Supplementary Material (ESI) for Chemical Communications

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*)$_3$] 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_3PO_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_2cat_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)]$_2$ (1.6 mg, 0.0024 mmol); 4,4´-di-*tert*-butyl-2,2´-bipyridine (1.3 mg, 0.0048 mmol), B_2cat_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 ºC. Upon heating, the B_2cat_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 ºC 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)]$_2$ (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 ºC. After heating for 24 h, the yield (24%, L = dcpe;

<5% L = dippe) of phenylboronate ester was determined by GC analysis using response factors calculated from pure samples of PhBpin.

Preparation of [(coe)Ir(dtbpy)(Bcat*)$_3$] (1b). In an oven-dried, 20-mL scintillation vial, [(*p*-xylene)Ir(Bcat*)$_3$] (254 mg, 0.308 mmol) and 4,4´-di-*tert*-butyl-2,2´-bipyridine (99 mg, 0.369 mmol) were combined with 4 mL of cyclohexane. The mixture was stirred while *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 -35ºC 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 ºC 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_2Cl_2 and COE. ^{11}B NMR (CD_2Cl_2): δ 37.6 (br s). ^{1}H NMR (CD_2Cl_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_2Cl_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 $C_{56}H_{74}B_3IrN_2O_6$: C, 61.38; H, 6.81; N, 2.56. Found: C, 61.08; H, 6.82; N, 2.69.

Preparation of [Ir(dippe)(Bcat*)$_3$] (3a). A 20-mL scintillation vial equipped with a stir bar was charged with [(*p*-xylene)Ir(Bcat*)$_3$] (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 ºC 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_6D_{12}): δ 42.4 (br s). ^{1}H NMR (C_6D_{12}): δ 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_6D_6): δ 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_6D_{12}): δ 84.5 (s).

Preparation of [Ir(dcpe)(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 ºC. 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_6D_{12}) : δ 44.4 (br, s); ^{1}H NMR (C_6D_6) : δ 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_6D_6) : δ 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_6D_{12}) : 78.4 (s). Anal. Calcd for $C_{56}H_{84}B_3IrO_6P_2$: 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)$_2$)$_3$(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 ν_{CO} values.

(dtbpy)Ir(Bpin)$_3$(CO) (4a) ν_{CO} (cyclohexane) = 1987 cm^{-1}; ^{1}H NMR (C_6D_6) : δ 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) ν_{CO} (cyclohexane) = 2017 cm^{-1}; ^{1}H NMR (C_6D_{12}) : δ 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[7-9] and carried out with the Gaussian 03 and 09 packages[10-11]. No symmetry restrictions were placed on any structure. Iridium was modeled with the LANL2DZ[12] basis set and all other atoms were modeled with the split valence 6-31G(d,p) basis set[13-14]. All optimized geometries were verified as minima by frequency calculations. The Molden program was used to visualize the structures[15].

Coordinates of Optimized Geometries

C_6H_6

C	-1.397406	0.000000	0.000000
H	-2.485503	0.000000	0.000000
C	-0.698703	1.210189	0.000000
H	-1.242751	2.152508	0.000000
C	0.698703	1.210189	0.000000
H	1.242751	2.152508	0.000000
C	1.397406	0.000000	0.000000
H	2.485503	0.000000	0.000000
C	0.698703	-1.210189	0.000000
H	1.242751	-2.152508	0.000000
C	-0.698703	-1.210189	0.000000
H	-1.242751	-2.152508	0.000000

