Pronounced Effects of Substituents on the Iridium-Catalyzed Borylation of Aryl C-H Bonds

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Supporting Information

Experimental

General Methods. All reactions were conducted under a nitrogen atmosphere using standard Schlenk and glovebox techniques, unless otherwise noted. All glassware were either flame-dried or oven-dried. Cyclohexane, benzene-$d_6$ and cyclohexane-$d_{12}$ were distilled from sodium/benzophenone solutions, and cis-cyclooctene and dichloromethane-$d_2$ were distilled from calcium hydride. Reaction solvents including dichloromethane and pentane were dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant, a supported copper catalyst for scavenging oxygen, under a positive pressure of N$_2$. 1,2-Bis(di-isopropylphosphino)ethane (dippe), $^{1}$[Ir(cod)Cl]$^2_2$, and [Ir(Bpin)$_3$(dtbpy)]$^3$ were prepared by published procedures. [(p-xylene)Ir(Bcat*)]$^4_3$ was prepared by a slight modification of the published procedure$^4$ from [(η$^5$-indenyl)Ir(cod)]$^5$, by using 4-tert-butylcatecholborane$^6$ in place of catecholborane and p-xylene as the arene. [Ir(cod)(OMe)]$_2$ was obtained as a gift from Johnson-Matthey. All other chemicals were used as received from commercial suppliers.

$^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded on 500 MHz spectrometers, and $^{11}$B NMR spectra were recorded at 96 MHz. All $^1$H and $^{13}$C chemical shifts are reported in ppm (δ) relative to tetramethylsilane and referenced using chemical shifts of residual solvent resonances. $^{31}$P NMR and $^{11}$B NMR spectra were referenced to external standards H$_3$PO$_4$ (0 ppm, $^{31}$P) and BF$_3$•OEt$_2$ (0 ppm, $^{11}$B). Analytical gas
chromatography (GC) was performed using a Hewlett-Packard 5890 Gas Chromatograph fitted with a flame ionization detector and a Hewlett-Packard HP5 (30m x 0.32 mm) capillary column.

Procedure for the borylation of benzene with bis(catecholato)diboron (B$_2$cat$_2$) catalyzed by [Ir(cod)(OMe)$_2$] and 4,4’-di-tert-butyl-2,2’-bipyridine. An oven-dried 4-mL vial equipped with a stir bar was charged with [Ir(cod)(OMe)$_2$]$_2$ (1.6 mg, 0.0024 mmol); 4,4’-di-tert-butyl-2,2’-bipyridine (1.3 mg, 0.0048 mmol), B$_2$cat$_2$ (23.1 mg, 0.0971 mmol), and dodecahydrotriphenylene (internal standard, 23.1 mg, 0.0961 mmol). These materials were then dissolved in 0.8 mL of neat benzene. The vial was sealed under an atmosphere of nitrogen with a Teflon-lined cap, removed from the glovebox, and heated in an oil bath at 120 °C. Upon heating, the B$_2$cat$_2$ dissolved in the reaction mixture to afford a homogeneous solution. After 1 h, the reaction was removed from the oil bath and cooled to room temperature. In the glovebox, 0.25 mL of the reaction solution was transferred to an NMR tube and flame-sealed under vacuum. Both the NMR tube and the vial containing the remaining reaction solution were returned to the oil bath and heated at 120 °C with periodic monitoring of the reaction by $^{11}$B NMR spectroscopy. After heating for 24 h, the yield (92%) of phenylboronate ester was determined by GC analysis using response factors calculated from pure samples of PhBcat.

