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Iridium Phosphane Complexes Containing Arylspiroboronate Esters for the Hydroboration of Alkenes

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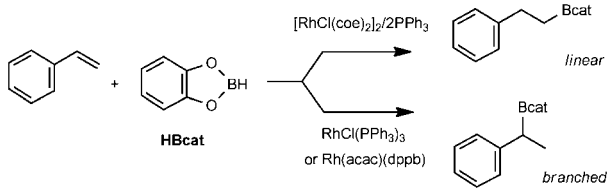
Keywords: Iridium / Boron / Hydroboration / Zwitterions

Iridium phosphane arylspiroboronate esters have been prepared by addition of B_2cat_3 (cat = 1,2-$O_2C_6H_4$) to the iridium precursors Ir(acac)(coe)$_2$/PR_3 (acac = acetylacetonato, coe = *cis*-cyclooctene) or Ir(acac)(coe)$_2$/P-P (chelating bidentate ligands) at elevated temperatures. These novel complexes have been characterized by a number of physical methods including X-ray diffraction studies for the PCy_3 (**2**) and dppp (**6**, 1,3-diphenylphosphanopropane) derivatives. The arylspiroboronate esters, as seen with the more common rhodium complexes, are bound to the metal centre via one of the benzene catecholato rings. These organometallic complexes can be used as precatalysts for the selective hydroboration of vinylarene derivatives with HBpin (pin = 1,2-$O_2C_2Me_4$) to give the corresponding linear hydroboration products. Reactions with methyl oleate proceed at elevated temperatures to give the isomerised/hydroboration product selectively along with equal amounts of hydrogenation product.

Introduction

The addition of boranes to unsaturated organic molecules has become a remarkably important synthetic methodology in organic synthesis.[1] Although borane reagents $H_3B{\cdot}X$ (X = THF, SMe_2) add readily to alkenes at –80 °C,[2] other hydroboration reagents, such as diorganyloxyboranes, are slow to react even at room temperature. For instance, catecholborane (HBcat, cat = 1,2-$O_2C_6H_4$) and pinacolborane (HBpin, pin = 1,2-$O_2C_2Me_4$) add to alkenes and alkynes only at elevated temperatures[3] or in the presence of a transition metal catalyst.[4] A considerable amount of research has therefore focused on investigating the mechanism and scope of these catalysed hydroboration reactions.[5] Although a number of transition metals have been found to catalyse hydroborations with HBcat and HBpin, rhodium complexes are usually the most effective for reactions with alkenes. For instance, the judicious choice of a rhodium precatalyst in hydroborations with HBcat can give exclusive formation of either the linear or branched product in the hydroboration of vinylarene derivatives (Scheme 1).[6] Indeed, the unusual branched product can be obtained in reactions employing either a catalytic amount of Wilkinson's catalyst, $RhCl(PPh_3)_3$, or phosphane acetylacetonato rhodium complexes of the type Rh(acac)(P_2) (where acac = acetylacetonato, P_2 is a bidentate phosphane).[7] These phosphane rhodium acetylacetonato complexes are remarkably active catalyst precursors for the hydroboration of a wide range of alkenes using HBcat, where catalyst resting states in these systems are believed to be the zwitterionic complexes of the type Rh(η^6-catBcat)(P_2), arising from the redistribution of borane substituents. The unusual arylspiroboronate ester $[Bcat_2]^-$ is bound to the rhodium fragment via all six carbons of one of the catecholato rings.



Scheme 1. The rhodium-catalysed hydroboration of styrene using catecholborane (HBcat).

More recently, there has been considerable interest in the use of iridium complexes in an effort to expand the scope of these catalysed hydroborations.[8] For instance, an elegant study by Suzuki, Miyata and co-workers[8b] has used the catalyst system of $[IrCl(cod)]_2$/diphosphane and HBpin as a key step in the synthesis of boron-containing histone deacetylases inhibitors containing a α-amino acid group. In light of this work, we decided to generate the zwitterionic iridium complexes of the type Ir(η^6-catBcat)(P_2) and examine their potential to catalyse the borylation of various alkenes, our findings are presented herein.