$bpyIr(Beg)_3$

	x	y	z
B	1.703405	12.935920	5.601246
B	2.000902	11.039752	3.599691
B	2.522606	10.489604	6.257929
C	-0.117510	11.475985	8.303129
H	0.959238	11.433128	8.435189
C	-0.987195	11.664410	9.374188
H	-0.592792	11.752847	10.382177
C	-2.355676	11.743408	9.117074
C	-2.801107	11.640077	7.801955
C	-1.870424	11.444559	6.772786
C	-2.256915	11.359193	5.339812
C	-3.591041	11.311116	4.915579
H	-4.399985	11.299266	5.638025
C	-3.877030	11.266730	3.553135
C	-2.822492	11.270764	2.641775
H	-2.997808	11.241924	1.570278
C	-1.516844	11.304466	3.129505
H	-0.646413	11.301644	2.476716
C	2.832651	14.912686	5.307858
C	2.243230	14.856662	6.734692
C	3.741252	10.741557	2.102473
C	2.489661	11.225338	1.333583
C	4.399652	10.309503	7.590870
C	3.959954	8.902687	7.125994
Ir	0.873979	11.149477	5.298306
N	-0.545504	11.355173	7.035640
N	-1.237852	11.343749	4.444453
O	2.589974	13.613345	4.767451
O	1.385179	13.714371	6.722697
O	3.363397	10.772046	3.475596
O	1.447590	11.230857	2.312090
O	3.342589	11.175630	7.170364
O	2.895708	9.140850	6.205352
H	-3.859771	11.726437	7.581870
H	-4.908977	11.228017	3.212824
H	-3.067155	11.894389	9.925102
H	3.909289	15.122564	5.301108
H	1.667022	15.753896	6.994263
H	2.331440	15.668119	4.684107
H	3.025805	14.715071	7.494273
H	4.527946	10.379098	8.678867
H	3.594315	8.286683	7.961843
H	4.028072	9.717006	1.823126
H	2.217615	10.560864	0.502794
H	4.609750	11.393114	1.941347
H	2.617577	12.240768	0.931956
H	5.339181	10.624338	7.114804
H	4.767184	8.351849	6.626915

$bpyIr(Beg)_3(H)(Ph)$

	x	y	z
B	1.583294	-0.900765	0.976120
B	1.168901	1.917223	0.064438

B	1.873833	-0.686640	-1.203142
C	-1.220032	-2.405141	-1.737230
H	-0.420342	-2.225635	-2.447756
C	-2.196828	-3.374916	-1.952927
H	-2.184156	-3.960749	-2.867379
C	-3.174859	-3.565549	-0.978268
C	-3.130798	-2.791599	0.176828
C	-2.114378	-1.837656	0.328708
C	-1.986167	-0.988281	1.535586
C	-2.809869	-1.148843	2.657884
H	-3.578990	-1.912477	2.664965
C	-2.634161	-0.335130	3.771554
C	-1.629564	0.629735	3.742327
H	-1.449387	1.291007	4.584581
C	-0.839352	0.743007	2.602577
H	-0.048093	1.481212	2.518584
C	3.025966	-1.217244	2.738931
C	2.399893	-2.572124	2.335816
C	2.520076	3.755766	-0.214806
C	1.667529	3.942309	1.058019
C	2.981180	-2.036781	-2.712389
C	3.995592	-1.133055	-1.972648
Ir	0.197614	0.160414	-0.287443
N	-1.181682	-1.649659	-0.630283
N	-1.010624	-0.042936	1.521867
O	2.341025	-0.248873	1.938006
O	1.622723	-2.279332	1.167398
O	1.992060	2.582999	-0.833583
O	1.012997	2.680720	1.231922
O	1.733337	-1.785563	-2.063458
O	3.197527	-0.259975	-1.175146
H	-3.885495	-2.925875	0.943687
H	-3.270001	-0.456578	4.644902
H	-3.959652	-4.306040	-1.110992
H	2.896654	-1.776602	-3.777078
H	4.663551	-1.711596	-1.318862
H	3.149986	-3.335719	2.096839
H	2.886872	-0.982489	3.801307
H	2.444002	4.605258	-0.904240
H	2.267632	4.174154	1.946189
H	3.582154	3.596198	0.020776
H	0.908299	4.727951	0.935458
H	3.228336	-3.103089	-2.637850
H	4.615838	-0.542402	-2.657712
H	4.100730	-1.172440	2.515761
H	1.739107	-2.976013	3.11567
H	0.788550	0.475720	-1.734138
C	-1.425478	1.376999	-1.029683
C	-2.010065	2.424701	-0.291147
H	-1.602314	2.683723	0.684976
C	-3.091781	3.169244	-0.775730
H	-3.512624	3.969632	-0.167349