Procedure for the borylation of benzene with pinacolborane (HBpin) catalyzed by [Ir(cod)(OMe)$_2$] and 1,2-bis(dicyclohexylphosphino)ethane (dcpe) or 1,2-bis(di-isopropylphosphino)ethane (dippe). An oven-dried 4-mL vial equipped with a stir bar was charged with [Ir(cod)(OMe)$_2$]$_2$ (1.5 mg, 0.0022 mmol, 2.5 mol%); phosphine (0.0044 mmol, 5.0 mol%), pinacolborane (22 µL, 0.15 mmol), and dodecahydrotriphenylene (internal standard, 11.7 mg, 0.049 mmol). These materials were then dissolved in 0.8 mL (60 equiv) of neat benzene to give a clear, light yellow solution. The vial was sealed under an atmosphere of nitrogen with a Teflon-lined cap, removed from the glovebox, and heated in an oil bath at 120 °C. After heating for 24 h, the yield (24%, L = dcpe;
<5% \text{L = dippe}) of phenylboronate ester was determined by GC analysis using response factors calculated from pure samples of PhBpin.

**Preparation of \([(\text{coe})\text{Ir(dtbpy)}(\text{Bcat^*})]\) (1b).** In an oven-dried, 20-mL scintillation vial, \([(p\text{-xylene})\text{Ir(}\text{Bcat^*})]\) (254 mg, 0.308 mmol) and 4,4'-\text{-di-}tert\text{-butyl-}2,2'\text{-bipyridine} (99 mg, 0.369 mmol) were combined with 4 mL of cyclohexane. The mixture was stirred while \text{cis-}cyclooctene (COE, 0.40 mL, 3.1 mmol) was added dropwise via a syringe. The heterogeneous reaction mixture was sealed under an atmosphere of nitrogen, then stirred for 6 h at ambient temperature to afford a clear orange-red solution. The volatile materials were evaporated from the reaction mixture, and the resulting red-orange oil was dissolved in pentane (~10 mL). A yellow powder immediately precipitated. The mixture was cooled to -35°C to precipitate more yellow powder. After filtering and rinsing with 2 x 5 mL of cold pentane, 291 mg (86%) of 1b as a yellow powder was obtained. Compound 1b is stable under a nitrogen atmosphere at -35 °C for months, but slowly decomposes at room temperature. Single crystals suitable for X-ray diffraction were obtained by a slow diffusion of pentane into a saturated solution of 1b in a mixture of CH$_2$Cl$_2$ and COE. $^{11}$B NMR (CD$_2$Cl$_2$): δ 37.6 (br s). $^1$H NMR (CD$_2$Cl$_2$): δ 9.36 (d, $J = 5.8$ Hz, 2H), 8.20 (d, $J = 1.8$ Hz, 2H), 7.50 (dd, $J = 1.8$ and 5.8 Hz, 2H), 7.09 (br s, 3H), 6.87 (br s, 6H), 5.11 (br s, 2H), 1.51 (br s, 4H) 1.47 (s, 18H), 1.38 (br s, 8H), 1.28 (s, 27H). $^{13}$C NMR (CD$_2$Cl$_2$): δ 161.7, 156.7, 154.1, 150.6, 148.4, 144.2, 123.7, 119.8, 117.0, 109.6, 108.6, 75.0, 35.6, 34.8, 31.9, 30.9, 30.5, 26.6, 25.5. Anal. Calc’d for C$_{56}$H$_{74}$B$_3$IrN$_2$O$_6$: C, 61.38; H, 6.81; N, 2.56. Found: C, 61.08; H, 6.82; N, 2.69.