Results and Discussion

Marder and co-workers have found that addition of B_2cat_3 to Rh(acac)(P_2) led to the zwitterionic complexes

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Rh(η^6-catBcat)(P_2) in high yields, along with concomitant formation of acacBcat.[7b] The diboron reagent B_2cat_3 can be readily prepared by the addition of catechol to solutions of $BH_3{\cdot}SMe_2$.[9] Although rhodium compounds containing arylspiroboronate esters are known,[7b,10] and a ruthenium example has been characterized by multinuclear NMR spectroscopy,[11] we have just begun to prepare a number of iridium complexes containing these unusual ligands and examine their potential to act as precatalysts in the hydroboration of alkenes and alkynes.[12] We have previously generated the starting iridium precursors from addition of phosphane to Ir(acac)$(coe)_2$ (coe = *cis*-cyclooctene).[13] Although the mixed phosphane cyclooctene complex Ir(acac)-(coe)(PCy_3) (**1**) has been characterized spectroscopically,[14] the molecular structure for this mixed ligand complex has not yet been reported. To confirm monosubstitution, we have carried out a single-crystal X-ray diffraction study on **1** and the molecular structure of which is shown in Figure 1. Bond lengths and angles are well within the expected range for similar iridium acetylacetonate phospane complexes.[13] Crystallographic data are presented in Table 1.

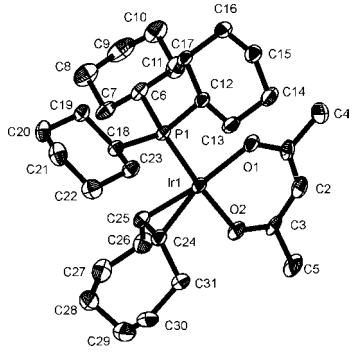


Figure 1. Molecular structure of **1** with atom labelling scheme, thermal ellipsoids are drawn at the 50% probability level with hydrogen atoms omitted for clarity. Selected bond lengths [Å]: Ir(1)–O(1) 2.065(3), Ir(1)–O(2) 2.093(4), Ir(1)–C(25) 2.106(5), Ir(1)–C(24) 2.118(5), Ir(1)–P(1) 2.2202(14); selected bond angles (°): O(1)–Ir(1)–O(2) 87.09(15), O(1)–Ir(1)–C(25) 159.30(18), O(2)–Ir(1)–C(25) 89.83(17), O(1)–Ir(1)–C(24) 160.60(18), O(2)–Ir(1)–C(24) 88.90(18), O(1)–Ir(1)–P(1) 88.39(11), O(2)–Ir(1)–P(1) 175.23(11).

We then used **1** to prepare the zwitterionic complex Ir(η^2-coe)(PCy_3)(η^6-catBcat) (**2**, cat = 1,2-$O_2C_6H_4$) in good yield (79%) by the addition of B_2cat_3. The $^{11}B\{^1H\}$ NMR spectrum shows a sharp singlet at δ = 13.8 ppm for the four coordinate boron anion[15] and the $^{31}P\{^1H\}$ NMR peak shifts from δ = 0.6 ppm in **1** to 7.6 ppm for complex **2**. More diagnostic, however, is the ^1H NMR spectroscopic data in [D_8]THF, as the resonances for the hydrogens on the Bcat group bound directly to iridium are observed at δ = 6.10 and 5.75 ppm, while the uncoordinated catecholato peaks remain downfield from δ = 6.46 to 6.52 ppm. In comparison, these catecholato proton peaks are observed at δ = 6.57 ppm for [NBu_4][$Bcat_2$].[16] The chemical shifts of the bound protons are quite dependent upon solvent as they move to δ = 5.93 and 5.55 ppm in $CDCl_3$ and δ = 5.47 and 4.78 ppm in C_6D_6. Significant upfield shifts are also observed in **2** by $^{13}C\{^1H\}$ NMR spectroscopy, where the carbon atoms of the Bcat group coordinated to the iridium fragment are located at δ = 139.4, 85.9, and 79.0 ppm. For comparison, the related carbon resonances in [NBu_4][$Bcat_2$] are observed at δ = 151.8, 117.9, and 108.5 ppm.

Complex **2** has also been characterised by a single-crystal X-ray diffraction study (Figure 2, Table 1), confirming that

Table 1. Crystallographic data collection parameters for **1**, **2** and **6**.

