500 MHz): δ 1.88-1.80 (m, 4 H), 1.28 (d, $^3J_{H-P}$ = 11.9 Hz, 36 H, 12 CH_3 of dtbpe), 1.19 (s, 36 H, 12 CH_3 of 3 BPin); ^{13}C NMR {^{1}H} (C_7D_8, 125 MHz): δ 81.1 (s, 6 C), 37.14-37.05 (m, 4 C), 30.5 (s, 12 C, 12 CH_3 of dtbpe), 26.4 (s, 12 C, 12 CH_3 of BPin), 25.50-25.28 (m, 2 C, 2 CH_2); ^{11}B NMR (C_7D_8, 160 MHz): δ 34.7; ^{31}P NMR (C_7D_8, 202 MHz): δ 93.0; Anal. Calcd for $C_{36}H_{76}IrB_3O_6P_2$: C, 48.50; H, 8.59. Found: C, 48.53; H, 8.65.

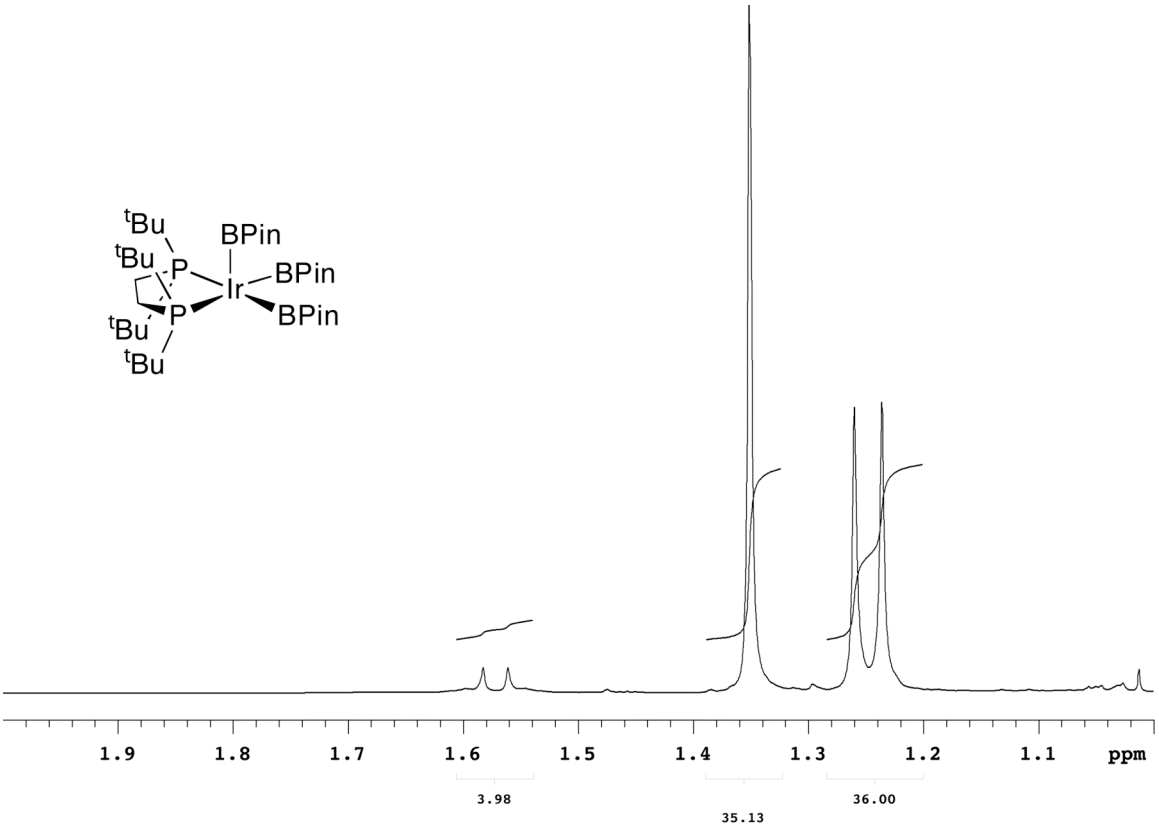


Figure S4. ^{1}H spectrum of (dtbpe)Ir(BPin)$_3$ (**5**).

