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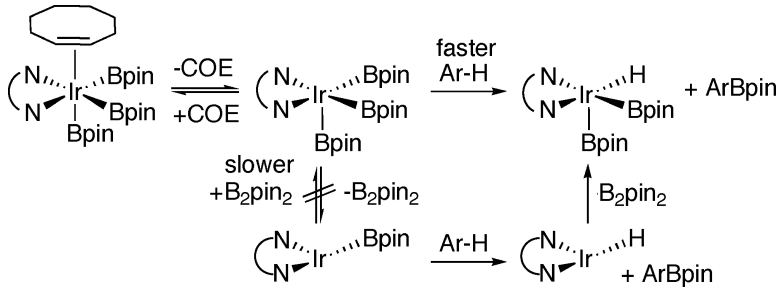

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Mechanism of the Mild Functionalization of Arenes by Diboron Reagents Catalyzed by Iridium Complexes. Intermediacy and Chemistry of Bipyridine-Ligated Iridium Trisboryl Complexes

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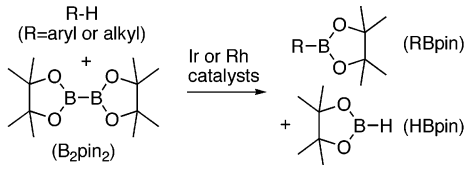
Abstract: This paper describes mechanistic studies on the functionalization of arenes with the diboron reagent B_2pin_2 (bis-pinacolato diborane(4)) catalyzed by the combination of 4,4′-di-*tert*-butylbipyridine (dtbpy) and olefin-ligated iridium halide or olefin-ligated iridium alkoxide complexes. This work identifies the catalyst resting state as [Ir(dtbpy)(COE)(Bpin)$_3$] (COE = cyclooctene, Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl). [Ir(dtbpy)(COE)(Bpin)$_3$] was prepared by independent synthesis in high yield from [Ir(COD)(OMe)]$_2$, dtbpy, COE, and HBpin. This complex is formed in low yield from [Ir(COD)(OMe)]$_2$, dtbpy, COE, and B_2pin_2. Kinetic studies show that this complex reacts with arenes after reversible dissociation of COE. An alternative mechanism in which the arene reacts with the Ir(I) complex [Ir(dtbpy)Bpin] after dissociation of COE and reductive elimination of B_2pin_2 does not occur to a measurable extent. The reaction of [Ir(dtbpy)(COE)(Bpin)$_3$] with arenes and the catalytic reaction of B_2pin_2 with arenes catalyzed by [Ir(COD)(OMe)]$_2$ and dtbpy occur faster with electron-poor arenes than with electron-rich arenes. However, both the stoichiometric and catalytic reactions also occur faster with the electron-rich heteroarenes thiophene and furan than with arenes, perhaps because η^2-heteroarene complexes are more stable than the η^2-arene complexes and the η^2-heteroarene or arene complexes are intermediates that precede oxidative addition. Kinetic studies on the catalytic reaction show that [Ir(dtbpy)(COE)(Bpin)$_3$] enters the catalytic cycle by dissociation of COE, and a comparison of the kinetic isotope effects of the catalytic and stoichiometric reactions shows that the reactive intermediate [Ir(dtbpy)(Bpin)$_3$] cleaves the arene C−H bond. The barriers for ligand exchange and C−H activation allow an experimental assessment of several conclusions drawn from computational work. Most generally, our results corroborate the conclusion that C−H bond cleavage is turnover-limiting, but the experimental barrier for this bond cleavage is much lower than the calculated barrier.

Introduction

The selective functionalization of arene and alkane C−H bonds under mild conditions with high efficiency has been sought for many years.[1,2] We and others have made progress toward this goal by developing the reaction of diborane(4) and dioxaborolane reagents with alkanes and arenes in the presence of rhodium and iridium catalysts to form alkyl- and arylboronate esters (eq 1).[3−26] These reactions occur under mild conditions with certain catalysts.



(1)

The organoboronate esters produced by this reaction are common reagents. They serve as precursors to alcohols[27] or participate in Suzuki−Miyaura couplings.[28] Arylboronate esters are typically prepared by converting an aryl halide to an aryl

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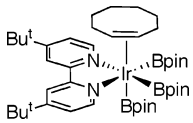

Figure 1. Trisboryl complex **1**.

Grignard reagent, trapping of the Grignard reagent with a borate, and hydrolyzing the arylboronate product to the boronic acid.[28] Alternatively, the aryl halide can be converted to the arylboronate ester by a transition metal catalyzed coupling of the aryl halide with a borane reagent.[29−33] This second method bypasses the need for Grignard reagents but still begins with an aryl halide. Thus, a synthesis of arylboronate esters from arenes would improve upon each of these methods by avoiding the need to prepare the halogenated arene and to generate any organometallic reagents.

The mildest direct borylation of arenes occurs with diborane(4) reagents and is catalyzed by an iridium complex generated from $[Ir(COE)_2Cl]_2$ or $[Ir(COD)OMe]_2$ (COE = cyclooctene, COD = cyclooctadiene) and di-*tert*-butylbipyridine.[12,14] This chemistry occurs at room temperature with a 1:1 molar ratio of arene to boron reagent in an inert alkane solvent.[14] The reactions occur with both arene and heteroarene substrates.[13] The regioselectivity of reactions with arenes is controlled by steric effects, while the borylation of heteroarenes occurs at the C−H bond α to the heteroatom, unless the heteroatom possesses a large group. Turnover numbers on the order of 8000 have been reported,[12] and this value exceeds that of most if not all homogeneous catalytic functionalizations of C−H bonds.

The mechanism of the borylation of alkanes and arenes has been shown in several cases to occur by C−H activation of the arene by a transition metal boryl complex.[4,8,9,11,12,20] The bipyridine-ligated iridium trisboryl complex **1** in Figure 1, which reacts readily with arenes to generate arylboronate esters, was isolated during preliminary studies on the mechanism of the iridium-catalyzed borylation of arenes.[12] Although studies on the selectivity of the reactions of this complex suggested that this species was competent to be an intermediate in the catalytic borylation of arenes, a reliable method to synthesize this complex was not available at that time. The inability to prepare this complex in appreciable amounts limited the scope and depth of mechanistic studies that could be pursued, and the mechanism by which this complex reacts with arenes was not deduced.

A computational study and two mechanistic studies of other groups have been published that are relevant to the work reported here. After we reported the isolation of the trisboryl complex **1**, a computational study was conducted of the mechanism of the catalytic borylation initiated with the 16-electron compound formed by dissociation of cyclooctene from isolated **1**.[34] These studies suggested that the catalytic reaction occurred by a mechanism in which the arene reacts with this trisboryl complex. The barriers calculated for the individual steps of the cycle implied that the turnover-limiting step was C−H bond cleavage of the arene and that a pentaboryl Ir(V) complex formed by addition of B_2pin_2 should be accessible.

A few experimental studies related to the borylation of aromatic substrates have also been reported. Smith and coworkers reported preliminary mechanistic data on the borylation of arenes by phosphine-ligated iridium complexes. Their data did not distinguish between reactions of arenes with Ir(I) monoboryl or Ir(III) trisboryl complexes.[20] A combined experimental and computational study on the borylation of benzylic C−H bonds catalyzed by a phosphine-ligated rhodium complex was also reported recently.[35] This study suggested that an analogous trisboryl rhodium intermediate was too high in energy to be part of the catalytic process and that the process occurred by C−H activation by a rhodium hydride, instead of a rhodium boryl complex.

Thus, we conducted studies to prepare the bipyridine-ligated trisboryl iridium complex **1** in high yield and to use material from such a synthesis to conduct a detailed mechanistic study of the mild borylation of arenes with this catalyst. We report such a high-yield synthesis of the trisboryl complex, kinetic studies on the catalytic reaction that reveal the turnover-limiting step, isotopic labeling studies that reveal whether an Ir(I) monoboryl or Ir(III) trisboryl complex reacts with the arene, and kinetic studies with labeled diborane(4) reagents that assess the possible generation of pentaboryl complexes. All of these data support the intermediacy of the trisboryl complex in the catalytic process and rate-limiting cleavage of the C−H bond of the arene by $[Ir(dtbpy)(Bpin)_3]$ (dtbpy = 4,4′-di-*tert*-butylbipyridine, Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl).

Results

1. Synthesis and NMR Characterization of (dtbpy)(η^2-COE)Ir(Bpin)$_3$ (1). We previously reported the isolation and solid-state structure of the Ir(III) trisboryl complex **1** from reaction of $[Ir(COE)_2Cl]_2$, dtbpy, and B_2pin_2 (bis-pinacolato diborane(4)).[12] However, compound **1** was formed in low yield from this reaction because of several factors, including the poor solubility of the iridium reagents and the bipyridine ligand in nonpolar alkane solvents and the need to separate **1** from excess B_2pin_2 and side products, such as pinBOBpin or B_2pin_3.

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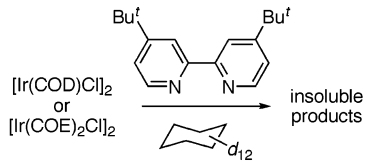
We investigated further reactions of $[Ir(olefin)_2Cl]_2$ complexes with dtbpy and borane reagents. However, the combination of dtbpy and either $[Ir(COD)Cl]_2$ or $[Ir(COE)_2Cl]_2$ in cyclohexane-d_{12} formed an insoluble material that reacted only slowly with B_2pin_2 or HBpin upon heating (eq 2). From this procedure,



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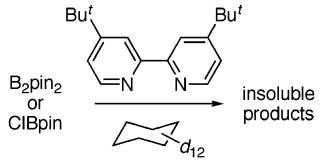
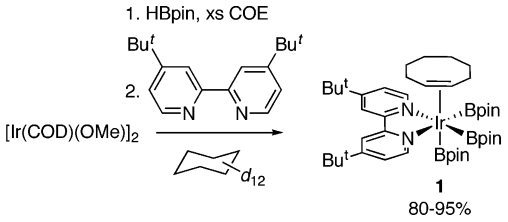


(3)

complex **1** was formed in less than 20% yield, as determined by ^{1}H NMR spectroscopy. Further complicating these reactions, dtbpy reacted with B_2pin_2 and the ClBpin that is generated from reaction of the iridium chlorides with the borane reagents to form insoluble Lewis acid−base complexes (eq 3). Similar reactions of ClBcat (cat = catecholate) with amines were reported by Marder.[36−38] Although these iridium complexes and Lewis acid−base adducts were slightly more soluble in hindered arenes, such as mesitylene, the conditions needed to evaporate the high boiling arene led to the decomposition of **1**. Benzene and toluene were not suitable solvents because they react rapidly with **1** (vide infra). Reactions in polar aliphatic solvents, such as THF, formed complex mixtures.

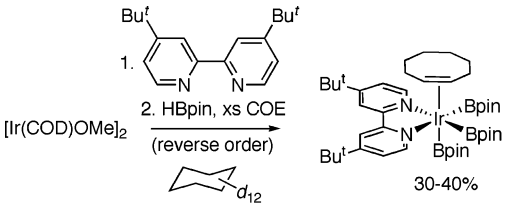
The detrimental effect of ClBpin was circumvented by conducting the synthesis of **1** from the iridium methoxide $[Ir(COD)(OMe)]_2$, and this precursor generated **1** in high yield under the appropriate conditions. The reaction of $[Ir(COD)(OMe)]_2$ with HBpin and COE, followed by dtbpy, generated a homogeneous solution, and **1** was formed in 80−95% yield (eq 4). In contrast, no reaction was observed between B_2pin_2 and



(4)

$[Ir(COD)Cl]_2$, $[Ir(COE)_2Cl]_2$, or $[Ir(COD)(OMe)]_2$ after 30 min at room temperature, as determined by ^{11}B NMR spectroscopy.[39]

A particular order of addition of HBpin and ligand was also necessary to form **1** in high yield. Although counterintuitive, reactions conducted by adding dtbpy to $[Ir(COD)(OMe)]_2$ after addition of HBpin (6 equiv at 20 °C in cyclohexane-d_{12}) generated the trisboryl complex **1** in much higher yields than reactions conducted by adding the ligand before the borane (eq 5), which formed **1** in only 30−40% yield, as determined by



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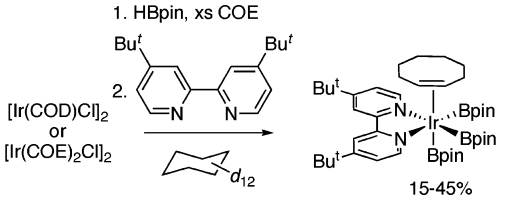

(6)

NMR spectroscopy with an internal standard. Even with this order of addition, the reaction of dtbpy with the combination of HBpin, COE, and either chloride dimer $[Ir(COD)Cl]_2$ or $[Ir(COE)_2Cl]_2$ formed **1** in only 40−45% and 15−20% yield, respectively (eqs 5 and 6). Because of the high solubility of **1**, even in methylcyclohexane at −30 °C, complex **1** was isolated in 55−65% yield by the addition of tetramethylsilane to a pentane solution of **1** at −30 °C. This procedure allowed for the preparation of **1** on a gram scale. Once pure, complex **1** is thermally stable in alkane solvent; no decomposition was observed by ^{1}H NMR spectroscopy after heating in cyclohexane-d_{12} at 80 °C for several hours.