Complex	**1**	**2**	**6**
Formula	$C_{31}H_{54}IrO_2P$	$C_{38}H_{55}BIrO_4P$	$C_{39}H_{34}BIrO_4P_2$
Formula mass	681.91	809.80	831.61
Dimensions [mm]	0.45 × 0.40 × 0.25	0.35 × 0.15 × 0.08	0.60 × 0.10 × 0.05
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Z	4	4	4
a [Å]	13.195(4)	16.071(3)	11.2363(12)
b [Å]	18.870(6)	9.6251(17)	20.635(2)
c [Å]	13.807(5)	23.247(4)	14.6540(17)
α [°]	90	90	90
β [°]	115.595(4)	108.381(2)	106.329(2)
γ [°]	90	90	90
Volume [Å^3]	3100.6(17)	3412.5(10)	3260.6(6)
$D_{calcd.}$ [mg m^{-3}]	1.461	1.576	1.694
T [K]	173(1)	173(1)	213(1)
Radiation [Å]	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)
μ [mm^{-1}]	4.382	3.999	4.236
Total reflections	20845	7642	22239
Number of variables	6912	7642	7188
Θ [°]	1.78 to 27.50	1.36 to 27.50	1.75 to 27.50
GoF on F^2	1.051	1.127	1.084
R_1[a] [$I > 2\sigma(I)$]	0.0514	0.0375	0.0256
wR_2[b] (all data)	0.1389	0.0974	0.0635
Largest difference peak & hole [Å]	4.335 & –3.765	3.145 & –1.383	1.018 & –0.566

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[F_o]^4\}^{1/2}$, where $w = 1/[\sigma^2(F_o)^2 + (0.0917\,P)^2 + (3.0571\,P)]$ (for **1**), $1/[\sigma^2(F_o)^2 + (0.058\,P)^2 + (1.8907\,P)]$ (for **2**), $1/[\sigma^2(F_o) + (0.0262\,P)^2 + (0.1357\,P)]$ (for **6**).

the arylspiroboronate ester is bound to the iridium fragment in a η^6 fashion. Within the bound Bcat group, four of the iridium carbon distances Ir(1)–C(30) 2.275(6), Ir(1)–C(31) 2.296(6), Ir(1)–C(29) 2.330(6), and Ir(1)–C(32) 2.338(6), are noticeably shorter than the other two at 2.420(6) Ir(1)–C(27) and 2.434(6) Ir(1)–C(28) Å. This slippage away from a true η^6 bonding mode has been observed in the rhodium analogues where the potential surface for such distortions is reputably quite shallow. Bond lengths and angles within the arylspiroboronate ester are similar to those reported previously.[17] Also of significance is that boron oxygen distances for the catecholato group bound to the metal centre, B(1)–O(1) 1.491(9) and B(1)–O(2) 1.532(9) Å,[18] are somewhat longer than the analogous distances for the unbound group at B(1)–O(4) 1.449(8) and B(1)–O(3) 1.463(8) Å. Not surprisingly, attempts to substitute the second coe ligand with another bulky PCy_3 group did not prove successful.

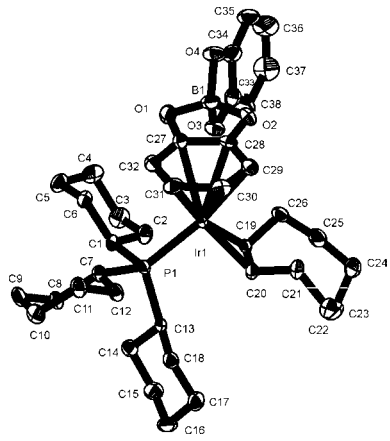
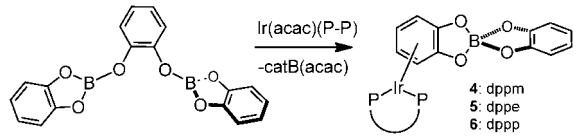


Figure 2. Molecular structure of **2** with atom labelling scheme, thermal ellipsoids are drawn at the 50% probability level with hydrogen atoms omitted for clarity. Selected bond lengths [Å]: Ir(1)–C(20) 2.104(5), Ir(1)–C(19) 2.128(6), Ir(1)–P(1) 2.2850(15), Ir(1)–C(30) 2.275(6), Ir(1)–C(31) 2.296(6), Ir(1)–C(29) 2.330(6), Ir(1)–C(32) 2.338(6), Ir(1)–C(27) 2.420(6), Ir(1)–C(28) 2.434(6), B(1)–O(4) 1.449(8), B(1)–O(3) 1.463(8), B(1)–O(1) 1.491(9), B(1)–O(2) 1.532(9); selected bond angles (°): C(20)–Ir(1)–C(19) 40.0(2), C(20)–Ir(1)–P(1) 93.18(17), C(19)–Ir(1)–P(1) 90.77(17), O(4)–B(1)–O(3) 107.2(5), O(4)–B(1)–O(1) 114.7(5), O(3)–B(1)–O(1) 111.7(6), O(4)–B(1)–O(2) 111.1(6), O(3)–B(1)–O(2) 109.4(5), O(1)–B(1)–O(2) 102.8(5).