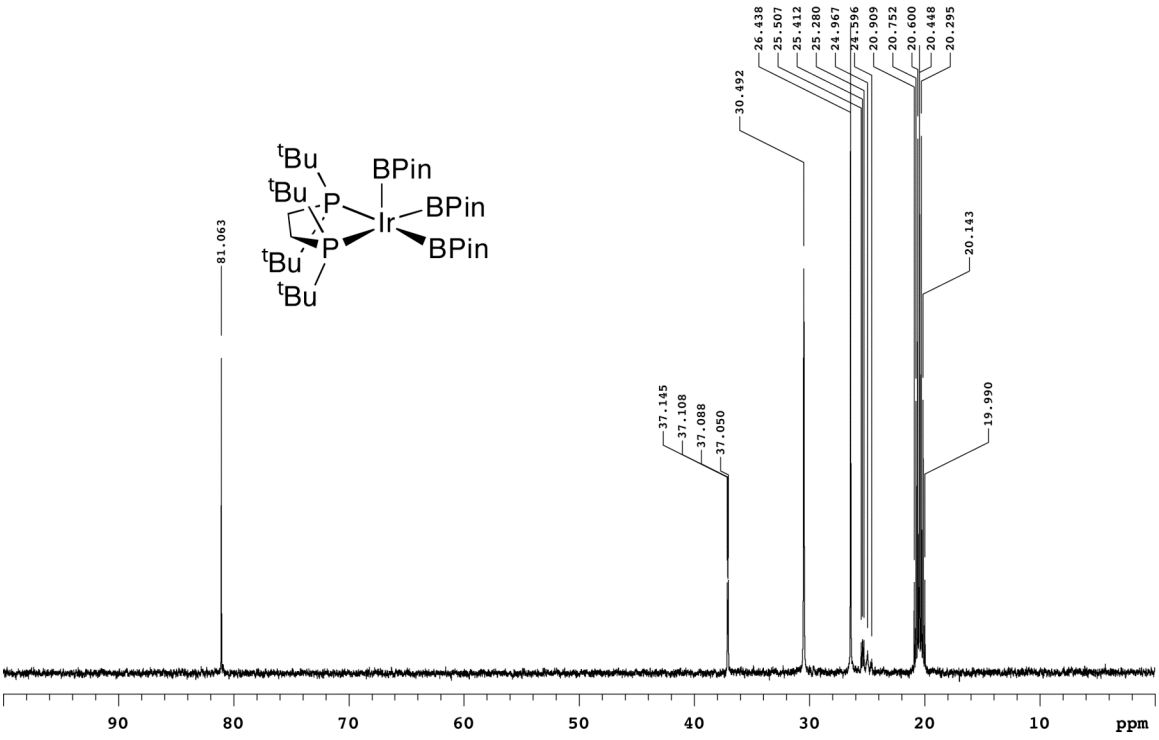
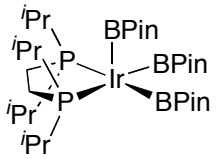


Figure S5. ^{13}C spectrum of (dtbpe)Ir(BPin)$_3$ (**5**).

Synthesis of (dippe)Ir(BPin)$_3$ (6)



In a 20 mL vial, equipped with a magnetic stirring bar, (η^6-MesH)Ir(BPin)$_3$ (**3**) (202 mg, 0.29 mmol, 1 equiv) was dissolved in THF (1 mL). Bis-(di-*iso*-propylylphosphino)-ethane (dippe) (76 mg, 0.29 mmol, 1 equiv) was weighed out in a test tube and was transferred to the reaction vial by dissolving in THF (1 mL × 2). The reaction was stirred at room temperature for 2 h. ^{31}P NMR showed full consumption of the starting phosphine ligand and the appearance of a single new peak. The crude reaction mixture was pumped down under high vacuum to give the desired complex **6** as a yellow-orange solid (yield 242 mg, quantitative, mp 114-116 °C dec). ^{1}H NMR (C_7D_8, 500 MHz): δ 2.52-2.42 (m, 4 H), 1.41-1.38 (m, 4 H), 1.33 (s, 36 H, 3 BPin), 1.12-1.06 (m, 24 H), ^{1}H NMR (C_6D_{12}, 500 MHz): δ 2.56-2.44 (m, 4 H), 1.68-1.60 (m, 4 H), 1.15 (s, 36 H, 3 BPin), 1.17-1.01 (m, 24 H); ^{13}C NMR {^{1}H} (C_7D_8, 500 MHz): δ 80.8 (s, 6 C), 27.01-26.85 (m, 4 C), 26.1 (s, 12 C, 12 CH_3 of BPin), 24.80-24.53 (m, 2 C, 2 CH_2), 19.7 (s, 6 C, 6 CH_3 of dippe), 19.4 (s, 6 C, 6 CH_3 of dippe); ^{11}B NMR (C_7D_8, 160 MHz): δ 39.1; ^{31}P NMR (C_7D_8, 202 MHz): δ 86.5; Anal. Calcd for $C_{32}H_{68}IrB_3O_6P_2$: C, 46.00; H, 8.20. Found: C, 46.23; H, 8.76.