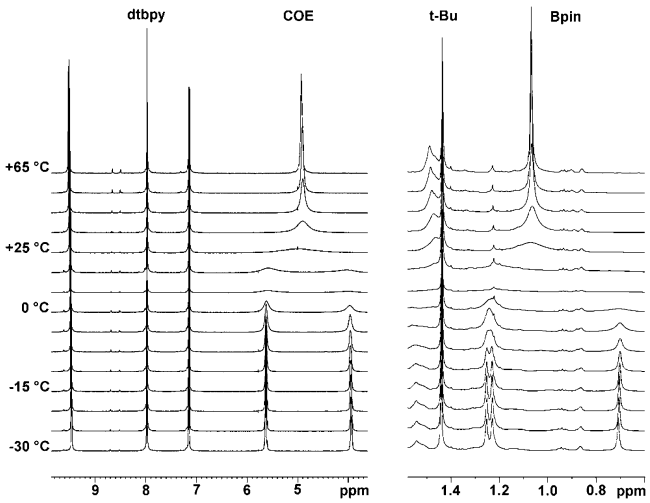

Figure 2. Variable-temperature ^{1}H NMR spectra (500 MHz) of complex **1** and 1 equiv of COE. The change in line shapes results from exchange between free (δ 5.61) and bound COE (δ 3.92) and exchange between Bpin groups located cis (δ 1.2) and trans (δ 0.6) to COE.

The ^{1}H NMR spectra of complex **1** are consistent with the structure we determined previously by X-ray diffraction.[12] The spectra at room temperature contained aromatic (δ 7.13, 7.96, and 9.45) and *tert*-butyl (δ 1.42) resonances for the coordinated dtbpy, and it contained an olefinic resonance for the η^2-COE at δ 3.92. However, the methyl resonances of the pinacolate groups and the methylene resonances of the COE ligand were not observed in the ^{1}H NMR spectrum at room temperature.

Thus, we obtained NMR spectroscopic data at various temperatures (Figure 2). Three pinacolate methyl resonances

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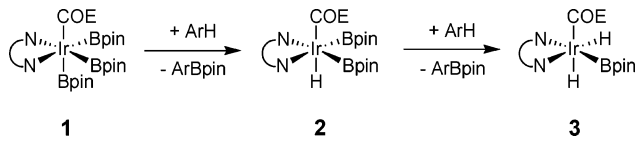
(39) Although HBpin reacted with $[Ir(COD)Cl]_2$ and $[Ir(COE)_2Cl]_2$, the nearly quantitative yield of **1** was obtained only from reaction with $[Ir(COD)(OMe)]_2$.

Scheme 1



in a 1:1:1 ratio were detected in the ^{1}H NMR spectrum of **1** at −20 °C in methylcyclohexane-d_{14}. The two resonances at δ 1.24 and δ 1.21 correspond to two inequivalent methyl groups of the mutually cis Bpin groups, and the third resonance at δ 0.69 corresponds to the Bpin group trans to the COE. Upon warming, the inequivalent methyl resonances of the mutually cis Bpin groups broadened, and near 30 °C they coalesced. At 65 °C, the methyl groups of all three boryl ligands were observed as one singlet at δ 0.99.

These data indicate that the Bpin groups located cis and trans to the bipyridine undergo site exchange at elevated temperatures. The coalescence of the pinacolate groups is likely to occur by dissociation of COE to form a 5-coordinate iridium complex, followed by Berry pseudorotation to exchange cis and trans Bpin groups. Consistent with this assertion, the resonances of the free and coordinated COE coalesce at temperatures similar to those that cause coalescence of the three Bpin signals. Using the temperature of the initial broadening[40] of the olefinic resonances for free and coordinated COE, one can estimate that $\Delta G^{\ddagger}$ is between 14 and 15 kcal/mol for the exchange of free and coordinated olefin.

2. Stoichiometric Reactions of Arenes with Isolated 1. A. Yields, Product Characterization, and Qualitative Rates. The reaction of complex **1** with benzene at room temperature for only 5 min generated 3 equiv of arylboronate ester in 80% yield. This complex also reacted with 1,2-dichlorobenzene (60 equiv) in cyclohexane upon mixing to give 3 equiv of the corresponding arylboronate ester in 70% yield. These reactions were much slower in the presence of added COE. In the presence of 0.21 M added COE, complex **1** generated only trace amounts of arylboronate ester upon reaction with 1,2-dichlorobenzene for 0.5 h and only 40% yield after 24 h. To compare the rate constant for reaction of **1** with arenes with the rate constant for reactions of **1** with labeled B_2pin_2 discussed later in this paper, we measured qualitatively the half-life for the reaction of **1** with benzene in cyclohexane-d_{12}. The half-life for reaction with 0.022 M benzene was between 0.5 and 1 h.

The reactions of **1** with arenes at room temperature to form 3 equiv of arylboronate ester did not produce a discrete iridium product, but reactions of **1** with arenes at lower temperatures did provide species that could be characterized in solution. A solution of **1** in a mixture of cyclohexane-d_{12} and methylcyclohexane-d_{14} containing 2.5 equiv of COE was allowed to react with 20 equiv of 1,3-bis(trifluoromethyl)benzene at 0 °C. The formation of arylboronate ester was observed over the course of 1−2 h, along with the formation of two additional iridium complexes tentatively assigned as the bisboryl hydride complex (dtbpy)(η^2-COE)Ir(Bpin)$_2$H (**2**) and the boryl dihydride complex (dtbpy)(η^2-COE)Ir(Bpin)(H)$_2$ (**3**) (Scheme 1).

Sections of the ^{1}H NMR spectra obtained during this reaction are shown in Figure 3. The structural assignment of the bisboryl hydride complex **2** was based on ^{1}H NMR spectroscopy. These

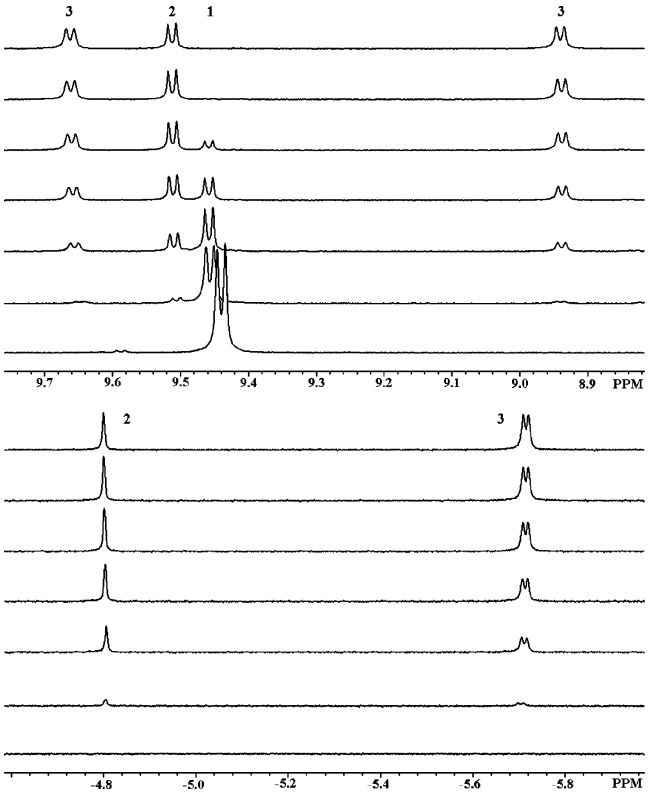


Figure 3. ^{1}H NMR spectra of the aromatic region for the dtbpy ligand and the more downfield portion of the hydride region during the reaction of **1** with 1,3-bis(trifluoromethyl)benzene at 0 °C. These spectra correspond to the decay of **1** and the formation of the iridium hydride species assigned as bisboryl monohydride **2** and monoboryl dihydride **3**.

data include resonances for a dtbpy ligand in a symmetrical environment, a singlet hydride resonance at δ −4.81, and two singlets from the boryl groups at δ 1.25 and 1.20. The structural assignment of the boryl dihydride complex **3** was also based on ^{1}H NMR spectroscopic data, and these data included a set of ^{1}H NMR resonances for a dtbpy group in an unsymmetrical environment and two mutually coupled hydride resonances at δ −5.72 and δ −23.1. The coupling constant of J = 5.3 Hz between the two hydrides is consistent with a mutually cis orientation of these two ligands. A singlet for the methyl groups of a Bpin ligand was observed at δ 1.24.

B. Isotope Effects on the Stoichiometric Reactions of Trisboryl 1 with Arenes. The isotope effect from the stoichiometric reaction of **1** with benzene, as well as from reactions of B_2pin_2 with benzene catalyzed by **1** (vide infra), were measured. An aggregate isotope effect of 4.6 ± 0.4 was obtained for the formation of the 3 equiv of PhBpin from the reaction of a 1:1 mixture of benzene and benzene-d_6. This number is similar to the value of 5.0 ± 0.4 obtained from reaction of a mixture of benzene and benzene-d_6 under catalytic conditions and presented in more detail in the section on reactions catalyzed by **1**.

C. Electronic Effects on the Reactions of Trisboryl 1 with Arenes. A series of competition reactions was conducted with trisboryl complex **1** and various arenes or heteroarenes to determine the factors that control the selectivity of the reactions of complex **1**. In parallel, reactions of B_2pin_2 with a mixture of the same arenes catalyzed by **1** were conducted to compare the selectivities of the stoichiometric and catalytic reactions of **1**. The stoichiometric reaction of **1** with an excess amount of a 1:1 mixture of *m*-xylene and 1,3-bis(trifluoromethyl)benzene

(40) Faller, J. W. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; John Wiley and Sons: New York, 1994; p 3914.

formed 1,3-bis(trifluoromethyl)benzene-5-pinacol boronate ester as the major product, as determined by GC and GC/MS. Similarly, the reaction of a 1:1 mixture of these two arenes with B_2pin_2 catalyzed by 1 mol % **1** formed 1,3-bis(trifluoromethyl)-benzene-5-pinacol boronate ester as the major product. In both cases, the borylated *m*-xylene product was formed in less than 6% yield by GC, while the 1,3-bis(trifluoromethyl)benzene-5-pinacol boronate ester was formed in greater than 65% yield. These data suggest that either the more electron-poor arene undergoes faster C−H bond cleavage or that an electron-poor arene forms a more stable precursor to the C−H bond cleavage or both. The precursor to C−H bond cleavage of arenes has been proposed to be a π-complex,[41] and Jones and Perutz have shown that 1,3-bis(trifluoromethyl)benzene forms more stable η^2-arene complexes than does benzene.[42]

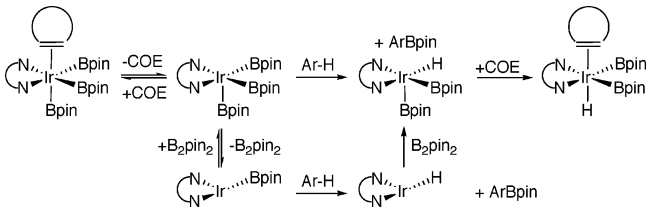
The analogous competition reactions between benzene and furan and between benzene and thiophene implied that the selectivity did not simply favor cleavage of the C−H bond of the more electron-poor aromatic system. The reaction occurred preferentially at the C−H bond of the more electron-rich, heteroaromatic ring. The reaction of **1** with an excess of a 1:1 mixture of benzene and furan formed 2-furanyl pinacol boronate ester as the major product, as determined by GC and GC/MS. The reaction of **1** with an excess of a 1:1 mixture of benzene and thiophene also formed 2-thienyl pinacol boronate ester as the major product. Likewise, the reaction of a 1:1 mixture of the two arenes with B_2pin_2 catalyzed by **1** formed the 2-furanyl pinacol boronate ester as the major product,[43] and the reaction of a 1:1 mixture of benzene and thiophene formed 2-thienyl pinacol boronate ester as the major product. In all four cases, the phenyl pinacol boronate ester product was formed in less than 2% yield.

The heteroaryl monoboronate esters were prepared independently by the iridium-catalyzed reaction of heteroarenes and B_2pin_2.[16] Both 2-thienyl pinacol boronate and 2-furanyl pinacol boronate ester were prepared in neat heteroarene to minimize the production of diborylated products.

Because these results show that the iridium complex does not simply react faster with the more electron-poor arene, we suggest that the reactivity is controlled by either the stability of an η^2-arene intermediate or by the electronic properties of the C−H σ-bond. At the same time, the high reactivity of thiophene over benzene is unlikely to be dominated by the polarity or electron-density in the C−H σ-bond, because the electronegativity of sulfur is similar to that of carbon. Thus, we favor an explanation for the relative reactivity of the arenes based on the stability of the respective π-complexes.

To see if the effect of the stability of the π-complex could override the steric preference for reaction at the less hindered C−H bond, we conducted reactions of phenanthrene. If the regioselectivity were controlled purely by the stability of the π-complex, then the borylation would occur at the 9-position, because the most stable π-complex is formed by coordination of the metal to the carbons at the 9- and 10-positions.[42] However, if the regioselectivity were controlled by steric effects, then a mixture of 2- and 3-borylated products would be observed. The 9-pinacol boronate ester of phenanthrene was prepared independently from 9-bromophenanthrene by lithiation with *tert*-butyllithium and quenching with isopropoxy pinacol boronate ester, in analogy to a reported procedure.[44] The catalytic borylation of phenanthrene did not form the 9-pinacol boronate ester, as determined by GC and NMR spectroscopic methods. Instead, two products that we assume to be the 2- and 3-borylated isomers were observed. During the course of this work, Coventry et al. reported the borylation of pyrene. Like the borylation of phenanthrene, the reaction occurred at the 2-position of the outer aryl groups and not at the 4-position of the central aryl rings.[26] Thus, the stability of the π-complex, if it is a controlling factor, does not override the steric effect on regioselectivity.