Addition of B_2cat_3 to $Ir(acac)(PPh_3)_2$ at elevated temperatures, however, lead to the bisphosphane complex $Ir(PPh_3)_2(\eta^6$-catBcat) (**3**) in high yield. Similar reactivity was observed with chelating bidentate systems $Ir(acac)(P\text{-}P)_2$ to give the corresponding species $Ir(dppm)(\eta^6$-catBcat) (dppm = 1,1-diphenylphosphanomethane, **4**), $Ir(dppe)(\eta^6$-catBcat) (dppe = 1,2-diphenylphosphanoethane, **5**) and $Ir(dppp)(\eta^6$-catBcat) (dppp = 1,3-diphenylphosphanopropane, **6**, Scheme 2). It should be noted that the precursor Ir(acac)(dppe) had to be prepared using microwave radiation[13] as conventional heating of $Ir(acac)(coe)_2$ with dppe lead to a mixture of products including $[Ir(dppe)_2]^+(acac)^-$.



Scheme 2. Synthesis of iridium arylspiroboronate esters using B_2cat_3.

In this study, complexes **3**–**6** have been characterized by a number of physical methods including multinuclear NMR spectroscopy. The ^{11}B NMR spectroscopic data for these species is consistently between δ = 14.8–15.2 ppm, which is only slightly different from the monophosphane PCy_3 species at δ = 13.9 ppm. Similar shifts for the ^1H and ^{13}C NMR peaks are observed for the bisphosphane complexes **3**–**6** as seen for **2**. Most noticeable are the shifts for bound catecholato hydrogens for **3**, which appear at δ = 4.91 and 4.11 ppm in C_6D_6. Likewise, these peaks are observed at δ = 4.60 and 4.44 ppm in C_6D_6 for complex **6**. Complex **6** has been characterized by a single-crystal X-ray diffraction study, the molecular structure of which is shown in Figure 3.

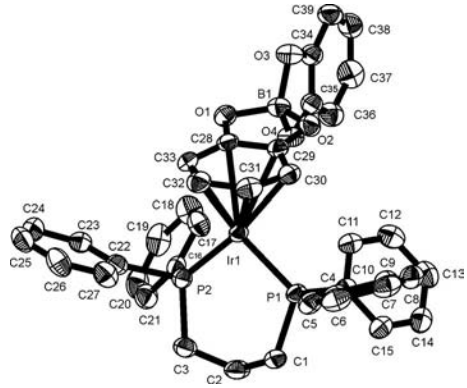
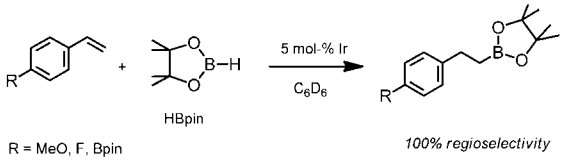


Figure 3. Molecular structure of **6** with atom labelling scheme, thermal ellipsoids are drawn at the 50% probability level with hydrogen atoms omitted for clarity. Selected bond lengths [Å]: Ir(1)–P(1) 2.2144(9), Ir(1)–P(2) 2.2185(9), Ir(1)–C(31) 2.284(4), Ir(1)–C(32) 2.293(4), Ir(1)–C(33) 2.304(3), Ir(1)–C(30) 2.306(3), Ir(1)–C(28) 2.449(3), Ir(1)–C(29) 2.455(3); selected bond angles (°): P(1)–Ir(1)–P(2) 92.67(3), P(1)–Ir(1)–C(31) 108.71(10), P(2)–Ir(1)–C(31) 142.30(10), P(1)–Ir(1)–C(32) 139.69(11), P(2)–Ir(1)–C(32) 110.81(10), O(3)–B(1)–O(4) 106.5(3), O(3)–B(1)–O(2) 111.9(3), O(4)–B(1)–O(2) 111.0(3), O(3)–B(1)–O(1) 112.9(3), O(4)–B(1)–O(1) 111.5(3), O(2)–B(1)–O(1) 103.2(3).