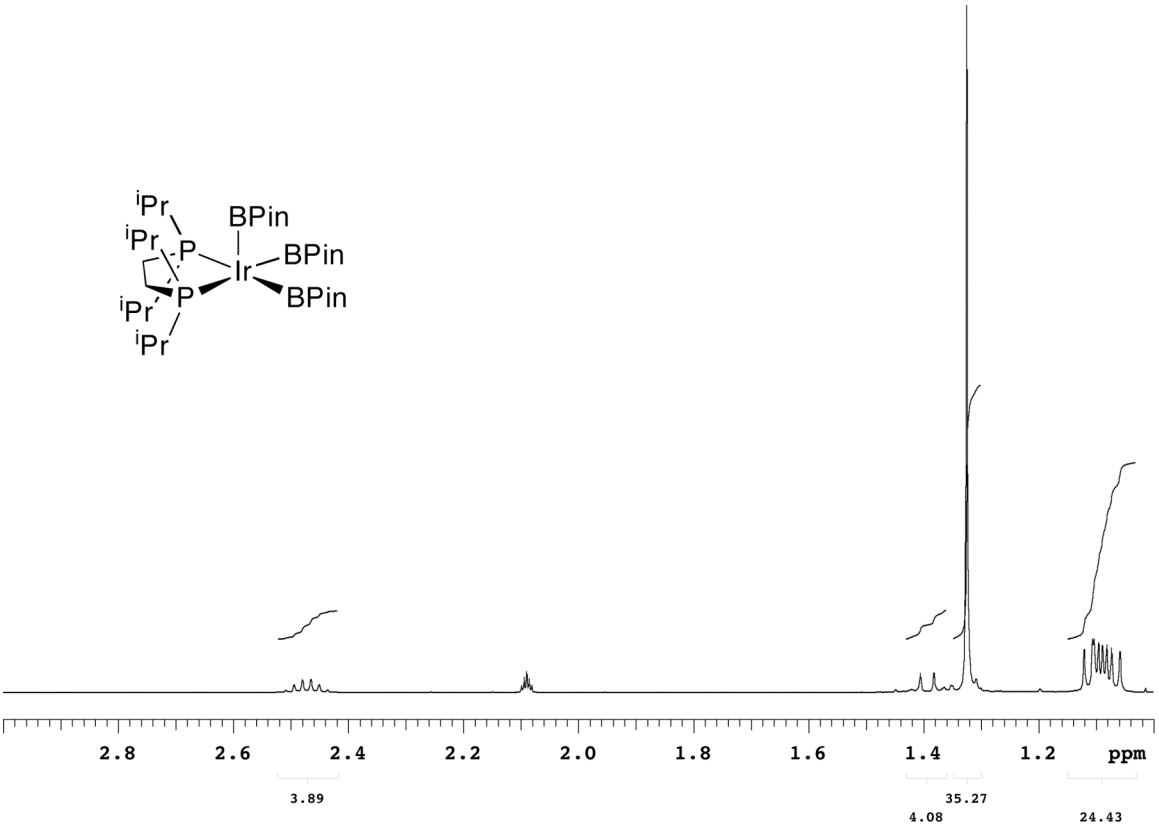


Figure S6. ^{1}H spectrum of (dippe)Ir(BPin)$_3$ (**6**).