Scheme 2



3. C−H Activation and Diboron Exchange Pathways. Two potential pathways for reactions of arenes with trisboryl complex **1** are shown in Scheme 2. Because C−H activation by Ir(III) species is less common than by Ir(I) species, we considered that the reaction could occur by reductive elimination of B_2pin_2 to generate an iridium(I) intermediate that would add arene and eliminate the arylboronate ester. Alternatively, the trisboryl complex could react directly with the arene by either an oxidative addition to generate an iridium(V) intermediate or by a σ-bond metathesis. With these mechanistic alternatives in mind, we conducted kinetic and isotopic labeling studies to determine the identity of the iridium complex that reacts with the arene. We conducted a set of experiments to test whether reaction of the trisboryl complex directly with arene was faster or slower than reaction of the trisboryl by elimination of B_2pin_2 to generate a monoboryl intermediate that reacts with the arene.

A. Relative Rates for Elimination of B_2pin_2 from 1 and for C−H Activation by 1. To assess the potential that an iridium(I) monoboryl complex is generated reversibly from **1**, a labeling experiment was devised. Reaction of **1** with 1,2-dichlorobenzene was conducted in the presence of B_2pin_2-d_{24}. If the reaction of **1** occurred by initial reversible elimination of B_2pin_2, then free protiated B_2pin_2 would be generated prior to formation of the arylboronate ester. If the reaction of **1** occurred by initial irreversible elimination of B_2pin_2, then free protiated B_2pin_2 would be generated on the same time scale as the arylboronate ester. If the reaction occurred directly from a trisboryl complex faster than an iridium(I) monoboryl complex is generated, then the arylboronate ester would form faster than free protiated B_2pin_2.

To conduct this experiment, a solution of **1** in cyclohexane-d_{12} was mixed with a solution of B_2pin_2-d_{24} (2.6 equiv) and 1,2-dichlorobenzene (3.3 equiv) in cyclohexane-d_{12} at 0 °C. The reaction was monitored by ^{1}H NMR spectroscopy at 7.5 °C for 60 min (Figure 4). Inconsistent with rapid reductive elimination

(41) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *106*, 1650.
(42) Chin, R. M.; Dong, L.; Duckett, S. B.; Partridge, M. G.; Jones, W. D.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685.
(43) A small amount of 2,5-borylated furan was also formed from the catalytic reaction, but this material was formed in less than 4% yield.
(44) Yang, R.; R.Tian; Yang, W.; Hou, Q.; Cao, Y. *Synth. Met.* **2003**, *135*−*136*, 197.

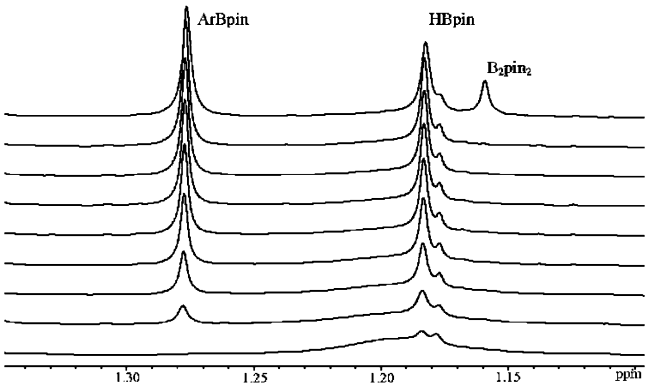


Figure 4. ^{1}H NMR spectra of pinacol methyl region during the reaction of **1** with 1,2-dichlorobenzene at 7.5 °C in the presence of B_2pin_2-d_{24}. The final spectrum contains added B_2pin_2 for reference. Small amounts of HBpin (δ 1.184) and pinBOBpin (δ 1.178) are present in solution at $t = 0$.

of B_2pin_2 from **1** and generation of an iridium(I) monoboryl intermediate, no labeled borane was incorporated into the arylboronate ester product under these conditions. The ^{1}H NMR spectra of reactions conducted with B_2pin_2-d_{24} contained only resonances from arylboronate ester (δ 1.28) and pinacolborane (δ 1.18).

We also addressed the potential that complex **1** could generate a different iridium complex that catalyzes the reaction of arenes with free B_2pin_2 without the intermediacy of **1** or complexes generated reversibly from **1**. If so, then the initial organoboronate ester formed from reactions of B_2pin_2-d_{24} catalyzed by unlabeled **1** would contain the deuterium label. In this case, the ratio of unlabeled to labeled product would be lower at the beginning of the catalytic reaction than at the end of the reaction. If the catalytic reaction occurred directly from **1** or a boryl complex generated from **1**, then the initial organic product would arise from **1** and would lack the deuterium label. In this case the ratio of unlabeled to labeled product would be higher at the beginning of the reaction than at the end of the reaction.

The reaction of B_2pin_2-d_{24} with benzene-d_6 catalyzed by 10 mol % unlabeled **1** (30% unlabeled Bpin groups) was conducted with 1 equiv of added COE at room temperature and was quenched at short and long times by dilution in ether. The isotopic composition of the PhBpin product was determined by GC and GC/MS.[45] Consistent with the reaction of arene with intact boryl complex **1** or with a boryl complex generated directly from **1**, the ratio of PhBpin to PhBpin-d_{12} was higher at low conversions than it was at high conversions. The ratio of PhBpin-d_5 to PhBpin-d_{17} after 4 h and 10% conversion was 68:32, after 17 h and 50% conversion was 47:53, and the ratio after complete conversion was 17:83.

The reaction of B_2pin_2-d_{24} with complex **1** was also studied in the absence of arene to gain information on the rate at which B_2pin_2 eliminated from **1**. This reaction was also conducted to assess a proposal that an Ir(V) pentaboryl complex would be generated from the combination of B_2pin_2 and **1**.[34] A solution of **1** was combined with B_2pin_2-d_{24} (14 equiv) in cyclohexane-d_{12}, and the appearance of signals from fully and partially protiated B_2pin_2 was monitored by ^{1}H NMR spectroscopy.

Fully and partially protiated B_2pin_2 were generated slowly from this reaction at room temperature. This slow rate contrasts with the fast rate of reaction of **1** with 1,2-dichlorobenzene at room temperature and reaction even below room temperature (vide supra). Thus, the rate of elimination of B_2pin_2 to generate a monoboryl complex is much slower than the rate of reaction of **1** with arene, and these data show again that a monoboryl iridium(I) complex cannot be an intermediate in the reaction of **1** with this arene.

B. Mechanism for Exchange of B_2pin_2 with 1. An exchange between B_2pin_2-d_{24} and **1** did occur at higher temperatures, however, and the mechanism of this exchange was shown by kinetic data to occur by addition of B_2pin_2 to the trisboryl complex. Because the exchange process is degenerate, an exchange process that occurred by reductive elimination of B_2pin_2-d_{24} after dissociation of COE would depend only on the rate of reductive elimination of B_2pin_2 from **1**. In this case, the reaction would be zero-order in the concentration of added B_2pin_2-d_{24} when conducted with varied amounts of an excess B_2pin_2-d_{24}. In contrast, reaction by addition of the B_2pin_2 to the trisboryl complex to form a pentaboryl complex would be first-order in B_2pin_2-d_{24} when conducted with varied amounts of excess B_2pin_2-d_{24}.

The relative rate constants for the exchange process were measured by monitoring the appearance of protiated Bpin groups in the ^{1}H NMR spectra of samples containing a mixture of **1** and 0.072, 0.143, and 0.216 M concentrations of B_2pin_2-d_{24} in a mixture of cyclohexane-d_{12} and methylcyclohexane-d_{14}. This mixture was monitored while being heated at 40 °C. The rate constant for the exchange process depended linearly on the concentration of B_2pin_2-d_{24}. These data show that the exchange process occurs by reaction of B_2pin_2-d_{24} with a trisboryl complex. We presume that the B_2pin_2-d_{24} reacts with the 16-electron trisboryl complex generated by dissociation of COE from **1**.

The rate constants for the exchange process were also measured over the temperature range 25−60 °C with [**1**] = 2.10×10^{-2} M and [B_2pin_2-d_{24}] = 2.88×10^{-1} M. The rate constant for the exchange process at 25 °C corresponded to a half-life of 2.8 ± 0.3 h. This half-life is between a factor of 2 and 5 longer than the half-life for the reaction of **1** with the same concentration of benzene presented in section 2.A.

The activation parameters for the exchange process were determined from the Eyring plot in Figure 5 to be $\Delta H^{\ddagger} = 25.9 \pm 1.3$ kcal mol^{-1}, $\Delta S^{\ddagger} = 9 \pm 1$ eu. The small positive entropy of activation is consistent with initial dissociation of COE, followed by a bimolecular second step. If the initial dissociation of COE were followed by a second dissociative step, then the entropy of activation would be large.

4. Kinetic Studies of the Reactions of Arenes with B_2pin_2 Catalyzed by Complex 1. A. Reaction Orders. Kinetic studies on the catalytic reaction were conducted to determine the mechanism of the overall process. Because kinetic data obtained on catalytic reactions in which the catalyst is generated in situ can provide misleading kinetic data, we measured the rate constants of reactions initiated with isolated complex **1** and a constant concentration of cyclooctene. The improved synthesis and isolation of **1** allowed for kinetic studies to be conducted with pure samples of this complex.

The rate constants of catalytic reactions of B_2pin_2 with 1-(trifluoromethyl)-3-methylbenzene in the presence of 5−10 mol % of **1** as catalyst were measured by NMR spectroscopy in a 5:1 mixture of cyclohexane and cyclohexane-d_{12} as solvent.

(45) PhBpin-d_5 and PhBpin-d_{17} are easily separated by GC.

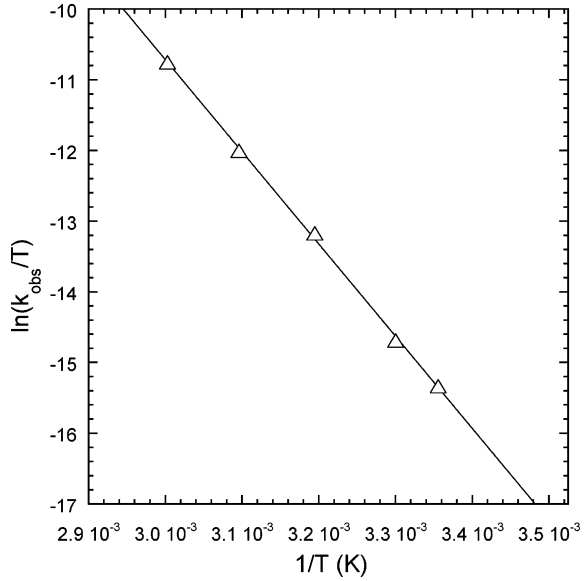


Figure 5. Eyring plot for exchange reaction of B_2pin_2/B_2pin_2-d_{24} with **1** between 25 and 60 °C.

The samples were prepared with concentrations of **1** = 0.0168 M and 1-(trifluoromethyl)-3-methylbenzene = 0.278 M. The simplest data were obtained when the concentration of B_2pin_2 exceeded the concentration of arene (B_2pin_2 = 0.472 and 1.32 M). The reactions were conducted at 30 °C and were monitored by $^{19}F\{^1H\}$ NMR spectroscopy in a mixture of cyclohexane and cyclohexane-d_{12}.

The concentration of arene decayed exponentially during all reactions with an excess of B_2pin_2. Plots of ln[arene] vs time were linear over 3−4 half-lives. These data show that the reaction is first order in arene. Rate constants for the reaction of 1-(trifluoromethyl)-3-methylbenzene (0.299 M) obtained at two different concentrations of B_2pin_2 (0.492 and 1.38 M) were within 10% of each other ($k_{obs} = 1.9 \pm 0.2 \times 10^{-4}$ s^{-1} and $k_{obs} = 1.7 \pm 0.2 \times 10^{-4}$ s^{-1}, respectively). These data indicate that the reaction is zero-order in B_2pin_2.

If the reaction rate is first-order in the concentration of arene, then it should depend on the identity of the arene. Indeed, the qualitative order of reactivity of four arenes in catalytic reactions with 1 mol % catalyst was 1,3-bis(trifluoromethyl)-benzene ($t_{1/2}$= about 1 h at 0 °C) > 1,2-dichlorobenzene ($t_{1/2}$= about 1 h at 10 °C) > benzene ($t_{1/2}$= about 1 h at 25 °C) > *m*-xylene ($t_{1/2}$= about 1 h at 40 °C).

The order of the reaction in added COE was determined with 1,2-dichlorobenzene as substrate in cyclohexane-d_{12} solvent by conducting reactions with varied concentrations of the added olefin and monitoring the reaction by ^1H NMR spectroscopy. Reactions with added COE were conducted with concentrations of **1** = 1.68×10^{-2} M, B_2pin_2 = 3.94×10^{-1} M, 1,2-dichlorobenzene = 2.84×10^{-1} M, and concentrations of COE ranging from 3.68×10^{-2} to 1.47×10^{-1} M. These reactions with added COE were conducted at 40 °C. The linear plot of $1/k_{obs}$ vs [COE] shown in Figure 6 (R^2 = 0.98) demonstrates that the reaction is inverse first-order in the concentration of olefin. This inverse dependence of the rate on the concentration of olefin implies that rapid and reversible dissociation of COE occurs prior to slower cleavage of the C−H bond. This reversible dissociation of COE is also consistent with the rapid exchange of free and bound COE detected by variable temperature ^1H NMR spectroscopy (vide supra).