bpyIr(Bcat)$_3$

	x	y	z
B	0.182955	-0.313569	1.320771
B	-0.733206	-1.225660	-1.004057
B	-1.170887	1.411760	-0.356518
C	1.899380	3.204865	-0.639446
H	0.863159	3.490215	-0.480578
C	2.905894	4.150487	-0.828401
H	2.660792	5.208254	-0.817010
C	4.209572	3.705235	-1.035530
C	4.462368	2.335524	-1.035342
C	3.408596	1.437562	-0.826053
C	3.607474	-0.035490	-0.787857
C	4.874762	-0.631753	-0.806925
H	5.772012	-0.024452	-0.853859
C	4.980457	-2.019129	-0.745761
C	3.817248	-2.781544	-0.654045
H	3.850112	-3.865137	-0.593605
C	2.590095	-2.123407	-0.631451
H	1.653329	-2.663644	-0.535438
C	-0.607835	-0.575832	3.390623
C	0.560867	-1.335225	3.273048
C	1.053914	-2.085030	4.328648
H	1.962732	-2.671695	4.226900
C	0.323175	-2.049158	5.528436
C	-0.845464	-1.289127	5.645420
C	-1.335633	-0.531538	4.568430
C	-2.055108	-2.506435	-2.284943
C	-1.760108	-3.220272	-1.118950
C	-2.259456	-4.492591	-0.892639
H	-2.026628	-5.033869	0.020143
C	-3.079842	-5.039540	-1.893749
C	-3.374244	-4.326960	-3.061332
H	-4.014502	-4.777785	-3.816071
C	-2.862199	-3.036995	-3.279222
H	-3.086937	-2.473243	-4.180229
C	-2.471025	3.238828	-0.093318
C	-3.297745	2.115389	-0.193759
C	-4.678676	2.220198	-0.126038
H	-5.311573	1.341026	-0.205333
C	-5.210604	3.507819	0.049739
C	-4.382154	4.631412	0.150365
C	-2.984159	4.514612	0.079274
H	-2.331905	5.380247	0.157791
Ir	0.508989	0.288156	-0.540272

N	2.139598	1.881470	-0.638869
N	2.483991	-0.786590	-0.706728
O	-0.853730	0.061017	2.201465
O	1.070591	-1.184840	2.007522
O	-1.433101	-1.287372	-2.238231
O	-0.938991	-2.459322	-0.323786
O	-1.164152	2.835549	-0.195875
O	-2.526010	1.001148	-0.360027
H	5.470003	1.973067	-1.205802
H	-6.289329	3.632511	0.109077
H	-1.388055	-1.283584	6.587812
H	-2.242053	0.061840	4.646040
H	0.674910	-2.625188	6.381184
H	-4.826792	5.614446	0.286847
H	5.958338	-2.493575	-0.760055
H	-3.494559	-6.035240	-1.754884
H	5.021208	4.410066	-1.197620

bpyIr(Bcat)$_3$(H)(Ph)