**Preparation of \([\text{Ir(dippe)}(\text{Bcat^*})]\) (3a).** A 20-mL scintillation vial equipped with a stir bar was charged with \([(p\text{-xylene})\text{Ir(}\text{Bcat^*})]\) (150 mg, 0.182 mmol). A solution of 1,2-bis(di-isopropylphosphino)ethane (57.3 mg, 0.219 mmol) in 3 mL of cyclohexane was then prepared and added to the iridium complex. The heterogeneous reaction mixture was sealed under an atmosphere of nitrogen and stirred overnight at ambient temperature to give a clear yellow solution. The volatile
materials were evaporated from the reaction mixture to give 174 mg (88%) of 3a as a yellow powder. Compound 3a is stable under a nitrogen atmosphere at -35 °C for weeks, but slowly decomposes at room temperature. Single crystals suitable for X-ray diffraction were obtained by the slow evaporation of a saturated solution of 3a in a mixture of pentane and COE. $^{11}$B NMR (C$_6$D$_{12}$): $\delta$ 42.4 (br s). $^1$H NMR (C$_6$D$_{12}$): $\delta$ 6.97 (d, $J = 1.4$ Hz, 3H), 6.77 (m, 6H), 2.46 (h, $J = 7.33$ Hz, 4H), 1.88 (d, $J = 12.1$ Hz, 4H), 1.27 (s, 9H), 1.09–1.03 (two overlapping peaks, m, 12H). $^{13}$C NMR (C$_6$D$_6$): $\delta$ 151.6, 149.5, 144.5, 118.2, 110.9, 108.8, 35.1, 32.4, 27.2 (m), 24.4 (t, $J_{CP} = 20.0$ Hz), 19.6, 19.4. $^{31}$P NMR (C$_6$D$_{12}$): $\delta$ 84.5 (s).

**Preparation of [Ir(dcppe)(Bcat*)$_3$] (3b).** A 20-mL scintillation vial equipped with a stir bar was charged with [(p-xylene)Ir(Bcat*)$_3$] (200 mg, 0.243 mmol), 1,2-bis(di-isopropylphosphino)ethane (103 mg, 0.243 mmol) and 3 mL of cyclohexane. The heterogeneous reaction mixture was sealed under an atmosphere of nitrogen and stirred for 1.5 h at ambient temperature to give a clear yellow-orange solution. The solvent was evaporated from the reaction mixture. Pentane (10 mL) was then added to the vial and the mixture was filtered. The filtrate was evaporated and dissolved in pentane (2 mL) and cooled to -35°C. After a yellow solid precipitated, the red-orange solution was decanted and the yellow solid was washed with cold pentane to yield 166 mg (60%) of a yellow powder. $^{11}$B NMR (C$_6$D$_{12}$) : $\delta$ 44.4 (br, s); $^1$H NMR (C$_6$D$_6$) : $\delta$ 7.00 (s, 3H), 6.80 (s, 6H), 2.39 (br m, 4H), 1.93 (d, 11.5 Hz, 4H), 1.84 (d, 9.0 Hz, 4H), 1.74 (br m, 8H), 1.66 (br m, 8H), 1.36-1.10 (multiple peaks, 47H) singlet from t-Bu at 1.32. $^{13}$C NMR (C$_6$D$_6$) : $\delta$ 151.7, 149.4, 144.5, 118.1, 110.8, 109.9, 37.9 (m), 35.1, 32.5, 29.9, 29.6, 28.3 (2 overlapping m), 26.9, 24.3 (t, $J_{CP} = 19.2$ Hz).$^{31}$P NMR (C$_6$D$_{12}$) : 78.4 (s). Anal. Calcd for C$_{56}$H$_{84}$B$_3$IrO$_3$P$_2$: C, 59.01; H, 7.43; N, 0.00 Found: C, 59.07; H, 7.57; N, 0.31.

**Generation of (dtbpy)Ir(B(OR)$_3$)$_3$(CO) complexes (4a, 4b) in situ.** The iridium-trisboryl complexes (0.010 mmol) were dissolved in cyclohexane (0.5 mL) and transferred to a J. Young tube. The tube was sealed and the solvent was frozen in a liquid N$_2$ bath. The tube was evaporated and refilled with CO (1
atm). Immediately upon thawing the color changed from orange to light yellow. A $^1$H NMR spectrum was obtained, and the samples were transferred to a solution IR cell to determine the $\nu_{CO}$ values.

**(dtbpy)Ir(Bpin)$_3$(CO) (4a)** $\nu_{CO}$ (cyclohexane) = 1987 cm$^{-1}$; $^1$H NMR ($C_6D_6$) : $\delta$ 10.17 (d, $J = 5.6$ Hz, 2H), 7.73 (d, 2.0 Hz, 2H), 6.83 (dd, $J = 6.2$ , 2.0 Hz, 2H), 1.58 (s, 18H), 1.00 (s, 12H), 0.98 (s, 12H), 0.95 (s, 12H).