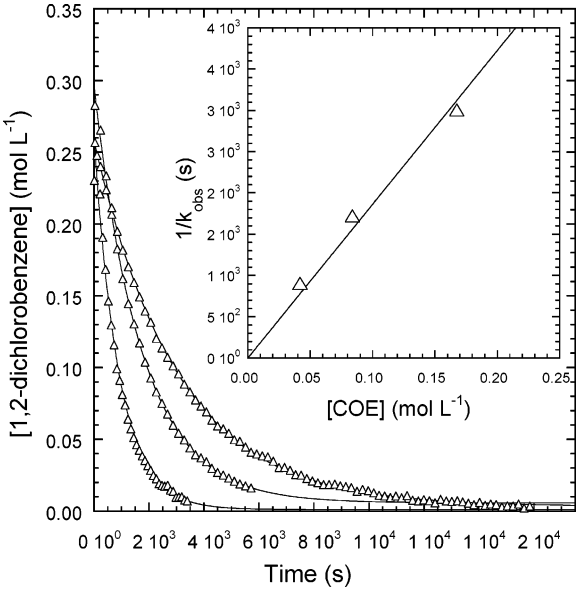


Figure 6. Decay of 1,2-dichlorobenzene during the reaction with B_2pin_2 catalyzed by **1** at 40 °C. Inset: Relationship between $1/k_{obs}$ and [COE] for the reaction of 1,2-dichlorobenzene with B_2pin_2 catalyzed by **1**.

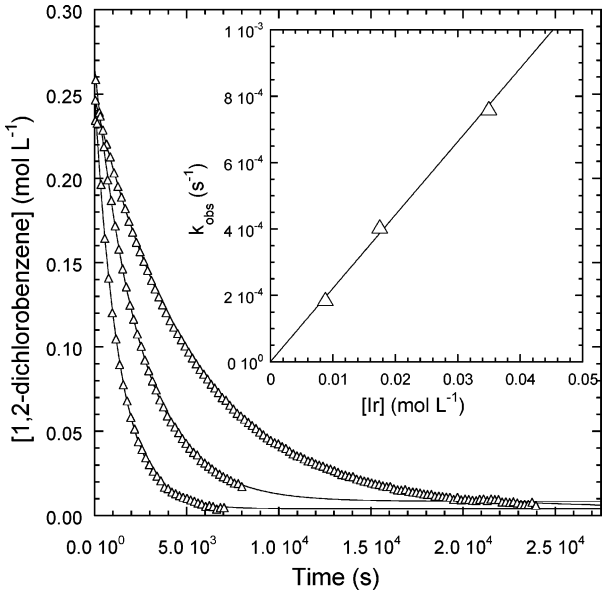


Figure 7. Decay of 1,2-dichlorobenzene during the reaction with B_2pin_2 catalyzed by **1** at 40 °C in the presence of added COE. Inset: Relationship between k_{obs} and [**1**] for the reaction of 1,2-dichlorobenzene with B_2pin_2 catalyzed by **1** with added COE.

The reaction was also first-order in catalyst when conducted with added COE. Reactions conducted with added COE contain a constant concentration of this olefin. Reactions at 40 °C in cyclohexane-d_{12} solvent with concentrations of 1,2-dichlorobenzene = 2.84×10^{-1} M, B_2pin_2 = 4.41×10^{-1} M, and of COE = 7.68×10^{-2} M were monitored by ^1H NMR spectroscopy. Variation of the concentration of **1** between 8.41×10^{-3} M and 3.36×10^{-2} M generated a linear plot of k_{obs} vs [**1**] (R^2 = 0.997) that reveals a first-order dependence of the reaction on the concentration of iridium (Figure 7).

The order of the reaction in catalyst differed when the reaction was conducted in the absence of added COE. In the absence of added olefin, the reaction was half-order in the concentration of **1**. The rate constants were determined for reactions containing

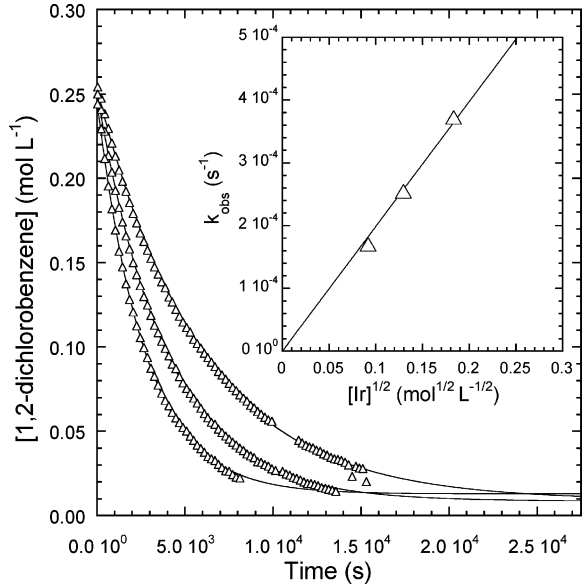


Figure 8. Decay of 1,2-dichlorobenzene during the reaction with B_2pin_2 catalyzed by **1** at 10 °C. Inset: Relationship between k_{obs} and [**1**] for the reaction of 1,2-dichlorobenzene with B_2pin_2 catalyzed by **1** in the absence of COE.

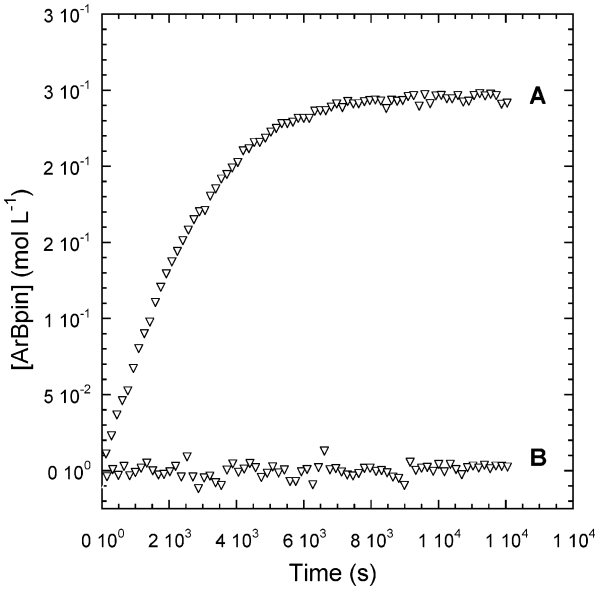


Figure 9. A comparison of the rate of the reaction of B_2pin_2 with 1,2-dichlorobenzene in cyclohexane-d_{12} at 25 °C catalyzed by 5 mol % [Ir(COD)Cl]$_2$ and 10 mol % dtbpy (relative to arene) initiated with 20 mol % of HBpin, relative to arene, (curve A) and initiated without added HBpin (curve B).

1,2-dichlorobenzene = 2.96×10^{-1} M, $B_2pin_2 = 4.27 \times 10^{-1}$ M, and [**1**] = 8.76×10^{-3}, 1.75×10^{-2} M, 3.50×10^{-2} M in cyclohexane-d_{12} at 10 °C. A plot of k_{obs} for the decay of arene vs [**1**]$^{1/2}$ that included the origin was linear ($R^2 = 0.990$), but a plot of k_{obs} vs [**1**] that included the origin was curved ($R^2 = 0.928$). These data show that the reaction is half-order in iridium under these conditions (Figure 8).

B. Isotope Effects on the Catalytic Reaction. Isotope effects on the catalytic borylation process were measured by several methods. First, the isotope effects from reactions of B_2pin_2 with a mixture of benzene and benzene-d_6 as solvent and reagent with 1 mol % **1** as catalyst were measured. These experiments led to a value of 5.0 ± 0.4. This value is indistinguishable from the isotope effect from the stoichiometric reaction of **1** with a mixture of benzene and benzene-d_6 as solvent (4.6 ± 0.4, see section 2B). The isotope effect for reaction of 1,2-dichlorobenzene was also measured by conducting the reaction with a mixture of 1,2-dichlorobenzene and 1,2-dichlorobenzene-d_4. These reactions occurred with a smaller, but nevertheless primary, isotope effect of 2.0 ± 0.4.

We also measured the isotope effect from the rate constants of two separate reactions of 1,2-dichlorobenzene and 1,2-dichlorobenzene-d_4. The rate constants of reactions of protiated and deuterated 1,2-dichlorobenzene at 25 °C were measured by ^{1}H NMR spectroscopy in cyclohexane-d_{12} with concentrations of **1** = 4.00×10^{-3} M, $B_2pin_2 = 0.315$ M, and arene = 0.284 M. Rate constants for reaction of protiated and deuterated arene were $7.5 \pm 0.7 \times 10^{-4}$ and $2.2 \pm 0.2 \times 10^{-4}$ s^{-1}, which correspond to a kinetic isotope effect of 3.3 ± 0.6. This isotope effect for separate catalytic reactions of protiated and deuterated 1,2-dichlorobenzene is slightly larger, but similar in magnitude, to the isotope effect from a mixture of dichlorobenzene and dichlorobenzene-d_4 in the same solution. The observation of a kinetic isotope effect from separate reactions of the two arenes implies that C−H bond cleavage is turnover-limiting and is consistent with the first-order dependence of the catalytic reaction on the concentration of arene.

5. Improvements in Turnover Frequencies and Assessment of Turnover Numbers. A. Improvements in Turnover Frequencies. We sought to use information on the synthesis and reactivity of **1** to develop improved procedures for conducting the catalytic reactions. We reported previously that the reaction of B_2pin_2 with benzene occurred with a significant induction period.[12] We proposed that this induction period resulted from the reduction of COD to COE and found that reactions initiated with 5 mol % of [Ir(COE)$_2$Cl]$_2$ occurred faster than those initiated with [Ir(COD)Cl]$_2$. However, the highest yields of **1** are generated from reactions of [Ir(COD)(OMe)]$_2$ and HBpin, in the presence of COE.

Thus, we considered that the reactions of B_2pin_2 with arenes catalyzed by these precursors would be faster if they were conducted with a small amount of HBpin to form the active catalyst **1**. As shown in Figure 9, the reactions of B_2pin_2 with 1,2-dichlorobenzene catalyzed by 5 mol % [Ir(COD)Cl]$_2$ and 10 mol % dtbpy, relative to arene initiated with 20 mol % of HBpin, relative to arene, occurred much faster than those initiated without added HBpin. Further, in contrast to previous reactions reported without added HBpin,[12] the reactions with added HBpin occurred without any induction period.

Our mechanistic studies also showed that COE inhibited the reaction. Thus, the rates of the catalytic reactions could be improved if the COE or COD of the starting complex could be consumed after the catalyst is generated. To consume the free olefin, we conducted the catalytic reactions with an added borane that would react with the free olefin in an uncatalyzed reaction. We examined catalytic reactions initiated with a small amount of added 9-borabicyclo[3.3.1]nonane (9-BBN dimer). The reaction of B_2pin_2 (0.430 M) with *m*-xylene (0.892 M, 2 equiv) catalyzed by **1** (2 mol % vs B_2pin_2) at room temperature in cyclohexane-d_{12} formed the arylboronate ester in 15% yield after 8 h and in 25% yield after 20 h. A parallel reaction conducted with identical concentrations of B_2pin_2, *m*-xylene, and catalyst **1**, but containing 20 mol % 9-BBN dimer, formed the

Table 1. Maximum Turnover Numbers for Borylation Reactions after 24 h at 100 °C

catalyst	catalyst loading (%)	yield (%)	turnover numbers
(dtbpy)(COE)Ir(Bpin)$_3$ (**1**)	0.0027	39	14 300
[Ir(COE)$_2$Cl]$_2$/dtbpy	0.0023	18	7 900
[Ir(COD)Cl]$_2$/dtbpy	0.0091	94	10 300
[Ir(COD)Cl]$_2$/dtbpy	0.0030	75	24 800
[Ir(COD)Cl]$_2$/dtbpy	0.0030	72	23 800[a]
[Ir(COD)(OMe)]$_2$/dtbpy	0.0091	100	10 900
[Ir(COD)(OMe)]$_2$/dtbpy	0.0030	49	16 000

[a] Sample contained 25 μL of pinacolborane to assist in catalyst initiation.

arylboronate ester in 44% and 80% yields after 8 and 20 h. Thus, a method to consume the COE ligand does lead to significant rate enhancements.

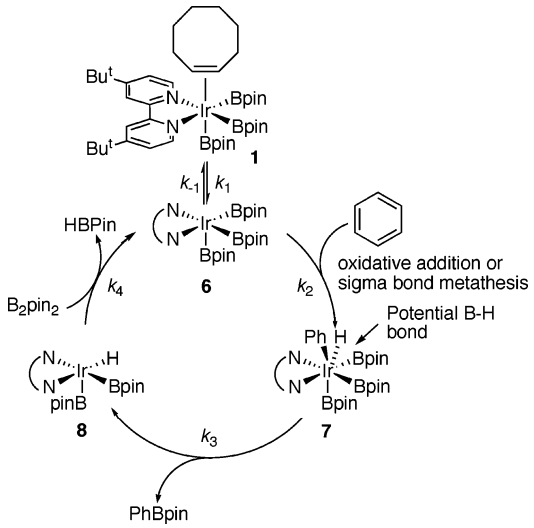
B. Assessment of the Maximum Turnover Numbers. Previously, we obtained 8000 turnovers for the borylation of arenes catalyzed by isolated **1**. As part of our current studies, we measured the maximum turnover numbers for reactions initiated with various catalyst precursors. Due to the water sensitivity of **1**, solvents and diboron reagent were rigorously dried. Reactions containing $(2.3-9.0) \times 10^{-5}$ M concentrations of one of the three iridium precursors [Ir(COE)$_2$Cl]$_2$, [Ir(COD)Cl]$_2$, or [Ir(COD)(OMe)]$_2$ and 2 equiv of dtbpy were conducted with $B_2pin_2 = 2.62$ M at 100 °C in benzene-d_6. Yields were recorded after 24 h.