The structure once again confirms that the arylspiroboronate ester is bound to the iridium fragment in a η^6 fashion where the bound catecholato group has four relatively short carbon distances: Ir(1)–C(31) 2.284(4), Ir(1)–C(32) 2.293(4), Ir(1)–C(33) 2.304(3), and Ir(1)–C(30) 2.306(3) along with two longer bonds of Ir(1)–C(28) 2.449(3) and Ir(1)–C(29) 2.455(3) Å. By comparison, four short bond lengths are also observed in the dppb derivative [2.270(3), 2.297(3), 2.302(3), and 2.312(3) Å].[12] Further studies are needed to see if this degree of slippage is a common trend observed in arylspiroboronate esters bound to transition metals.[19]

We then decided to examine these iridium arylspiroboronate complexes for their potential to catalyse the addition of HBcat and HBpin to a number of vinylarenes (4-R-$C_6H_4CH{=}CH_2$, where R = MeO, F, Bpin). Contrary to results using the highly active and selective rhodium analogues, no significant reaction was observed with HBcat using a catalytic amount of these species at room temperature after 16 h. Interestingly, however, reactions of HBpin and the vinylarenes proceeded smoothly at room temperature to the exclusive formation of the corresponding linear hydroboration product (4-R-$C_6H_4CH_2CH_2$Bpin), along with minor amounts (<2% by ^{1}H NMR spectroscopy) of the saturated hydrogenation product 4-R-$C_6H_4CH_2CH_3$ (Scheme 3). The nature of the para substituent R had negligible effect on product selectivities. Unfortunately, attempts to add either HBcat or HBpin to the more hindered substrates α- and β-methylstyrene proceeded with no clear selectivites and gave a complicated mixture of products.



Scheme 3. The iridium arylspiroboronate ester catalysed hydroboration of vinyl arenes using pinacolborane (HBpin).

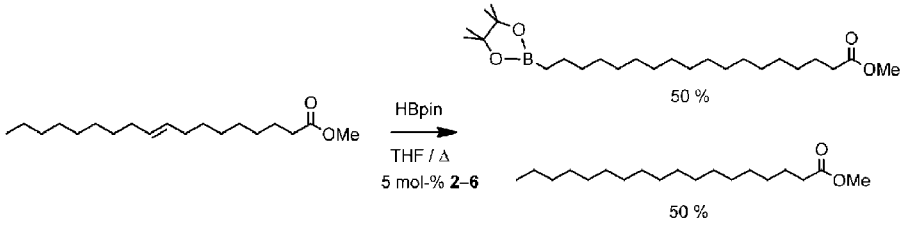
Recent interests into the catalytic functionalization of methyl oleate [$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_3$] are of considerable interest in biomass research.[20] In a recent elegant study by Ghebreyessus and Angelici,[21] it was shown that $[IrCl(coe)_2]_2$/dppe can be used to isomerise and hydroborate methyl oleate with HBpin to give the organoboronate ester pin$BCH_2(CH_2)_{16}CO_2CH_3$ in 45% yield. This remarkable reaction prompted us to investigate our new iridium complexes for this possible transformation. Although no reaction was observed with methyl oleate and HBpin using 5 mol-% of catalyst precursors **2**–**6** at room temperature, we were able to affect this reaction at elevated temperatures (Scheme 4). Indeed, complete conversion of methyl oleate was observed in THF at reflux after 18 h using three equivalents of HBpin. Complex **2** gave the best yields (ca. 50%) of the desired hydroboration product pin$BCH_2(CH_2)_{16}CO_2CH_3$, but unfortunately, as was observed by Ghebreyessus and Angelici, equal amounts of the saturated hydrogenation product $CH_3(CH_2)_{16}CO_2CH_3$ was also observed. Competing hydrogenation reactions during hydroborations are well documented, and believed to arise from the degradation of the borane into B_2pin_3 (δ = 23 ppm in the ^{11}B NMR spectra) and H_2.[5a,5b] The molecular structure of B_2pin_3 has been reported by Marder, Norman and co-workers.[22] The dihydrogen adds to the starting alkene in the presence of an active catalyst system. Although the iridium complexes **2**–**6** could be used to effectively catalyse this isomerisation/hydroboration reaction, we will continue to investigate this reaction using other metal systems in an effort to reduce the amount of competing hydrogenation, the results of which will be presented in due course.