	x	y	z
B	1.240300	-0.220300	0.895400
B	-0.891700	1.728300	-0.013000
B	1.412000	0.277600	-1.156400
C	0.195200	-3.003800	-1.959500
H	0.720700	-2.320200	-2.617200
C	0.097500	-4.363900	-2.244100
H	0.535400	-4.758100	-3.156200
C	-0.570900	-5.187100	-1.339800
C	-1.101800	-4.623800	-0.183500
C	-0.959100	-3.247700	0.041500
C	-1.474200	-2.575900	1.257700
C	-2.049400	-3.285500	2.319500
H	-2.141000	-4.364100	2.268700
C	-2.494800	-2.607600	3.449200
C	-2.350700	-1.223300	3.499000
H	-2.676400	-0.645700	4.358600
C	-1.771200	-0.570600	2.415200
H	-1.641500	0.506000	2.397700
C	2.404400	0.241300	2.740600
C	2.695900	-1.071200	2.359900
C	-1.191700	3.932700	-0.227800
C	-1.643200	3.563200	1.041800
C	3.245000	0.074100	-2.431000
C	3.186900	1.382800	-1.942800
Ir	-0.472500	-0.216600	-0.419300
N	-0.324800	-2.456700	-0.851600
N	-1.345800	-1.224700	1.317700
O	1.512800	0.778000	1.846800
O	1.988300	-1.371700	1.221300
O	-0.733800	2.822700	-0.885900
O	-1.470400	2.207700	1.194400
O	2.165300	-0.629500	-1.956100
O	2.075000	1.524000	-1.155600
H	-1.628000	-5.250900	0.527400
H	-2.940700	-3.154600	4.275900
H	-0.678100	-6.252200	-1.528000
H	-0.126000	0.430600	-1.837300
C	-2.449400	-0.311200	-1.247900
C	-3.611600	0.043700	-0.536900
H	-3.528500	0.432200	0.477100
C	-4.889700	-0.064200	-1.096700
H	-5.761300	0.223900	-0.510100
C	-5.049500	-0.529100	-2.402500
H	-6.041200	-0.611700	-2.843100
C	-3.914800	-0.876200	-3.138800
H	-4.017600	-1.230000	-4.164000
C	-2.643000	-0.764800	-2.568700
H	-1.782200	-1.037000	-3.178700
C	3.572900	-1.866700	3.080500
C	4.157000	-1.288600	4.218600
C	3.864500	0.026800	4.600400
C	2.975500	0.823100	3.861700
C	4.272300	-0.355400	-3.255100
C	5.259100	0.590200	-3.580600
C	5.201200	1.899900	-3.091700
C	4.154700	2.323300	-2.256100
C	-2.164000	4.485300	1.934000
C	-2.219900	5.821200	1.502100
C	-1.769000	6.192900	0.230900
C	-1.242700	5.246900	-0.664200
H	2.743800	1.845700	4.145100
H	4.337900	0.442900	5.486400
H	4.852800	-1.875200	4.813700
H	3.795300	-2.884300	2.772300
H	6.083600	0.295300	-4.225100
H	4.309300	-1.375400	-3.627200
H	5.981500	2.606800	-3.363200
H	4.097800	3.336800	-1.870000
H	-2.510800	4.185800	2.919300
H	-2.621800	6.578800	2.170900
H	-1.826600	7.235500	-0.072800
H	-0.890000	5.523400	-1.653600

dmpeIr(Beg)$_3$

C	0.961306	0.867576	3.662347
C	0.548044	-0.615841	3.788142
C	2.750629	-2.990610	-1.617627
C	3.013094	-3.076639	-0.097666

C	2.491826	3.303035	-1.269040
C	3.521688	2.378155	-0.585490
C	-3.554572	-0.527999	-0.348528
H	-3.807069	-0.419141	-1.412368
H	-4.389342	-1.065845	0.119605
C	-3.364466	0.861653	0.288757
H	-3.271663	0.765972	1.379008
H	-4.232967	1.505268	0.093534
C	-2.196354	-2.711945	-1.710366
H	-3.123343	-3.293486	-1.638516
C	-2.252785	-2.685340	1.158025
H	-1.434581	-3.411757	1.189720
C	-2.263181	2.482685	-1.891854
H	-1.385142	3.017086	-2.268575
B	0.311630	0.058143	1.605724
B	1.360563	-1.521408	-0.503872
B	1.461172	1.338159	-0.588293
O	0.910093	1.137395	2.258753
O	-0.045126	-0.930388	2.525547
O	1.594691	-2.152916	-1.736459
O	2.204273	-2.045326	0.472162
O	1.235479	2.640736	-1.080125
O	2.823933	1.149485	-0.377686
P	-1.976257	-1.558157	-0.278244
P	-1.777159	1.672603	-0.298254
Ir	-0.084611	-0.040676	-0.358414
C	-1.591507	3.126685	0.819693
H	-1.312602	2.779383	1.818598
H	-2.546077	1.725237	-2.630974
H	-3.095144	3.185449	-1.762051
H	-1.337336	-3.389694	-1.742220
H	-2.201650	-2.139442	-2.644207
H	-3.211445	-3.211710	1.075930
H	-2.206351	-2.107388	2.083644
H	-2.503527	3.733278	0.870505
H	-0.763260	3.727887	0.432673
H	2.455139	4.304072	-0.821138
H	3.853583	2.775426	0.384583
H	3.591434	-2.530421	-2.155879
H	2.713934	-4.049562	0.320302
H	0.265887	1.538601	4.188414
H	1.414689	-1.270995	3.950987
H	1.972787	1.059673	4.039279
H	-0.175749	-0.791301	4.593863
H	2.548679	-3.968801	-2.072607
H	4.065798	-2.905599	0.159465
H	2.685473	3.417098	-2.345581
H	4.410194	2.201241	-1.204294

dmpeIr(Beg)$_3$(H)(Ph)