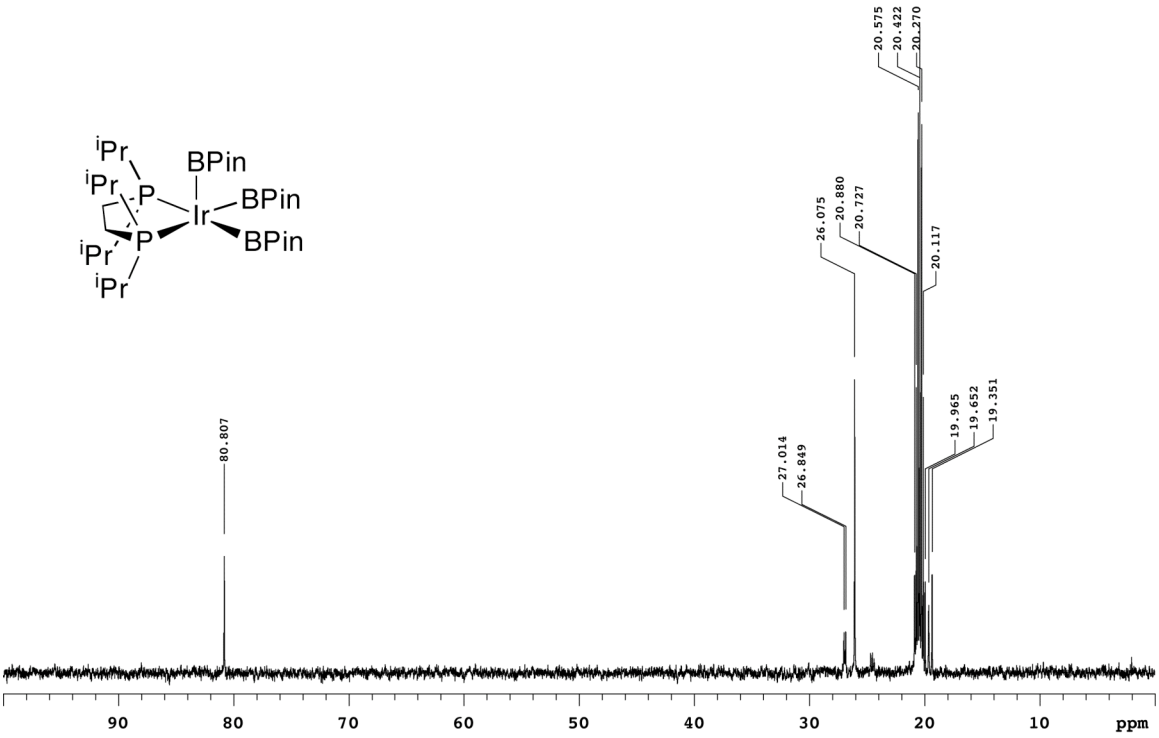


Figure S7. ^{13}C spectrum of (dippe)Ir(BPin)$_3$ (**6**).

Stoichiometric borylation of 1,3-bis-trifluromethylbenzene with (dtbpe)Ir(BPin)$_3$ (5)

Compound **5** (dtbpe)Ir(BPin)$_3$ (36 mg, 0.04 mmol, 1 equiv) was weighed out in a test tube and was transferred to a J. Young NMR tube using C_6D_{12} (175 μL × 4). 1,3-bis-trifluoromethylbenzene (6.2 μL, 0.04 mmol, 1 equiv) was syringed in to the J. Young NMR tube. 1,4-bis-trifluoromethylbenzene (6.2 μL, 0.04 mmol, 1 equiv) was also syringed in to the J. Young NMR tube as an internal standard. The J. Young NMR tube was capped and the reaction was monitored by ^{1}H, ^{31}P, and ^{11}B NMR. The NMR yield after 48 h at room temperature was 10%.

Stoichiometric borylation of 1,3-bis-trifluromethylbenzene with (dippe)Ir(BPin)$_3$ (6)

Compound **6** (d^{i}ppe)Ir(BPin)$_3$ (33 mg, 0.04 mmol, 1 equiv) was weighed out in a test tube and was transferred to a J. Young NMR tube using C_6D_{12} (175 μL × 4). 1,3-bis-trifluoromethylbenzene (6.2 μL, 0.04 mmol, 1 equiv) was syringed in to the J. Young NMR tube. 1,4-bis-trifluoromethylbenzene (6.2 μL, 0.04 mmol, 1 equiv) was also syringed in to the J. Young NMR tube as an internal standard. The J. Young NMR tube was capped and the reaction was monitored by ^{1}H, ^{31}P, and ^{11}B NMR. The NMR yield of 2-(3,5-bis(trifluoromethyl)phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[4] after 48 h at room temperature was 104%.