Conclusions

Iridium phosphane arylspiroboronate ester complexes have been prepared by addition of B_2cat_3 (cat = 1,2-$O_2C_6H_4$) to the iridium precursors Ir(acac)$(coe)_2$/PR_3 or Ir(acac)$(coe)_2$/P-P (chelating bidentate ligands) at elevated temperatures. These novel complexes have been prepared in good to high yields and have been characterized by a number of physical methods including X-ray diffraction studies for the PCy_3 (**2**) and dppp [**6**, 1,3-bis(diphenylphosphanyl)propane] derivatives. The work represents the first iridium complexes containing these unusual arylspiroboronate ester ligands. Solid state and solution data show that the arylspiroboronate ester is bound to the metal via the six-membered ring of the catecholato group. The potential of these zwitterionic species to change in hapticity from an η^6 to an η^4 or even an η^2 to an η^0 bonding mode, could facilitate catalysis without loss of a ligand. Indeed, we have found that these novel iridium species can be used for the selective hydroboration of vinylarenes using pinacolborane (HBpin) to give the corresponding terminal hydroboration products. However, elevated temperatures are required for these complexes to be used as catalyst precursors for the isomerisation and subsequent hydroboration of methyl oleate, an important feedstock in biomass research. We are investigating the nature of the arylspiroboronate ester metal bond but further work is needed, however, to design a more effective catalyst for these reactions and the results of which will be published in due course.

Experimental Section

General: Reagents and solvents were purchased from Aldrich Chemicals and used as received. Ir(acac)$(\eta^2$-coe$)_2$[13] and B_2cat_3[9] were prepared by known procedures. Ir(acac)$(PPh_3)_2$, Ir(acac)(dppm), Ir(acac)(dppe), and Ir(acac)(dppp) were synthesized as previously reported.[13] NMR spectra were recorded on a JEOL



Scheme 4. Isomerisation and hydroboration of methyl oleate with HBpin using iridium arylspiroboronate esters **2**–**6**.

JNM-GSX270 FT NMR (^{1}H: 270 MHz; ^{11}B: 87 MHz; ^{13}C: 68 MHz; ^{31}P: 109 MHz) spectrometer. Chemical shifts (δ) are reported in ppm [relative to residual solvent peaks (^{1}H and ^{13}C) or external $B(OH)_3$ (^{11}B) and H_3PO_4 (^{31}P)] and coupling constants (J) in Hz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), multiplet (m), broad (br), and overlapping (ov). Melting or decomposition points were determined using a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Guelph Chemical Laboratories (Guelph, ON). All reactions were performed under an atmosphere of dinitrogen.

Ir(acac)(η²-coe)(PCy$_3$) (1): To a toluene (5 mL) solution of Ir(acac)(η²-coe)$_2$ (300 mg, 0.59 mmol) was added a toluene (3 mL) solution of tricyclohexylphosphane (164 mg, 0.59 mmol). The reaction was allowed to proceed for 18 h at which point solvent was removed under vacuum. The residual oil was dissolved in a minimum amount of hexane and stored at –30 °C. The resulting yellow-orange precipitate was collected by suction filtration and washed with cold hexane (1 mL) to afford **1**; yield 315 mg (79%), m.p. 145–148 °C. Selected spectroscopic NMR data: ^{13}C{^{1}H} NMR (C_6D_6): δ = 184.7, 180.6, 101.0, 43.9, 30.9, 30.6 (d, J_{CP} = 28.7 Hz), 30.1, 28.2 (d, J_{CP} = 10.7 Hz), 27.9, 27.3, 27.0, 26.4 ppm.

Ir(η²-coe)(PCy$_3$)(η⁶-catBcat) (2): To a toluene (5 mL) solution of Ir(acac)(η²-coe)(PCy$_3$)(250 mg, 0.37 mmol) was added a toluene (5 mL) solution of B_2cat_3 (128 mg, 0.37 mmol). The reaction was allowed to proceed for 18 h at which point solvent was removed under vacuum. The resulting yellow solid was washed with Et_2O (3 × 15 mL) before being collected by suction filtration to afford **2** as a pale yellow solid; yield 237 mg (79%), m.p. 191–193 °C. Spectroscopic NMR data: ^{1}H NMR ([D$_8$]THF): δ = 6.52–6.46 (ov m, 4 H, catechol), 6.10 (m, 2 H, η⁶-C$_6H_4O_2$), 5.74 (m, 2 H, η⁶-C$_6H_4O_2$), 2.30–2.21 (m, 3 H), 1.84–1.57 (ov m, 30 H), 1.41–1.27 (ov m, 12 H) . ^{11}B ([D$_8$]THF): δ = 13.9 (sharp) ppm. ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 150.0, 149.8, 138.0, 115.9, 115.7, 106.2, 84.9, 76.2, 39.1, 32.6 (d, J_{CP} = 29.7 Hz), 30.9, 28.5, 28.0, 25.8, 25.6, 24.6 ppm. ^{31}P{^{1}H} ([D$_8$]THF): δ = 7.5. $C_{38}H_{55}BIrO_4P$ (809.94): calcd. C 56.35, H 6.86; found C 56.58, H 6.99.