C	-3.502719	-1.242710	1.769857
C	-3.279028	0.066893	2.549075
C	0.002172	3.956275	1.516169
C	0.361059	4.356710	0.072731
C	-3.605282	0.060762	-2.648303
C	-3.666574	1.499168	-2.101215
C	1.394133	-2.524963	1.592853
H	2.311346	-2.610290	0.921257
H	1.602047	-3.034656	2.591144
C	0.188392	-3.202675	0.910954
H	-0.749530	-3.051107	1.540977
H	0.397801	-4.316548	0.788343
C	2.539603	0.238025	2.279716
H	2.792635	0.937889	1.416139
C	-0.253288	-0.482508	3.254942
H	-0.617414	0.597767	3.259140
C	1.456068	-2.755616	-1.836543
H	2.329351	-3.083191	-1.181050
B	-1.617812	-0.253960	1.079814
B	0.149846	2.131600	0.227740
B	-1.870499	0.435327	-1.286919
O	-2.096374	-1.594403	1.352242
O	-2.389701	0.850408	1.612923
O	0.504680	2.534094	1.574254
O	-0.157233	3.181215	-0.722860
O	-2.792202	-0.640665	-1.586603
O	-2.219686	1.760619	-1.757985
P	0.985107	-0.717855	1.872339
P	-0.024447	-2.378165	-0.759259
Ir	0.011479	0.087410	-0.429249
C	-1.591138	-2.971606	-1.589930
H	-1.521897	-4.094565	-1.773697
H	-1.721816	-2.431045	-2.585077
H	-2.484822	-2.750996	-0.917428
H	1.748923	-1.821538	-2.420782
H	1.192743	-3.592285	-2.564721
H	3.401356	-0.490021	2.443823
H	2.372583	0.849001	3.227563
H	0.242378	-0.720325	4.253620
H	-1.139386	-1.181568	3.094490
C	2.171669	0.156334	-0.654181
H	0.342883	0.394857	-2.422039
H	-4.160930	-1.061262	0.856931
H	-3.974062	-2.019067	2.458846
H	-2.743060	-0.138532	3.534032
H	-4.282790	0.573841	2.736333
H	-1.126045	3.991973	1.675706

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	-1.132235
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	-0.494999
C	1.993004	5.886093	-0.427660
C	0.615203	6.133995	-0.431795
H	0.256536	7.158957	-0.373352
C	-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
H	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
C	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