Turnover numbers equal to or exceeding 14 000 were obtained for reactions catalyzed by **1** and for reactions catalyzed by a combination of dtbpy and the chloride dimer or methoxide dimer (Table 1). One reaction produced nearly 25 000 turnovers and 75% yield with 0.0030 mol % of the catalyst (mol % iridium) generated from the chloride dimer. Turnover numbers were clearly lower for reactions initiated with [Ir(COE)$_2$Cl]$_2$ as the source of iridium. The yields of these reactions tended to reflect conversions, rather than the amounts of side products formed. The differences in turnover numbers with **1**, or a combination of dtbpy and [Ir(COD)Cl]$_2$ or [Ir(COD)(OMe)]$_2$ are small, and for this reason we do not think it is appropriate to comment on the relationship between the precursor and these small differences. The purity of reagents from run to run are likely to account for at least some of these differences. Regardless of the precise relationship between the turnover numbers and catalyst precursor, these turnover numbers exceed any previous value for a homogeneous arene functionalization by at least an order of magnitude if not more.

Discussion

1. Evidence for the Intermediacy of Trisboryl Complex 1. A. Direct Observation of 1 in the Catalytic Reactions. A catalytic cycle that is consistent with our synthetic studies and with our qualitative and quantitative kinetic data is shown in Scheme 3. Several qualitative observations suggested that trisboryl complex **1** was the active catalyst or led to the active catalyst by a facile and reversible process. First, trisboryl **1** was observed in the catalytic reaction mixture. Although the direct observation of a complex in a catalytic system does not require that the complex be relevant to the catalytic process, this observation, in combination with the high reactivity of this complex with arenes to form arylboronate esters, provided initial strong support for the relevance of **1** to the catalytic process.

Scheme 3



Several more quantitative pieces of kinetic data provided further support for the relevance of **1** to the catalytic process. First, an induction period was observed when the catalyst was generated in situ from [Ir(COD)(OMe)]$_2$ and di-*tert*-butylbipyridine, but the induction period was absent when the reactions were initiated with isolated trisboryl complex **1**. Second, the isotope effects were similar for the catalytic reactions and the stoichiometric reactions of complex **1**. Third, the selectivities for reactions of B_2pin_2 with different arenes and heteroarenes were similar for the catalytic reactions and the stoichiometric reactions of complex **1**.

B. Kinetics of the Catalytic Reactions. Quantitative kinetic data provided strong evidence that the trisboryl complex rapidly and reversibly dissociates cyclooctene to form a 16-electron trisboryl complex that lies on the catalytic cycle (Scheme 3). The rate equation for the catalytic cycle under conditions with added COE is shown in eq 7.

$$\text{rate} = K_1 k_2 [\text{Ir}][\text{benzene}]/[\text{COE}] \tag{7}$$

The complex rate equation for the overall process (see Experimental Section) simplified to eq 7 when the reassociation of COE to 16-electron intermediate **6** is much faster than the catalytic process. This assumption is supported by the exchange of free and bound olefin on the NMR time scale and a catalytic reaction with added COE on the time scale of hours at 40 °C, as well as the inhibition of the stoichiometric reaction of **1** with benzene by added COE. This rate equation shows that the reaction would be first-order in catalyst, first-order in arene, and inverse-first-order in COE. These reaction orders were observed experimentally.

The somewhat counterintuitive observation of a half-order dependence of the rate on the concentration of catalyst without added COE is illustrated by eqs 8−11.

$$\text{rate} = k_2[\mathbf{6}][\text{benzene}] \tag{8}$$

$$K_1 = \frac{[\mathbf{6}][\text{COE}]}{[\mathbf{1}]} \quad \text{or} \quad K_1 = \frac{[\mathbf{6}]^2}{[\mathbf{1}]} \quad \text{because} \quad [\mathbf{6}] = [\text{COE}] \tag{9}$$

therefore,

$$[\mathbf{6}] = K_1^{1/2}[\mathbf{1}]^{1/2} \quad (10)$$

and

$$\text{rate} = K_1^{1/2}k_2[\mathbf{1}]^{1/2}[\text{benzene}] \quad (11)$$

These equations show the derivation of the rate expression for the catalytic process with rapid and reversible dissociation of COE and a 1:1 molar ratio of COE and complex **6** that results from the stoichiometry of the initial dissociation process and the constant concentrations of the starting iridium complexes that result from the catalytic property of the reaction. Under these conditions, the reaction would be half-order in the concentration of **1**. This half-order behavior was observed under the conditions when COE is not added to the system and further support reaction by the pathway in Scheme 3.

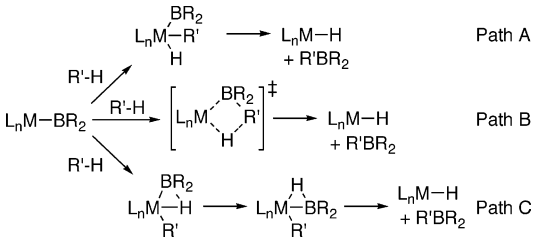
The 16-electron trisboryl complex **6** that results from the dissociation of COE would then react with arene in the turnover-limiting step, perhaps through aryl hydride **7**, to generate a bisboryl iridium hydride complex **8** and the aryl boronate ester product. Reaction of the bisboryl monohydride with the diboron reagent would then generate pinacolborane and regenerate the trisboryl complex.

Kinetic studies on the catalytic reaction support the assertion that the C−H activation step is turnover-limiting. First, trisboryl complex **1** was observed directly in the catalytic system, and the species that lies before the turnover-limiting step typically accumulates in the highest concentration. Second, the catalytic reaction was first-order in the concentration of arene and zero-order in the concentration of diboron compound. Third, a primary isotope effect was observed when comparing the rates of separate reactions of 1,2-dichlorobenzene and 1,2-dichlorobenzene-d_4 catalyzed by isolated **1**.

2. Mechanism of the C−H Bond Cleavage by Trisboryl Complex 1. A. C−H Activation by Ir(III) Trisboryl or Ir(I) Monoboryl Complexes. Although iridium(I) monoboryl and iridium(III) trisboryl complexes are both likely to be capable of undergoing C−H activation of the arene, isotopic labeling studies and kinetic studies of the stoichiometric reactions of **1** with arenes imply that addition of the arene occurs to an iridium(III) trisboryl complex. The barrier for C−H activation by the monoboryl complex was calculated in separate theoretical work to be lower than the barrier for C−H activation by the trisboryl complex.[34] However, the concentration of the trisboryl complex **1** is much higher in the catalytic system than any monoboryl complexes, and our experimental results show clearly that the barrier for elimination of B_2pin_2 from the trisboryl complex formed by dissociation of COE from **1** is higher than the barrier for C−H bond cleavage by the trisboryl complex. Thus, the labeling studies show that an iridium(III) boryl complex, not an iridium(I) boryl complex, reacts with the arene.

This conclusion is consistent with the reaction orders measured for the catalytic reactions. If rate-limiting dissociation of B_2pin_2 occurred from the trisboryl complex and reaction of the arene occurred with the resulting iridium(I) monoboryl intermediate, then the reaction would be zero-order in arene. If reversible dissociation of B_2pin_2 occurred and cleavage of the C−H bond were rate limiting, then the stoichiometric and catalytic reactions would be inverse-first-order in the concentration of B_2pin_2. Thus, the first-order dependence of the catalytic reaction on the concentration of arene and the zero-order dependence on the concentration of B_2pin_2 are inconsistent with rate-limiting and irreversible elimination of B_2pin_2, or with reversible elimination of B_2pin_2 to generate an iridium(I) monoboryl complex prior to C−H bond cleavage.

Scheme 4



B. Comments on the Mechanism of C−H Bond Cleavage. The selectivity for reaction of various arenes suggests that the C−H bond cleavage by the iridium(III) complex occurs through an η^2-arene complex. This assertion, although tentative, explains the relative reactivity of **1** with arenes possessing different electronic properties and with arenes vs electron-rich, five-membered heteroarenes. Complex **1** reacted faster with electron-poor arenes than with the electron-neutral arenes but reacted faster with electron-rich, five-membered heteroarenes than with electron−neutral arenes. The greater stability of η^2-arene complexes with electron-poor arenes than η^2-arene complexes with electron−neutral arenes and the greater stability of η^2-heteroarene complexes of five-membered heteroarenes than η^2-arene complexes[46] would account for this seemingly disparate set of relative rate data.

At the same time, our data do not reveal the detailed mechanism by which the C−H bond cleavage occurs. Several pathways for C−H bond cleavage by transition metal boryl complexes have been proposed and evaluated by computational studies. Three such mechanisms are shown in Scheme 4. One mechanism involves oxidative addition of the C−H bond, followed by reductive elimination to form a carbon−boron bond. The second pathway involves C−H bond cleavage by a σ-bond metathesis process that forms a carbon−boron bond in the organoborane product and a metal hydride in the transition metal product through a single transition state. A third mechanism involves cleavage of the C−H bond by a σ-bond metathesis process that first generates a borane complex. This borane complex subsequently rearranges to place the boron and carbon atoms cis to each other, if necessary, and undergoes B−C bond formation. Both σ-bond metathesis processes would involve the p-orbital of boron.

Computational studies reported recently concluded that C−H bond cleavage by the 16-electron trisboryl complex **6** generated by COE dissociation from **1** occurred by oxidative addition to generate an iridium(V) intermediate and reductive elimination to form the carbon−boron bond (path A).[34] In contrast, computational studies on the reactions of a rhodium trisboryl complex, a tungsten monoboryl complex, and an iron monoboryl complex imply that C−H bond cleavage occurs by a σ-bond metathesis to generate a borane complex as the initial product (path C).[47] Thus, the energies for the oxidative addition pathway

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(47) Hartwig, J. F.; Cook, K. S.; Hapke, M.; Incarvito, C.; Fan, Y.; Webster, C. E.; Hall, M. B. *J. Am. Chem. Soc.* **2005**, *127*, 2538.

A and the σ-bond metathesis pathway C are likely to be similar and we are unable to distinguish between these pathways from the experimental data. By computational studies, the σ-bond metathesis pathway B that forms the carbon−boron bond in a single step appears to have a higher activation energy than the σ-bond metathesis that first generates a borane complex prior to formation of the carbon−boron bond.[48,49]

One might imagine that the unoccupied p-orbital on the boryl ligand could lead to an electrophilic C−H activation process. Although the selectivities for arenes vs heteroarenes are different than the selectivities between two arenes, we have shown clearly that more electron-poor arenes react much faster than the more electron-rich arenes. This finding contradicts potential mechanisms in which the boryl complex would be the electrophilic component in a C−H activation process.

The magnitude of the electronic effects on the C−H bond cleavage by trisboryl complex **1** are larger than and opposite to those on the C−H bond cleavage by iron monoboryl complexes studied previously.[6] The photochemical reactions of CpFe(CO)$_2$Bcat with different arenes occurred faster with more electron-rich arenes, but the magnitude of this difference was small. For example, the reaction of a mixture of toluene and chlorotoluene or a mixture of toluene and trifluorotoluene gave nearly 1:1 ratios of products from reaction with the two arenes, while reaction of a mixture of toluene and anisole or a mixture of *tert*-butylbenzene and *N*,*N*-dimethylaniline gave 1:3 ratios of products in favor of the more electron-rich arene.

3. Comparison of Experimental and Computational Studies of Trisboryl Complex 1. The experimental work in the current paper corroborates several of the conclusions drawn from computational studies of the catalytic process initiated with complex **1**, but it also reveals some differences. Most generally, the experimental work and the computational work both show that the turnover-limiting step of the catalytic process with diboron reagents is cleavage of the C−H bond of the arene and that this cleavage occurs by the 16-electron complex formed by dissociation of olefin from trisboryl complex **1**.

More specifically, the experimental activation energy for the C−H bond cleavage step is significantly different from the computed value. The computed activation energy for C−H activation by the computed 16-electron complex with three boryl ligands and two dative nitrogen ligands is roughly 20 kcal/mol. The experimental free energy of activation for the borylation by **1** is close to this value. However, the borylation of arenes by **1** corresponds to a combination of dissociation of COE and activation of the C−H bond. Thus, one cannot compare these numbers directly. Instead, one must estimate the activation energy for the C−H bond cleavage step from the overall experimental activation energy and the binding energy of COE. Although we cannot provide a precise value, we can provide a valuable estimate.

The overall enthalpy of activation should be similar to the overall free energy of activation, because the entropy of activation for the overall two-step process should be small. This entropy should be small because the two steps of the mechanism for C−H activation by **1** involve one dissociative step (dissociation of COE) and one associative step (reaction of the 16-electron intermediate with benzene). Consistent with this prediction, the related combination of dissociation of COE and addition of Bpin$_2$ occurs with entropy of activation less than 10 eu.