Ir(PPh$_3$)$_2$(η⁶-catBcat) (3): To a toluene (5 mL) solution of Ir(acac)(PPh$_3$)$_2$ (250 mg, 0.31 mmol) was added a toluene (5 mL) solution of B_2cat_3 (106 mg, 0.31 mmol). The reaction was heated at 100 °C for 18 h. Upon cooling to room temp. a precipitate formed and was collected by suction filtration. The solid was washed with toluene (3 × 1 mL) to afford **3** as a brick-red solid; yield 262 mg (90%), m.p. 192 °C (decomp.). Spectroscopic NMR data: ^{1}H NMR (C_6D_6): δ = 7.54 (m, 12 H, Ar), 7.34–7.10 (ov m, 4 H, C$_6H_4O_2$), 6.96–6.85 (ov m, 18 H, Ar), 4.91 (m, 2 H, η⁶-C$_6H_4O_2$), 4.11 (m, 2 H, η⁶-C$_6H_4O_2$); ^{11}B δ: 15.1 (sharp) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 152.8, 152.6, 141.6, 136.1 (t, J_{C-P} = 28.6 Hz), 134.5 (t, J_{C-P} = 5.7 Hz), 129.6, 127.5 (t, J_{C-P} = 4.7 Hz), 125.4, 119.1, 118.8, 109.9, 108.9, 85.1, 80.3 ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 8.4 ppm. $C_{48}H_{38}BIrO_4P_2$ (943.89): calcd. C 61.07, H 4.07; found C 61.33, H 4.15.

Ir(dppm)(η⁶-catBcat) (4): To a toluene (5 mL) solution of Ir(acac)(dppm) (163 mg, 0.24 mmol) was added a toluene (5 mL) solution of B_2cat_3 (83 mg, 0.24 mmol). The reaction was heated at 100 °C for 18 h. Upon cooling to –30 °C, a solid precipitated and was collected by suction filtration. The solid was redissolved in hot toluene (10 mL) and stored at –30 °C. After 3 days, a precipitate was collected by suction filtration and washed with Et_2O (3 × 1 mL) to afford **4** as an orange-yellow solid; yield 95 mg (49%), m.p. 158–162 °C. Spectroscopic NMR data: ^{1}H NMR (C_6D_6): δ = 7.56 (m, 8 H, Ar), 7.13–6.97 (ov m, 14 H, Ar & C$_6H_4O_2$), 6.87–6.80 (ov m, 2 H, C$_6H_4O_2$), 5.84 (2nd order m, 2 H, η⁶-C$_6H_4O_2$), 4.52 (2nd order m, 2 H, η⁶-C$_6H_4O_2$), 3.99 (t, J_{H-P} = 11.1 Hz, 2 H, P CH_2) ppm. ^{11}B NMR (C_6D_6): δ = 14.8 (sharp); ^{13}C {^{1}H} δ: 152.5, 152.4, 137.1, 136.2 (t, J_{C-P} = 26.6 Hz), 132.0 (t, J_{C-P} = 6.1 Hz), 130.3, 128.4 (t, J_{C-P} = 5.6 Hz), 125.4, 118.8, 118.6, 109.7, 108.8, 80.0, 77.2, 21 (br. m, CH$_2$-P) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = –55.8 ppm. $C_{37}H_{30}BIrO_4P_2$ (803.70): calcd. C 55.29, H 3.77; found C 55.44, H 3.98.

Ir(dppe)(η⁶-catBcat) (5): To a toluene (5 mL) solution of Ir(acac)(dppe) (160 mg, 0.23 mmol) was added a toluene (5 mL) solution of B_2cat_3 (80 mg, 0.23 mmol) and the reaction mixture was heated at 100 °C for 18 h. Upon cooling to –30 °C, a solid precipitated and was collected by suction filtration. The solid was dissolved in toluene (5 mL) and Et_2O (1 mL) and the solution stored at –30 °C. A precipitate was collected by suction filtration to afford **5** as a yellow solid; yield 75 mg (40%), m.p. 171–174 °C (decomp.). Spectroscopic NMR data: ^{1}H NMR (C_6D_6): δ = 7.50 (m, 8 H, Ar), 7.19–7.01 (ov m, 14 H, Ar & C$_6H_4O_2$), 6.97–6.84 (ov m, 2 H, C$_6H_4O_2$), 5.24 (2nd order m, 2 H, η⁶-C$_6H_4O_2$), 4.42 (2nd order m, 2 H, η⁶-C$_6H_4O_2$), 1.66 (d, J_{H-P} = 17.3 Hz, 4 H, P-CH_2) ppm. ^{11}B NMR (C_6D_6): δ = 14.8 (sharp) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 152.7, 152.5, 139.5, 136.9 (m, C-P), 132.7 (t, J_{C-P} = 5.7 Hz), 130.2, 128.3 (t, J_{C-P} = 5.7 Hz), 125.4, 118.9, 118.6, 109.7, 108.7, 83.0, 76.9, 30.2 (t, J_{C-P} = 28.1 Hz) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 41.6 ppm. $C_{38}H_{32}BIrO_4P_2$ (817.73): calcd. C 55.81, H 3.95; found C 56.12, H 4.09.