C	-1.550800	4.723600	1.506500
H	-1.392500	4.740400	2.581000
C	-1.904100	5.877500	0.787700
C	-2.104100	5.840800	-0.596600
H	-2.376100	6.752600	-1.122900
C	-1.959900	4.646800	-1.323000
H	-2.111300	4.607600	-2.398200
C	2.812600	-0.772100	2.687100
C	2.650100	0.615700	2.650800
C	3.525800	1.471900	3.298800
H	3.388100	2.548500	3.263500
C	4.588200	0.877000	3.998200
C	4.750300	-0.512700	4.035000
C	3.856600	-1.370800	3.373500
H	3.972300	-2.450600	3.397600
C	-1.568200	-2.536900	-2.602800
H	-2.537900	-2.911000	-2.254200
H	-1.571200	-2.619400	-3.697600
C	-0.421800	-3.353800	-1.990100
H	0.530500	-3.070400	-2.455600
H	-0.567700	-4.427200	-2.168200
C	-3.146100	-0.069000	-2.499300
H	-3.445200	-0.349900	-3.515800
C	-0.473800	0.026100	-3.479800
H	-0.348900	1.088600	-3.254400
C	-1.253300	-4.256300	0.696900
H	-0.997600	-4.240700	1.762200
B	1.230100	-0.057100	-0.859700
B	-1.056500	1.453700	0.091200
B	1.008200	-0.300800	1.454700
O	2.155700	-0.967800	-1.440200
O	1.664700	1.247200	-1.171800
O	-1.406600	2.231600	-1.046600
O	-1.077400	2.297400	1.218900
O	1.801300	-1.359500	1.966700
O	1.539200	0.921900	1.910400
P	-1.471300	-0.731600	-2.128600
P	-0.177500	-3.022100	-0.163200
Ir	-0.624200	-0.572300	0.081800
C	1.481900	-3.787200	0.104500
H	5.583900	-0.939500	4.587300
H	2.239000	-3.188200	-0.405700
H	5.298600	1.511500	4.522300
H	5.400100	2.473400	-3.596100
H	-2.023800	6.818000	1.320300
H	1.706100	-3.787000	1.173600
H	1.492700	-4.815700	-0.276400
H	-1.087600	-5.267500	0.306600
H	-2.307500	-3.987200	0.607800
H	-3.096300	1.019300	-2.414500
H	-3.870600	-0.445900	-1.775100
H	-0.987100	-0.090000	-4.441200
H	0.512500	-0.442500	-3.539400
H	-0.361300	-0.479100	1.725500
C	-2.653500	-0.883200	0.892700
C	-3.626700	-1.778800	0.401000
H	-3.423200	-2.381900	-0.482000
C	-4.882200	-1.952200	0.998300
H	-5.590800	-2.658100	0.566200
C	-5.221900	-1.227800	2.139400
H	-6.193400	-1.356600	2.611900
C	-4.285500	-0.333500	2.661400
H	-4.524000	0.245500	3.552500
C	-3.039100	-0.166500	2.049700
H	-2.355000	0.557500	2.484400

Crystallographic data of [(coe)Ir(dtbpy)(Bcat*)$_3$] (1b)

Crystal data and structure refinement for **1b**.

Identification code	g08vas	
Empirical formula	C61 H86 B3 Ir N2 O6	
Formula weight	1167.95	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.849(4) Å	α= 79.705(4)°.
	b = 14.181(4) Å	β= 79.622(4)°.
	c = 15.889(4) Å	γ = 74.051(4)°.
Volume	2923.4(14) Å^3	
Z	2	
Density (calculated)	1.327 Mg/m^3	
Absorption coefficient	2.333 mm^{-1}	
F(000)	1212	
Crystal size	0.20 x 0.12 x 0.06 mm^3	
Theta range for data collection	1.86 to 25.40°.	
Index ranges	-16<=h<=16, -17<=k<=17, -19<=l<=19	
Reflections collected	30653	
Independent reflections	10724 [R(int) = 0.0684]	
Completeness to theta = 25.40°	99.6 %	
Absorption correction	Integration	
Max. and min. transmission	0.8819 and 0.5881	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10724 / 932 / 840	
Goodness-of-fit on F^2	0.953	
Final R indices [I>2sigma(I)]	R1 = 0.0423, wR2 = 0.0806	
R indices (all data)	R1 = 0.0709, wR2 = 0.0863	
Largest diff. peak and hole	1.477 and -1.172 e.Å^{-3}	

Crystallographic data of [Ir(dippe)(Bcat*)$_3$] (3a).

Identification code	ga39zas	
Empirical formula	C49 H80 B3 Ir O6 P2	
Formula weight	1051.70	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 20.5747(8) Å	α= 90°.
	b = 16.6713(7) Å	β= 90°.
	c = 30.6305(10) Å	γ = 90°.
Volume	10506.5(7) Å^3	
Z	8	
Density (calculated)	1.330 Mg/m^3	
Absorption coefficient	2.646 mm^{-1}	
F(000)	4352	
Crystal size	0.16 x 0.14 x 0.06 mm^3	
Theta range for data collection	1.33 to 28.30°.	
Index ranges	-27<=h<=27, -22<=k<=22, -40<=l<=40	
Reflections collected	153721	
Independent reflections	12930 [R(int) = 0.1203]	
Completeness to theta = 28.30°	98.9 %	
Absorption correction	Integration	
Max. and min. transmission	0.8227 and 0.6650	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12930 / 1347 / 820	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0395, wR2 = 0.0693	
R indices (all data)	R1 = 0.0872, wR2 = 0.0833	
Largest diff. peak and hole	1.468 and -0.602 e.Å^{-3}	

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