**(dtbpy)Ir(Bcat*)$_3$(CO) (4b)** $\nu_{CO}$ (cyclohexane) = 2017 cm$^{-1}$; $^1$H NMR ($C_6D_{12}$) : $\delta$ 9.82 (d, $J = 5.5$ Hz, 2H), 8.11 (s, 2H), 7.33 (d, $J = 5.0$ Hz, 2H), 7.09 (s, 2H), 6.88 (d, $J = 8.0$ Hz, 2H), 6.81 (d, $J = 8.0$ Hz, 2H), 6.70 (s, 1H), 6.59 (d, $J = 7.5$ Hz, 1H), 6.46 (d, $J = 7.5$ Hz, 1H), 1.46 (s, 9H), 1.34 (s, 9H), 1.30 (s, 18H), 1.14 (s, 9H).
Computational Methods

In this study DFT calculations were carried out using the B3LYP hybrid functional\textsuperscript{7-9} and carried out with the Gaussian 03 and 09 packages\textsuperscript{10-11}. No symmetry restrictions were placed on any structure. Iridium was modeled with the LANL2DZ\textsuperscript{12} basis set and all other atoms were modeled with the split valence 6-31G(d,p) basis set\textsuperscript{13-14}. All optimized geometries were verified as minima by frequency calculations. The Molden program was used to visualize the structures\textsuperscript{15}.

Coordinates of Optimized Geometries

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Supplementary Material (ESI) for Chemical Communications
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\text{C} & -1.769000 & 6.192900 & 0.230900 \\
\text{C} & -1.242700 & 5.246900 & -0.664200 \\
\text{H} & 2.743800 & 1.845700 & 4.145100 \\
\text{H} & 4.337900 & 0.442900 & 5.486400 \\
\text{H} & 4.852800 & -1.875200 & 4.813700 \\
\text{H} & 3.795300 & -2.884300 & 2.772300 \\
\text{H} & 6.083600 & 0.295300 & -4.225100 \\
\text{H} & 4.309300 & -1.375400 & -3.627200 \\
\text{H} & 5.981500 & 2.606800 & -3.363200 \\
\text{H} & 4.097800 & 3.336800 & -1.870000 \\
\text{H} & -2.510800 & 4.185800 & 2.919300 \\
\text{H} & -2.621800 & 6.578800 & 2.170900 \\
\text{H} & -1.826600 & 7.235500 & -0.072800 \\
\text{H} & -0.890000 & 5.523400 & -1.653600 \\
\end{align*}

\begin{align*}
\text{C} & 0.961306 & 0.867576 & 3.662347 \\
\text{C} & 0.548044 & -0.615841 & 3.788142 \\
\text{C} & 2.750629 & -2.990610 & -1.617627 \\
\text{C} & 3.013094 & -3.076639 & -0.097666 \\
\end{align*}