Stoichiometric borylation of 2-methylthiophene with (dippe)Ir(BPin)$_3$ (6)

Compound **6** (dippe)Ir(BPin)$_3$ (33 mg, 0.04 mmol, 1 equiv) was weighed out in a test tube and was transferred to a J. Young NMR tube using C_6D_{12} (175 μL × 4). 2-methylthiophene (3.9 μL, 0.04 mmol, 1 equiv) was syringed in to the J. Young NMR tube. The J. Young NMR tube was capped and the reaction was monitored by ^{1}H, ^{31}P, and ^{11}B NMR. The NMR yield of

4,4,5,5-tetramethyl-2-(5-methylthiophen-2-yl)-1,3,2-dioxaborolane[5] after 4 h at room temperature was 98%.

Borylation of 2-methylthiophene with catalysts generated in situ from (η^5-indenyl)Ir (η^4-1,5-cyclooctadiene) and dtbpe

dtbpe (7.8 mg, 0.025 mmol, 0.1 equiv) was weighed out in a test tube and was transferred to a second test tube containing (Ind)Ir(COD) (10.4 mg, 0.025 mmol, 0.1 equiv) using C_6D_{12} (100 μL × 4). This solution was then transferred to a J. Young NMR tube. 2-methylthiophene (194 μL, 2 mmol, 8 equiv) and HBPin (36 μL, 0.25 mmol, 1 equiv) syringed in to the J. Young NMR tube. The J. Young NMR tube was capped and heated in an oil bath at 100 °C. The reaction was monitored by ^{1}H and ^{11}B NMR. The NMR yield of 4,4,5,5-tetramethyl-2-(5-methylthiophen-2-yl)-1,3,2-dioxaborolane after 2 h at 100 °C was 11%.

Borylation of 2-methylthiophene with catalysts generated in situ from (η^5-indenyl)Ir (η^4-1,5-cyclooctadiene) and dippe

dippe (6.6 mg, 0.025 mmol, 0.1 equiv) was weighed out in a test tube and was transferred to a second test tube containing (Ind)Ir(COD) (10.4 mg, 0.025 mmol, 0.1 equiv) using C_6D_{12} (100 μL × 4). This solution was then transferred to a J. Young NMR tube. 2-methylthiophene (194 μL, 2 mmol, 8 equiv) and HBPin (36 μL, 0.25 mmol, 1 equiv) syringed in to the J. Young NMR tube. The J. Young NMR tube was capped and heated in an oil bath at 100 °C. The reaction was monitored by ^{1}H and ^{11}B NMR. The NMR yield of 4,4,5,5-tetramethyl-2-(5-methylthiophen-2-yl)-1,3,2-dioxaborolane after 2 h at 100 °C was 81%.

Catalytic borylation of 2-methylthiophene with 5

(dtbpe)Ir(BPin)$_3$ (22.2 mg, 0.025 mmol, 0.1 equiv) was weighed out in a test tube and then transferred to a J. Young NMR tube using C_6D_{12} (100 μL × 4). 2-methylthiophene (194 μL, 2 mmol, 8 equiv) and HBPin (36 μL, 0.25 mmol, 1 equiv) syringed in to the J. Young NMR

tube. The J. Young NMR tube was capped and heated in an oil bath at 100 °C. The reaction was monitored by ^{1}H and ^{11}B NMR. The NMR yield of 4,4,5,5-tetramethyl-2-(5-methylthiophen-2-yl)-1,3,2-dioxaborolane after 1 h at 100 °C was 16%.

Catalytic borylation of 2-methylthiophene with 6

(dippe)Ir(BPin)$_3$ (20.8 mg, 0.025 mmol, 0.1 equiv) was weighed out in a test tube and then transferred to a J. Young NMR tube using C_6D_{12} (100 μL × 4). 2-methylthiophene (194 μL, 2 mmol, 8 equiv) and HBPin (36 μL, 0.25 mmol, 1 equiv) syringed in to the J. Young NMR tube. The J. Young NMR tube was capped and heated in an oil bath at 100 °C. The reaction was monitored by ^{1}H and ^{11}B NMR. The NMR yield of 4,4,5,5-tetramethyl-2-(5-methylthiophen-2-yl)-1,3,2-dioxaborolane after 1 h at 100 °C was 109%.