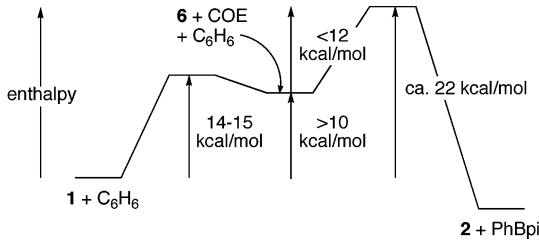

Figure 10. Qualitative energy diagram (enthalpy) that allows an estimate of the enthalpy of activation for the C−H bond cleavage by the 16-electron intermediate **6** generated by dissociation of COE from trisboryl complex **1**.

The estimate of the enthalpy for the C−H activation process is illustrated in Figure 10. The overall free energy of activation for the C−H functionalization process starting with **1** can be estimated to be about 22 kcal/mol, because it is a fast reaction ($k \sim 10^{-3}$) at room temperature with a 1 M concentration of arene (1 M is standard state). The enthalpy of activation will also be about 22 kcal/mol because the entropy of activation is small. Because the COE complex is stable, the Ir−COE bond strength (the enthalpy to cleave the Ir−COE linkage) should be at least 10 kcal/mol.[50] Consistent with this assertion, the rate of exchange between free and coordinated COE is between 14 and 15 kcal/mol. By subtracting the estimated binding energy of COE from the overall enthalpy of activation, the experimental activation energy for the elementary C−H bond cleavage process by the 16-electron intermediate should be between 8 and 12 kcal/mol instead of the calculated value of 20 kcal/mol.

The computational work also suggested that the trisboryl complex and a pentaboryl complex would be similar in energy in the presence of a high concentration of the diboron reagent. Although we cannot compare the relative ground-state energies of a pentaboryl complex vs the unsaturated 16-electron trisboryl complex formed after dissociation of COE, because we cannot observe either species, we did obtain evidence that the pentaboryl complex lies at an accessible energy. The studies on the isotopic exchange of trisboryl **1** with B$_2$pin$_2$-d_{24} were consistent with an exchange by association of the diboron reagent with the 16-electron intermediate **6**. Thus, our data imply that addition of B$_2$pin$_2$ to the 16-electron species to generate a pentaboryl complex is more favorable than elimination of B$_2$pin$_2$ from the same 16-electron species to generate a monoboryl intermediate. These findings are consistent with the computational work.

In addition to a small difference in energy between the pentaboryl complex and the combination of the trisboryl complex and free diboron reagent, the reaction of the 16-electron species with the diboron reagent was computed to have a barrier of only 5.6 kcal/mol, relative to the free energy of the two separate reagents. This barrier lies about 15 kcal/mol lower than the computed one for C−H activation by the same 16-electron intermediate.

Our experimental work shows that the difference in energy for C−H activation of benzene and oxidative addition of B$_2$-

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(49) Lam, W. H.; Lin, Z. Y. *Organometallics* **2003**, *22*, 473.
(50) This bond strength is based on a free energy of binding of at least 3 kcal/mol and an entropy for the bimolecular event that would be 20−30 eu and would correspond to a TΔS term of 6−9 kcal/mol near room temperature.

pin_2 is much different from the 15 kcal/mol difference determined by the computational work. Moreover, inconsistent with a higher barrier for C−H activation than for addition of the boron reagent, the stoichiometric borylation of benzene by isolated **1** was faster than the exchange of Bpin groups between **1** and B_2pin_2-d_{24}. From the observation that the rate constant for C−H activation of benzene by **1** was a factor of 2−5 larger than the rate constant for exchange of the diboron reagent with **1**, one can conclude that the transition state for C−H activation of benzene lies 0.5−1 kcal/mol below the transition state for reaction with B_2pin_2. Further studies will be needed to determine whether these large differences in relative energies between the experimental and computational work result from differences in the true mechanism for C−H bond cleavage and the computed mechanism or simply from truncation of the bipyridine ligand and the substituents on the boryl group to allow computational studies.

4. Comparison of C−H Activation by Iridium Boryl and Hydrocarbyl Complexes. We have shown clearly in previous work on C−H activation by $CpM(CO)_nR$ (R═Ar, Bcat) compounds that the boryl complexes are more reactive for C−H bond cleavage than the analogous alkyl or aryl complexes. This type of comparison between the reactivity of iridium(III) alkyl or aryl complexes and the iridium(III) boryl complexes toward C−H bond cleavage is more difficult to make because few bpy-ligated Ir(III) alkyl complexes are known.[51] A looser comparison can be made between these complexes and other iridium(III) alkyl complexes, however. For example, the 16-electron (PCP-pincer)Ir(H)(Ph) compound reacts with arenes by first generating Ir(I),[52] and this mechanism contrasts with the mechanism involving activation of arenes by the Ir(III) trisboryl complex over activation by an Ir(I) monoboryl complex. The different mechanisms for reaction of **1** and (PCP-pincer)Ir(H)(Ph) with arenes may result from the severe steric hindrance of the PCP-pincer ligand containing *tert*-butyl groups. Another comparison can be made between the activation of hydrocarbons by the 16-electron iridium(III) fragment $[Cp^*Ir(PMe_3)(Me)]^+$ generated by dissociation of CH_2Cl_2 from $[Cp^*Ir(PMe_3)(Me)(CH_2Cl_2)]^+$.[53] This compound cannot eliminate alkane prior to C−H activation and does appear to react with benzene and methane at room temperature by oxidative addition.[54]

One factor that clearly distinguishes the C−H activation of arenes by **1** and the C−H activation of arenes by these complexes is the subsequent formation of functionalized product. This functionalization by the formation of arylboronate esters results from the strong thermodynamic driving force for B−C bond formation and the overall favorable thermodynamics for the reaction of B_2pin_2 with arenes to form ArBpin and HBpin.[55,56] These favorable thermodynamics create a catalytic process that allows the direct generation of arylboronate esters without the intermediacy of halogenated reagents, Grignard reagents, or a hydrolytic workup that are characteristic of the conventional synthesis of arylboronate esters. Further, the regiochemistry of the borylation process is controlled by steric effects,[12,14,15] and the control of regioselectivity by steric effects complements the predominant control of regiochemistry by electronic effects in electrophilic aromatic substitution.

Thus, the mild temperatures, lack of byproducts, and regiochemistry that complements that of electrophilic substitution generate a useful catalytic process. Information on the factors that control the generation of the catalyst in situ allowed conditions to be developed in which the borylation of arenes with B_2pin_2 occurs under conditions that are even milder than those published previously. Studies on the scope and utility of the reaction under these conditions will be reported as part of future studies.

Experimental Section

General Methods. All the experiments were carried out in a glovebox under a nitrogen atmosphere or by using standard Schlenk techniques. Kinetic experiments were carried out under nitrogen in screw-capped NMR tubes with a PTFE septum or flame-sealed NMR tubes. The temperature of the NMR spectrometer probe was measured with a calibrated thermocouple inserted through the magnet into an NMR sample tube containing the appropriate solvent. Deuterated solvents were distilled from sodium benzophenone solutions or Na/K alloy (75 wt % K), and arenes were distilled from calcium hydride. All commercially available chemicals were used as received or purified as described in the individual sections. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared by a slight modification of the literature procedure.[57] $[Ir(COE)Cl]_2$ and $[Ir(COD)Cl]_2$ were made by known methods,[58] and $[Ir(COD)OMe]_2$ was prepared by a recently published protocol.[59] ^1H NMR spectra were recorded on samples in C_6D_{12}, C_7D_{14} or a mixture of C_6D_{12} and C_7D_{14} at 400 or 500 MHz, with Me_4Si or residual protiated solvent as an internal chemical shift reference. ^2H NMR spectra were recorded at 46 MHz and were referenced to C_6D_6 as internal standard at 7.15 ppm. $^{19}F\{^1H\}$ NMR spectra were recorded at 376 MHz. ^{11}B NMR were recorded at 160 MHz with $BF_3{\cdot}OEt_2$ as an external standard. NMR yields were measured with an internal standard of either dodecahydrotriphenylene (DHT, Aldrich) or 1,3,5-tris(trimethylsilyl)benzene.[60]

Reaction of 4,4′-Di-*tert*-butyl-2,2′-bipyridine (dtbpy) with B_2pin_2 and ClBpin. To an NMR tube was added dtbpy (25 mg, 0.093 mmol) and B_2pin_2 (25 mg, 0.098 mmol) in cyclohexane-d_{12} (0.5 mL). The sample was sonicated for 15 min (25 °C) to dissolve solids and then allowed to stand at room temperature. Slow formation of a white precipitate was observed, presumed to be the Lewis acid−base adduct dtbpy·B_2pin_2 (not detectable by ^1H or ^{11}B NMR spectroscopy, only starting materials observed). The NMR sample was heated in an oil bath (50 °C) for 10 min, redissolving the precipitate. Upon cooling to room temperature, white precipitate was again observed. An NMR sample containing identical concentrations of dtbpy and B_2pin_2 prepared in benzene-d_6 remained homogeneous, as any adduct formation remained soluble.

In an NMR tube, dtbpy (25 mg, 0.093 mmol) was dissolved in pentane (0.7 mL). 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (ClBpin, 75 mg, 0.46 mmol) was added, resulting in immediate congealing of the entire sample as a white solid. Only excess ClBpin was observed by ^{11}B NMR spectroscopy. The material was dried in vacuo and dissolved in CH_3CN, and an ^{11}B NMR spectrum was acquired to reveal an unidentified resonance at δ 11.3. An NMR sample containing identical concentrations of dtbpy and ClBpin in benzene-d_6 resulted in immediate precipitation to afford a white suspension, indicating that the adduct dtbpy·ClBpin is insoluble, even in arene solvent.

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Monitoring of the Borylation Reactions of Complex 1 Generated from [Ir(COD)Cl]$_2$ with and without Added HBpin (Data in Figure 9). A 4-mL vial equipped with a stir bar was charged with iridium dimer (0.0091 mmol), which was dissolved in cyclohexane-d_{12} (0.75 mL). The solution was stirred while pinacolborane (0.083 mmol) was added via microsyringe. After 1 min, the mixture was transferred to a second 4-mL vial containing 4,4′-di-*tert*-butyl-2,2′-bipyridine (0.0205 mmol) and stirred for 5 min at room temperature. The red solution was added to B_2pin_2 (0.236 mmol) and TMS_3Ph (internal standard, 5 μL, 0.016 mmol) in an NMR tube equipped with a screw-cap and septum. 1,2-Dichlorobenzene (0.18 mmol) was then added through the septum via microsyringe, and the reaction course was monitored by ^{1}H NMR spectroscopy at room temperature for 160 min. The experiment without added HBpin was conducted in an identical fashion but without adding HBpin prior to addition of ligand.

Synthesis of Trisboryl Complex 1 from Pinacolborane and [Ir(COD)(OMe)]$_2$, [Ir(COD)Cl]$_2$, and [Ir(COE)$_2$Cl]$_2$. An NMR tube equipped with a screw-cap and septum was charged with iridium dimer (0.0091 mmol) and dodecahydrotriphenylene (7.5 mg, 0.031 mmol) as an internal standard. The solid materials were dissolved in C_6D_{12} (0.5 mL). *cis*-Cyclooctene (25 μL, 0.18 mmol) was added to the tube, the sample was mixed, and pinacolborane (25 μL, 0.24 mmol) was added. To the resulting solution was added 4,4′-di-*tert*-butyl-2,2′-bipyridine (0.019 mmol), and the sample was heated in an oil bath at 40 °C for 30 min. At this time, the sample was analyzed by ^{1}H NMR spectroscopy at 25 °C. Aromatic resonances for complex **1** were observed at δ 7.10 (d, 2H, J = 5.5 Hz, 3,3′), 7.92 (s, 2H, 3,3′), and 9.45 (d, 2H, J = 6.0 Hz, 6,6′). The yield of **1** was determined by integrating the resonances of the dtbpy ligand vs those of dodecahydrotriphenylene as internal standard: [Ir(COD)(OMe)]$_2$ = 95%, [Ir(COD)Cl]$_2$ < 10%, [Ir(COE)$_2$Cl]$_2$ < 2%.

Synthesis of Trisboryl Complex 1 from [Ir(COD)(OMe)]$_2$: Importance of the Order of Addition of Reagents. The effect of the order of addition of reagents on the yield of **1** was assessed by reactions performed in three screw-capped NMR tubes containing [Ir(COD)(OMe)]$_2$ (9.5 mg, 0.014 mmol), dtbpy (7.5 mg, 0.028 mmol), HBpin (25 μL, 0.17 mmol), *cis*-COE (25 μL, 0.19 mmol), dodecahydrotriphenylene (internal standard, 7.5 mg, 0.0312 mmol), and cyclohexane-d_{12} (0.6 mL).

Sample A. The solids [Ir(COD)(OMe)]$_2$, dtbpy, and dodecahydrotriphenylene were dissolved in C_6D_{12} to yield a brown solution. Pinacolborane was added, and the sample was shaken. A ^{1}H NMR spectrum was acquired at room temperature, which indicated a ~30% yield of **1** (by integration vs internal standard) and unreacted dtbpy, accompanied by low yields of multiple, unidentified dtbpy-ligated iridium complexes with resonances in the aromatic region. Subsequent addition of COE and mixing increased the yield of **1** slightly to 38% vs internal standard.

Sample B. The solids [Ir(COD)OMe]$_2$, dtbpy, and dodecahydrotriphenylene were combined in an NMR tube, to which COE was added followed by solvent, C_6D_{12}. The sample was shaken vigorously, affording a brown solution with a significant quantity of insoluble material. Pinacolborane was added. Upon mixing a homogeneous brown solution was generated. A ^{1}H NMR spectrum was acquired at room temperature, which indicated a 50% yield of **1** (by integration vs internal standard) and small quantities of unidentified dtbpy-ligated iridium complexes with resonances in the aromatic region.