\begin{align*}
\text{dmpe}Yr(Beg)$_3$
\end{align*}
H 0.534746  4.650701  2.246743
H 1.490282  4.456689  -0.047522
H -0.159305  5.336291  -0.190407
H -3.065442  0.034299  -3.652032
H -4.662795  -0.352976  -2.748745
H -4.317472  1.547371  -1.166545
H -4.068862  2.196048  -2.908756
C 3.026156  -1.090114  -0.350599
C 4.555317  -1.035421  -0.531671
C 5.227846  0.257701  -1.026923
C 4.374092  1.504368  -1.322660
C 2.847085  1.454103  -1.132325
H 2.530502  -2.048911  0.004941
H 5.187734  -1.955898  -0.302054
H 6.358090  0.293244  -1.172875
H 4.872625  2.464603  -1.683106
H 2.216886  2.376574  -1.348368
dmpeIr(Bcat)₃
C 1.127739  -1.362637  3.112124
C 1.000276  0.024333  3.228542
C 1.200458  0.676112  4.434431
H 1.097200  1.754312  4.513293
C 1.538659  -0.124191  5.538282
C 1.666134  -1.512469  5.421035
H 1.928078  -2.102434  6.296028
C 1.460534  -2.162767  4.192435
H 1.555291  -3.240394  4.090519
C 0.194596  3.798628  -0.576651
C 1.570558  3.551129  -0.573014
C 2.498891  4.578034  -0.499422
H 3.566335  4.374675  -0.499499
C 1.993004  5.886093  -0.427660
C 0.615203  6.133995  -0.431795
H 0.256536  7.158957  -0.373352
H -0.315792  5.085784  -0.508251
H -1.387039  5.265501  -0.510504
C -4.001773  0.134094  -0.630174
C -3.738195  0.247402  0.738439
C -4.745771  0.488120  1.658709
H -4.528072  0.575721  2.719394
C -6.050269  0.615936  1.153162
C -6.313853  0.504309  -0.216455
C -5.284042  0.259576  -1.140495
H -5.476903  0.174279  -2.206375
C 2.569892  -2.716104  -2.064072
H 2.291306  -2.776805  -3.125214
H 3.608781  -3.062694  -1.989150
C 1.629931  -3.596369  -1.220346
H 1.984379  -3.648401  -0.182936

C 1.596974  -4.623286  -1.608231
C 3.187999  -0.032674  -3.029807
H 4.193178  -0.405267  -3.259542
C 3.743882  -0.695420  -0.288373
H 3.749416  0.356507  0.013484
C -0.871220  -3.387439  -2.728235
H -1.908001  -3.035179  -2.740377
B 0.573916  -0.523746  1.105319
B 0.492772  1.577181  -0.692181
B -1.796878  -0.128402  -0.308922
O 0.877058  -1.726453  1.807536
O 0.670560  0.552706  2.007262
O -0.475585  2.607733  -0.657017
O 1.779209  2.197898  -0.657478
O -2.825177  -0.112783  -1.293688
O -2.394209  0.081357  0.954031
P 2.444432  -0.905359  -1.581924
P -0.089915  -2.862984  -1.132408
Ir 0.166033  -0.464349  -0.843578
C -0.949771  3.928372  0.100206
H -7.334886  0.610547  -0.575572
H -0.527208  -3.725726  1.087787
H 2.686884  6.721204  -0.366327
H -6.869814  0.807492  1.841892
H 1.703302  0.347786  6.503897
H -0.349467  -2.923700  -3.572405
H -0.856157  -4.476714  -2.852852
H 3.238398  1.033594  -2.788562
H 2.547473  -0.157079  -3.909455
H 4.734897  -0.981300  -0.660395
H 3.490035  -1.304703  0.584338
H -0.847395  -4.992668  -0.142419
H -2.012129  -3.663642  0.116578
dmpeIr(Bcat)₃(H)(Ph)
C 3.118800  -0.217000  -2.076200
C 2.814600  1.135300  -1.908900
C 3.612600  2.135400  -2.442500
H 3.368200  3.184300  -2.303000
H 4.744800  1.722100  -3.162000
C 5.048900  0.365600  -3.330000
H 5.935600  0.081700  -3.891500
C 4.233000  -0.638500  -2.784500
H 4.462300  -1.693600  -2.904700
C -1.611200  3.516500  -0.602300
C -1.410700  3.552400  0.779700
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### Crystallographic data of [(coe)Ir(dtbp)(Bcat*)$_3$] (1b)

Crystal data and structure refinement for 1b.

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<tr>
<td>Wavelength</td>
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<tr>
<td>Crystal system</td>
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<td>Space group</td>
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<td></td>
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<tr>
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<tr>
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<td>$\gamma = 74.051(4)^\circ$</td>
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<td>Integration</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
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<td>Data / restraints / parameters</td>
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<td>Goodness-of-fit on $F^2$</td>
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<td>Final R indices [$I&gt;2\sigma(I)$]</td>
<td>$R1 = 0.0423$, $wR2 = 0.0806$</td>
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### Crystallographic data of [Ir(dippe)(Bcat*)₃] (3a).

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<td>P b c a</td>
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References