Ir(dppp)(η⁶-catBcat) (6): To a toluene (5 mL) solution of Ir(acac)(dppp) (200 mg, 0.28 mmol) was added a toluene (5 mL) solution of B_2cat_3 (98 mg, 0.28 mmol). Following 18 h of stirring at room temp. a precipitate was collected by suction filtration. The solid was washed with toluene (3 × 3 mL) to afford **6** as an orange solid; yield 200 mg (86%), m.p. 172–174 °C (decomp.). Spectroscopic NMR data: ^{1}H NMR (C_6D_6): δ = 7.47 (m, 8 H, Ar), 7.29–7.10 (ov m, 14 H, Ar & C$_6H_4O_2$), 7.00–6.79 (ov m, 2 H, C$_6H_4O_2$), 4.60 (2nd order m, 2 H, η⁶-C$_6H_4O_2$), 4.44 (2nd order m, 2 H, η⁶-C$_6H_4O_2$), 2.08 (m, 4 H, P-CH_2), 1.36 (br. m, 2 H, CH$_2$CH_2CH$_2$); ^{11}B δ: 15.2 (sharp) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 153.0, 152.9, 141.1, 136.9 (t, J_{C-P} = 28.2 Hz), 132.8 (t, J_{C-P} = 5.6 Hz), 130.0, 128.7 (t, J_{C-P} = 6.7 Hz), 125.4, 119.0, 118.7, 109.8, 108.7, 84.2, 77.8, 27.6 (t, J_{C-P} = 24.0 Hz), 19.1 ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = –10.1 ppm. $C_{39}H_{34}BIrO_4P_2$ (831.74): calcd. C 56.31, H 4.13; found C 56.67, H 4.08.

General Procedure for the Hydroboration of Alkenes: To a stirred C_6D_6 (0.5 mL) solution of alkene and the desired iridium catalyst (2 mol-%) was added the appropriate borane (1 molar equiv.) in C_6D_6 (0.5 mL). The reaction was allowed to proceed at room temp. for 18 h at which point the reaction was analyzed by multinuclear NMR spectroscopy and compared to known compounds.[5a]

Isomerizing Hydroboration of Methyl Oleate: To a stirred THF (1 mL) solution of methyl oleate (50 mg, 0.17 mmol) and Ir(η²-coe)(PCy$_3$)(η⁶-catBcat) (3 mg, 0.003 mmol) was added a THF (1 mL) solution of pinacolborane (65 mg, 0.51 mmol). The reaction was heated at reflux for 18 h at which point solvent was removed under vacuum and the resultant oil analyzed by multinuclear NMR spectroscopy in $CDCl_3$. Selected spectroscopic ^{13}C{^{1}H} NMR spectroscopic data: δ: 11.3 (br., C-B).

X-ray Crystallography: Crystals of **1**, **2**, and **6** were grown from saturated THF solutions, at –30 °C. Single crystals were coated with Paratone-N oil, mounted using a polyimide MicroMount and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and 10 s exposure times. The detector distances were 5 cm. All data collection was performed at 173 K with the exception of **6** which was

carried out at 213 K due to loss of crystallinity at lower temperatures. The data were reduced (SAINT)[23] and corrected for absorption (SADABS).[24] For **1**, the crystal was twinned and the orientation matrixes for two components were determined (CELL_NOW).[25] The data were reduced (SAINT) and corrected for absorption (TWINABS).[26] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXTL).[27] All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined using a riding model.

CCDC-777409 (for **1**), -777408 (for **2**), and -807116 (for **6**) contain the supplementary crystallographic data for this and are available free of charge at http://www.ccdc.cam.ac.uk/data_request/cif.

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