Sample C. [Ir(COD)OMe]$_2$ and dodecahydrotriphenylene were dissolved in C_6D_{12}. *cis*-COE and HBpin were then added, and a dark yellow solution resulted. Subsequent addition of dtbpy, followed by vigorous shaking, generated a dark red solution. A ^{1}H NMR spectrum was acquired at room temperature, indicating an 80% yield of **1** (by integration vs internal standard). The NMR tube was then heated at 60 °C in the spectrometer probe for 0.5 h, and the yield of **1** was found to be ca. 95% vs internal standard.

Synthesis of Trisboryl Complex 1 from Pinacolborane and [Ir(COD)OMe]$_2$. In a 200-mL Schlenk flask, [Ir(COD)(OMe)]$_2$ (0.950 g, 1.43 mmol) was dissolved in cyclohexane (60 mL). To this solution was added *cis*-cyclooctene (2.5 mL, 19 mmol). The yellow solution was stirred while pinacolborane (2.5 mL, 17 mmol) was added dropwise. The solution turned red. 4,4′-Di-*tert*-butyl-2,2′-bipyridine (0.750 g, 2.79 mmol) was added in one portion as a white solid. The solution immediately became dark red. The flask was sealed with a rubber septum and stirred for 15 min at ambient temperature and then at 40 °C for 20 min. The mixture was evaporated to dryness while the temperature was maintained at 40 °C, and the resulting solid was heated under vacuum for 30 min at 40 °C to afford a brown solid. The material was dissolved in pentane, concentrated in vacuo, and cooled to −30 °C. A yellow powder precipitated. The dark brown pentane supernatant was removed via pipet, and the remaining yellow powder was rinsed with 2 × 10 mL of cold (−30 °C) tetramethylsilane and dried in vacuo to afford 1.69 g (62%) of **1**. This material was further purified for kinetic studies and stoichiometric reactions at low temperature by dissolving about 500 mg of material in ether, cooling at −30 °C for 1 h, and adding tetramethylsilane (precooled at −30 °C) to the cold ether solution while it stirred. After stirring for about 2 min, the sample was returned to the −30 °C freezer for 1 h. After removing the supernatant with a pipet, about 20% of further purified **1** was recovered. Additional material was obtained by combining the mother liquors from several reactions and isolating **1** from pentane/TMS at −30 °C. ^{1}H NMR (C_6D_{12}, 60 °C): δ 9.51 (d, J = 5.9 Hz, 2H, 6,6′), 7.93 (d, J = 1.2 Hz, 2H, 3,3′), 7.11 (d, J = 5.8 Hz, 2H, 5,5′), 4.33 (br s, 2H, =C*H*), 1.40 (s, 18H, ^{t}Bu), 1.04 (s, 36H, $Bpin_3$); the aliphatic resonances of the COE ligand were broad at the temperatures at which the Bpin resonances were resolved, and they overlapped with the solvent and larger Bpin resonances. Thus, we were unable to confidently assign these resonances, even by 2-dimensional methods. The presence of the COE ligand is shown by the resolved olefinic resonances and the X-ray diffraction study published previously.[12] ^{11}B (C_6D_{12}, 60 °C): δ 34 (br s, $\omega_{1/2}$ = 500 Hz). ^{1}H NMR ($C_6D_{11}CD_3$, −60 °C): δ 9.44 (d, J = 5.6 Hz, 2H, 6,6′), 7.95 (s, 2H, 3,3′), 7.13 (d, J = 5.5 Hz, 2H, 5,5′), 3.90 (d, J = 7.6 Hz, 2H, =C*H*), 1.42 (s, 18H, ^{t}Bu), 1.23 (s, 12H, Bpin), 1.20 (s, 12H, Bpin), 0.69 (s, 12H, Bpin). ^{13}C NMR ($C_6D_{11}CD_3$, −60 °C): δ 156.1 (C-2,C-2′), 155.6 (C4,C-4′), 153.1 (C-6,C-6′), 120.0 (C-3,C-3′), 116.5 (C-5,C-5′), 78.3, 78.1 (C_{quart}, Bpin), 74.3 (*C*=*C*, COE), 30.2 (CH_2, COE), 29.2 (CH_3, *t*-Bu), 25.4 (CH_2, COE), 24.5 (CH_3, Bpin), 24.1 (CH_3, Bpin), 23.6 (CH_2, COE), 23.3 (CH_3, Bpin). Anal. Calcd for $C_{44}H_{74}B_3IrN_2O_6$: C, 55.53; H, 7.84; N, 2.94. Found: C, 55.43; H, 7.64; N, 2.87.

Kinetic Isotope Effect of the Reaction of Benzene with (dtbpy)Ir(COE)(Bpin)$_3$. In a reaction vial equipped with a stir bar, complex **1** (0.015 mmol, 0.011 g), benzene (3.00 mmol, 268 μL), benzene-d_6 (3.00 mmol, 266 μL), and DHT (0.10 mmol, 0.028 g) were combined. The reaction mixture stirred overnight at room temperature. After 24 h, one product was observed by GC trace and GC/MS. The kinetic isotope effect was calculated by taking the ratios of the parent mass peak for protiated and deuterated products. The same procedure was followed to determine the kinetic isotope effect for a 1:1 mixture of 1,2-dichlorobenzene:1,2-dichlorobenzene-d_4 and 1,3,5-benzene-d_3; the kinetic isotope effect was determined by normalizing the MS peak intensities to the mass spectrum of a sample of pure 2-(3,4-dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane, respectively.

Kinetic Isotope Effect of a Catalytic Reaction of Benzene with B_2pin_2 Catalyzed by (dtbpy)Ir(COE)(Bpin)$_3$. In a reaction vial equipped with a stir bar, catalyst **1** (1 mol %, 0.01 g), benzene (3.00 mmol, 268 μL), benzene-d_6 (3.00 mmol, 266 μL), B_2pin_2 (1.50 mmol, 0.200 g) and DHT (0.100 mmol, 0.028 g) were combined. The reaction mixture stirred overnight at room temperature. After 24 h, one product was observed by GC trace and GC/MS. The kinetic isotope effect was calculated by taking the ratios of the parent mass peak for protiated

and deuterated products. The same procedure was followed to determine the kinetic isotope effect for a 1:1 mixture of 1,2-dichlorobenzene:1,2-dichlorobenzene-d_4 and 1,3,5-benzene-d_3; the kinetic isotope effect was determined by normalizing the MS peak intensities to the mass spectrum of a sample of pure 2-(3,4-dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane, respectively.

Stoichiometric Reaction of 1 with Arene. Into an NMR tube was placed complex **1** (10 mg, 0.011 mmol), *cis*-COE (3.0 μL, 0.023 mmol), and an internal standard (TMS_3Ph, 3 μL). These materials were dissolved in a mixture of 0.32 mL of C_6D_{12} and 0.25 mL of C_7D_{14}. The sample was placed in a precooled spectrometer probe. An initial ^{1}H NMR spectrum was recorded at −15 °C. 1,3-Bis(trifluoromethyl)-benzene (32 μL, 0.21 mmol) was then added to the sample via microsyringe and quickly returned to the spectrometer. The sample was warmed to 0 °C, and the reaction was monitored by ^{1}H NMR spectroscopy. Trisboryl **1** reacted with the arene to produce an equivalent of arylboronate ester and (dtbpy)(η^2-COE)Ir(H)$(Bpin)_2$ (**2**). ^{1}H NMR (C_6D_{12}/C_7D_{14}, 0 °C): δ 9.51 (d, J = 5.6 Hz, 2H, 6,6′), 7.91 (d, J = 1.7 Hz, 2H, 3,3′), 7.13 (dd, J = 6.1, 2.1 Hz, 2H, 5,5′), 3.38 (m, 2H, η^2-COE C*H*), −4.81 (s, 1H, Ir*H*). Subsequently, complex **2** reacted with arene to afford an additional equivalent of arylboronate ester and (dtbpy)(η^2-COE)Ir$(H)_2$(Bpin) (**3**). ^{1}H NMR (C_6D_{12}/C_7D_{14}, 0 °C): δ 9.66 (d, J = 6.1 Hz, 1H, 6 or 6′), 8.94 (d, J = 5.6 Hz, 1H, 6 or 6′), −5.72 (d, J = 5.3 Hz, 1H, Ir*H*), −23.1 (d, J = 5.3 Hz, 1H, Ir*H*).

Determination of the Half-Life of the Reaction of 1 with Benzene. In a reaction vial were placed **1** (0.011 mmol, 0.010 g) and DHT (0.050 mmol, 0.014 g). Cyclohexane-d_{12} (0.5 mL) was added to the reaction vial, and the solution was mixed until **1** and DHT were dissolved. Benzene (0.144 mmol, 13.0 μL) was added, and the solution was then transferred to a screw-capped NMR tube. The tube was removed from the glovebox, and ^{1}H NMR spectra of the reaction mixture were obtained once every 60 min for 6 h. The borylated product was monitored by the appearance of a peak at δ 1.26, corresponding to the methyl groups of the phenyl pinacol boronate ester. The decay of **1** was monitored by integrating the doublet at δ 9.44, which corresponded to the bound dtbpy ligand on **1**.

Reactions of 1 with a mixture of two Arenes. In a reaction vial equipped with a stir bar were placed complex **1** (0.015 mmol, 0.010 g) and dodecahydrotriphenylene (DHT) (0.10 mmol, 0.023 g). Into a second reaction vial were mixed benzene (3.0 mmol, 0.27 mL) and thiophene (3.0 mmol, 0.24 mL); the diluted arene was then added to the vial that contained **1** and DHT. The reaction mixture was stirred at room temperature overnight in the glovebox. After 24 h, an aliquot of the reaction mixture was removed, and a GC trace of the reaction mixture was obtained. The identity of each product was determined by comparison of the GC/MS to that of authentic material prepared independently (vide infra) or purchased from chemical suppliers, and the yield of each product was determined by using GC. The same procedure was also followed for the reactions of a mixture of benzene and furan, and *m*-xylene and 1,3-bis(trifluoromethyl)benzene.

Reactions of B_2pin_2 with a Mixture of Two Arenes Catalyzed by 1. In a reaction vial equipped with a stir bar were placed catalyst **1** (1 mol %, 0.001 g), B_2pin_2 (0.005 mmol, 0.003 g), and dodecahydrotriphenylene (DHT) (0.050 mmol, 0.011 g). Into a second reaction vial, benzene (0.10 mmol, 9.0 μL) and thiophene (0.10 mmol, 8.0 μL) were mixed; the diluted arene was then added to the vial that contained **1**, B_2pin_2, and DHT. The reaction mixture was stirred at room temperature overnight in the glovebox. After 24 h, an aliquot of the reaction mixture was removed, and a GC trace of the reaction mixture was obtained. The identity of each product was determined by comparison of the GC/MS to authentic material (see the next paragraph), and the yield of each product was determined by GC. The same procedure was also followed for the reactions with the combination of benzene and furan, and *m*-xylene and 1,3-bis(trifluoromethyl)benzene.

Independent Synthesis of 4,4,5,5-Tetramethyl-2-(thiophene-2-yl)-1,3,2-dioxaborolane, 4,4,5,5-Tetramethyl-2-(furanyl-2-yl)-1,3,2-dioxaborolane, 4,4,5,5-Tetramethyl-2-(3,5-dimethylphenyl)-1,3,2-dioxaborolane, and 2-(3,5-Bis(trifluoromethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Representative Procedure for the Synthesis of 4,4,5,5-Tetramethyl-2-(thiophene-2-yl)-1,3,2-dioxaborolane. In a reaction vial equipped with a stir bar were combined $[Ir(COD)(OMe)]_2$ (0.015 mmol, 0.0093 g), dtbpy (0.030 mmol, 0.0081 g), thiophene (2.00 mmol, 159 μL), and B_2pin_2 (0.500 mmol, 0.127 g). Cyclohexane (approximately 2.0 mL) was added to the reaction vial, and the reaction mixture was stirred at room temperature overnight. The reaction mixture was monitored using GC. The product was purified by column chromatography, eluting with 1:1 ethyl acetate:hexane. The same procedure was also followed for the synthesis of 4,4,5,5-tetramethyl-2-(3,5-dimethylphenyl)-1,3,2-dioxaborolane and 2-(3,5-bis-(trifluoromethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The 4,4,5,5-tetramethyl-2-(furanyl-2-yl)-1,3,2-dioxaborolane was purchased from Lancaster chemicals. The *m*-xylylBpin was isolated by column chromatography, and the 1,3-bis(trifluoromethyl)phenylBpin was isolated by Kugelrohr distillation. Spectroscopic data for 2-thienylBpin: ^{1}H NMR (C_6D_6, 400 MHz): δ 7.87 (d, J = 3.6 Hz), 6.89 (dd, J = 3.6, 4.4 Hz, 1H), 1.07 (s, 12H). ^{11}B (C_6D_6): δ 30.8 (br s). GC/MS (intensity, *m*/*z*): 210 (97, M^+), 195 (100, $M - CH_3^+$). 2-FuranylBpin: ^{1}H NMR (C_6D_6, 400 MHz): δ 7.29 (d, J = 4.2 Hz), 7.20 (d, J = 3.2 Hz, 1H), 6.08 (dd, J = 3.2, 3.2 Hz, 1H), 1.05 (s, 12H). ^{11}B (C_6D_6): δ 27.1 (br s). GC/MS (*m*/*z*): 194 (100, $M)^+$, 179 (90, $M - CH_3)^+$. 3,5-dimethylphenylBpin: ^{1}H NMR (CD_3Cl, 400 MHz): δ 7.34 (s, 2H), 7.03 (s, 1H), 2.25 (s, 6H), 1.42 (s, 12H). ^{11}B (C_6D_6): δ 30.8 (br s). GC/MS (intensity, *m*/*z*): 232 (100, M^+), 217 (77, $M - CH_3^+$). 1,3-Bis(trifluoromethyl)phenylBpin: ^{1}H NMR (C_6D_6, 400 MHz): δ 8.3 (s, 2H), 7.7 (s, 1H), 1.0 (s, 12H). ^{11}B (C_6D_6): δ 31.4 (br s). GC/MS (intensity, *m*/*z*): 340 (2, M^+), 325 (100, $M - CH_3^+$).