Crystallographic Details:

Data were collected using a Bruker CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173 K. Data were measured using omega and phi scans of 0.5° per frame for 30 s. Cell parameters were retrieved using ASTRO software[6] and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software[7] which corrects for Lp. Scaling and absorption corrections were applied using SADABS[8] multi-scan technique, supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97[9] program and refined by least squares method on F^2, SHELXL- 97, [10] incorporated in SHELXTL-PC V 6.10.[11]

All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The refinement for **5** is reported without any absorption correction. Applying absorption corrections resulted in a worse refinement. Rotational disorder along the Ir-B2 bond vector in compound **6** was modeled using standard commands in the SHELXTL suite. Attempts to restrain the bond lengths to reasonable values still resulted in two long C-C bonds in the minor component, C7B-C8B (1.7160 Å) and C10B-C11B (1.8340 Å). The conformer population was optimized by least squares analysis and the major conformer consists of 73% of the total population. The crystals used for the diffraction study showed no decomposition during data collection. All drawings are done at 50% probabilities for the thermal ellipsoids.

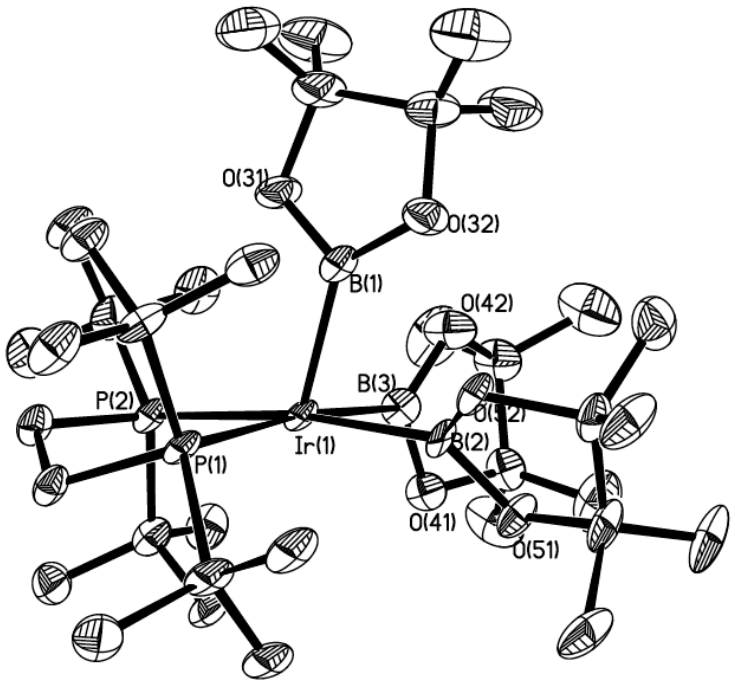


Figure S8. ORTEP diagram for **5** (H atoms are omitted). Thermal ellipsoids are shown at the 50% probability level.

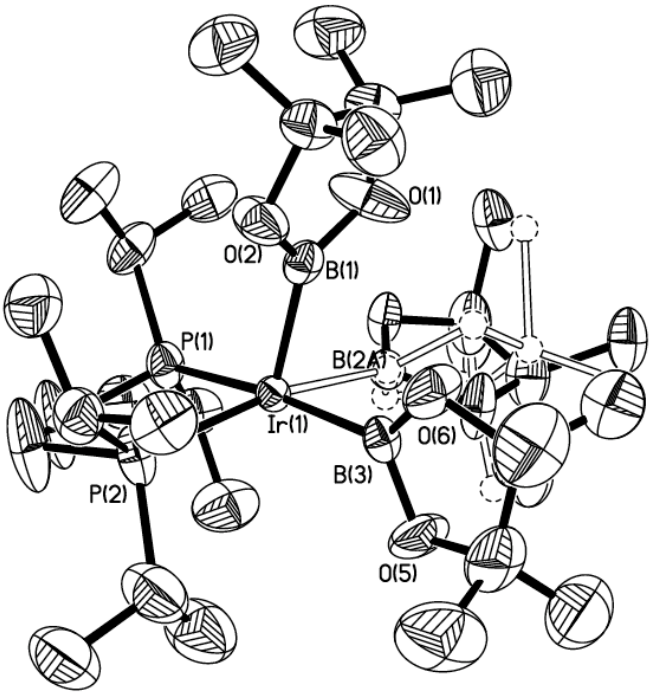


Figure S9. ORTEP diagram for **6** (H atoms are omitted, minor contributor to boryl disorder shown as ball and stick model). Thermal ellipsoids are shown at the 50% probability level.

References:

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