Reaction of $[Ir(COD)(OMe)]_2$ with Phenanthrene. In a reaction vial equipped with a stir bar were placed $[Ir(COD)(OMe)]_2$ (0.002 mmol, 0.001 g), dtbpy (0.003 mmol, 0.001 g), phenanthrene (0.20 mmol, 0.034 g), B_2pin_2 (0.10 mmol, 0.026 g), and DHT (0.10 mmol, 0.026 g). Cyclohexane (approximately 0.6 mL) was added to the reaction vial, and the reaction mixture was stirred at room temperature overnight. The reaction mixture was monitored by GC and GC/MS.

Independent Synthesis of 9-Phenanthryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. To a solution of *tert*-butyllithium (1.4 M, 3.2 mL, 4.48 mmol) in 15 mL of THF was added a solution of 9-bromophenanthrene (575 mg, 2.24 mmol) in 4 mL of THF at −78 °C via syringe in small portions. The mixture was stirred for a further 1.5 h at −78 °C to give a green suspension. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.9 mL, 11.2 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature over 24 h, at which time the solution was clear yellow. The reaction mixture was poured into water and extracted several times with dichloromethane, and the combined organic phases were subsequently washed with water and brine and dried over $MgSO_4$. After evaporation of the solvent, the crude product was obtained as an oil. This crude material was purified by column chromatography on silica gel with *n*-hexane/ethyl acetate (30:1 v/v) as eluent to give a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.86−8.84 (m, 1H), 8.71 (dd, J = 3.5, 9.6 Hz, 1H), 8.69 (d, J = 8.2 Hz, 1H), 8.41 (s, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.69 (ddd, J = 1.3, 7.1, 8.2 Hz, 1H), 7.66−7.64 (m, 2H), 7.60 (ddd, J = 0.9, 7.0, 7.9 Hz, 1H). The position of the boryl group was confirmed by ^{1}H−^{1}H COSY spectroscopy. ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 138.3, 134.7, 132.1,131.2, 130.2, 129.5, 129.3, 128.0, 126.9, 126.6, 126.3, 122.8, 122,7, 84.1, 25.2 (the carbon atom attached to the boron could not be detected). ^{11}B ($CDCl_3$, 160.4 MHz): δ 31.6 (br s). GC/MS (*m*/*z*) (intensity, fragment): 304 (100, M^+), 289 (10, $M^+ - CH_3$), 204 (100, $M^+ - C_6H_{12}O$). Anal. Calcd for $C_{20}H_{21}BO_2$: C, 78.97; H, 6.96. Found: C, 78.74; H, 7.12.

Pinacol-d_{12}. This material was prepared from acetone-d_6 by procedures reported for the synthesis of pinacol from acetone.[61] In a glovebox, magnesium powder (0.500 g, 20.6 mmol) was added to mercury (20.0 g, 100 mmol) in a 20-mL DRAM vial. The mixture was warmed on a hot plate (100 °C) and triturated with a spatula to form a molten amalgam. The amalgam was transferred to a Schlenk flask containing acetone-d_6 (10.5 mL, 143 mmol) in 80 mL of dry benzene. The flask was sealed with a septum under nitrogen and stirred in a 60 °C oil bath for 10 h, resulting in a white suspension. The mixture was cooled to room temperature, quenched with distilled water (35−40 mL), and heated for an additional hour at 60 °C. The mixture was extracted with diethyl ether (2 × 100 mL), and the solvent was removed by distillation at ambient pressure to afford a yellow oil. The oil was dissolved in 15 mL of distilled water and cooled to 0 °C to afford a white solid. The solid was collected and dried azeotropically by refluxing in benzene in a Dean−Stark trap. Evaporation of the benzene provided clear, oily crystals (1.62 g, 60%). ^{2}H NMR (toluene): δ 0.98. ^{13}C NMR (toluene-d_8): 65.9 (s), 24.0 (septet, 1:3:6:7:6:3:1, J = 18.9 Hz).

B_2pin_2-d_{24}. This material was made by simple modification of the preparation of B_2pin_2.[62] In a Schlenk flask, tetrakis(dimethylamino)-diboron (2.66 g, 13.4 mmol) and pinacol-d_{12} (3.50 g, 26.9 mmol) were dissolved in 40 mL of toluene and cooled to 0 °C. The solution was stirred as HCl was added dropwise (1.0 M in ether, 54 mL, 54 mmol), forming a white precipitate. The mixture was stirred at 0 °C for 60 min and then at room temperature for 3 h. The suspension was extracted with pentane (2 × 120 mL) and filtered through a coarse frit to remove insoluble material. The solution was washed with degassed water (3 × 75 mL) and dried over $MgSO_4$. The solvent volume was reduced in vacuo, and the concentrated pentane solution was cooled to −30 °C. White crystals (1.49 g, 40%) formed and were isolated by filtration. Additional material was obtained from the mother liquor. The crystals were dried azeotropically by refluxing in benzene in a Dean−Stark trap, followed by sublimation (60 °C, 0.1 mm). ^{2}H NMR (C_6H_6): 0.94. ^{11}B NMR (C_6D_6): 31.5. ^{13}C NMR: 82.7 (s), 24.2 (septet, 1:3:6:7:6:3:1, J = 19.0 Hz).

Low-Temperature Reactions of Arenes with 1 in the Presence of B_2pin_2-d_{24}. In a glovebox, a stock solution of complex **1** was prepared by dissolving 50 mg of **1** in 1.5 mL of cyclohexane-d_{12} ([**1**] = 0.0350 M). An aliquot of stock solution of **1** (0.4 mL, 0.0140 mmol) was added to a screw-capped NMR tube and was frozen at −30 °C. To the NMR was added B_2pin_2-d_{24} (10 mg, 0.0360 mmol) in 0.35 mL of C_6D_{12} to form a second layer above the frozen solution of **1**. The sample was again frozen at −30 °C and then placed in a 0 °C ice bath outside of the drybox. The sample was transferred to a NMR spectrometer probe that had been precooled to 7.5 °C, and an ^{1}H NMR spectrum was acquired. The NMR tube was removed from the spectrometer to a 0 °C ice bath, injected with 1,2-dichlorobenzene (5.0 μL, 0.044 mmol), shaken, and reinserted into NMR probe. The reaction course was monitored at 7.5 °C for 70 min (50% conversion of 1,2-dichlorobenzene). The pinacol-methyl region showed new resonances only for the arylboronate ester (δ 1.28, 2-(3,4-dichloro-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane) and pinacolborane (δ 1.18, HBpin). The tube was removed from the spectrometer, and a small quantity of bis(pinacolato)-diboron (approx. 1.0 mg, 0.0041 mmol) in C_6D_{12} (50 μL) was injected to confirm the assignment of the new resonances. The sample was quickly returned to the probe. A new pinacol-methyl resonance at δ 1.16 for the added B_2pin was observed, confirming the peak assignments and that no exchange of Bpin groups from the iridium center and the labeled B_2pin_2-d_{24} occurred prior to functionalization.

Temperature Dependence of the Reactions of Trisboryl Complex 1 with Deuterium-Labeled B_2pin_2. In a glovebox, B_2pin_2-d_{24} (40 mg, 0.144 mmol) and tris(trimethylsilyl)benzene (internal standard, 5.0 μL, 0.016 mmol) in cyclohexane-d_{12} (0.5 mL) were added to an NMR tube. The sample was frozen at −30 °C, and trisboryl complex **1** (10 mg, 0.0105 mmol) was added to the NMR tube as a yellow powder. The NMR tube was removed from the glovebox and placed in a 0 °C ice bath. The sample was thawed and mixed at 0 °C to give a red solution. The NMR tube was then transferred to an NMR spectrometer probe, and the formation of bis(pinacolato)diboron (δ 1.14, mixture of pinB−Bpin-d_{12} and B_2pin_2) was monitored at various temperatures. The observed rates measured at the respective temperatures were 25 °C, 6.5×10^{-5} s^{-1}; 30 °C, $k_{obs} = 1.3 \times 10^{-4}$ s^{-1}; 40 °C, $k_{obs} = 6.0 \times 10^{-4}$ s^{-1}; 50 °C, $k_{obs} = 2.0 \times 10^{-3}$ s^{-1}; 60 °C, $k_{obs} = 7.1 \times 10^{-3}$ s^{-1}. A plot of ln[k_{obs}/T (K)] vs $1/T$ (K) was linear (R^2 = 0.999), which provided the thermodynamic parameters $\Delta H^{\ddagger} = 25.9 \pm 1.3$ kcal·mol^{-1} and $\Delta S^{\ddagger} = 9 \pm 1$ eu.

Concentration Dependence of the Exchange Reactions of Trisboryl Complex 1 with Deuterium-Labeled B_2pin_2. In a glovebox, B_2pin_2-d_{24} (10.0 mg, 36.0 μmol, 7 equiv) and DHT (internal standard, 0.10 mL of a 78.8 mM stock solution in cyclohexane-d_{12}) was added to an NMR tube. The sample was frozen at −30 °C, and a solution of trisboryl complex **1** (5.0 mg, 5.2 μmol) in 0.4 mL cyclohexane-d_{12} was added. The NMR tube was removed from the glovebox and placed in an ice bath at 0 °C. The sample was thawed and mixed until all the solids had dissolved, and a red solution was generated. The NMR tube was then transferred to an NMR spectrometer probe at 40 °C, and the formation of bis(pinacolato)diboron (δ 1.14, mixture of pinB−Bpin-d_{12} and B_2pin_2) was monitored. An exponential fit of the approach to equilibrium gave an observed rate constant $k_{obs} = 3.24 \times 10^{-4}$ s^{-1}. Samples with 20.0 mg (72.0 μmol, 14 equiv) and 30.0 mg (108 μmol, 21 equiv) of B_2pin_2-d_{24} were prepared in the same way and inserted into the preheated NMR spectrometer proble. The resonance for protio-B_2pin_2 was monitored, and the observed rates were: 14 equiv of B_2pin_2-d_{24}, $k_{obs} = 6.7 \times 10^{-4}$ s^{-1}; 21 equiv of B_2pin_2-d_{24}, $k_{obs} = 1.2 \times 10^{-3}$ s^{-1}.

Kinetics of the Catalytic Borylation: Dependence of the Rate on the Concentration of B_2pin_2. The rate constants were measured for reactions of 1-(trifluoromethyl)-3-methylbenzene by ^{19}F NMR spectroscopy. NMR samples were prepared containing **1** (10 mg, 0.0105 mmol) and C_6F_6 (15 μL, internal standard) in C_6D_{12}:C_6H_{12} (0.1 mL:0.5 mL). To the sample was added 75 mg (0.30 mmol) or 210 mg (0.827 mmol) of B_2pin_2. To the sample containing B_2pin_2 was added 1-(trifluoromethyl)-3-methylbenzene (25 mL, 0.179 mmol), and the reaction was monitored at 30 °C by ^{19}F{^{1}H} NMR spectroscopy. Plots of ln[arene] vs time were linear over five half-lives. The first-order rate constants for reactions with the two concentrations of B_2pin_2 were $1.9 \pm 0.2 \times 10^{-4}$ s^{-1} and $1.7 \pm 0.2 \times 10^{-4}$ s^{-1}, respectively.

Catalytic Borylation: Dependence on Added Olefin. To test the order of the reaction in added *cis*-cyclooctene, three reactions were performed in screw-capped NMR tubes. The reactions were conducted with **1** (10 mg, 0.0105 mmol), B_2pin_2 (62.5 mg, 0.246 mmol), and tris-(trimethylsilyl)benzene (internal standard, 5 μL, 0.0157 mmol) in cyclohexane-d_{12} (0.5 mL). *cis*-COE (3.0 μL, 0.023 mmol; 6.0 μL, 0.046 mmol; or 12 μL, 0.092 mmol) was added to each NMR tube. Each sample was inserted into a preheated NMR spectrometer at 40 °C, and an initial ^{1}H NMR spectrum was acquired. The sample was removed, injected with 1,2-dichlorobenzene (20 μL, 0.20 mmol), mixed, and returned to the probe. The borylation reaction was monitored for more than five half-lives at 40 °C. A first-order decay of arene was observed. The rate constants, as a function of the concentration of COE were [COE] = 0.037 M, $k = 1.1 \times 10^{-3}$ s^{-1}; [COE] = 0.074 M, $k = 5.8 \times 10^{-4}$ s^{-1}; [COE] = 0.15 M, $k = 3.3 \times 10^{-4}$ s^{-1}. A plot of k_{obs}^{-1} vs [COE] was linear (R^2 = 0.976).

Catalytic Borylation: Dependence on Catalyst 1 in the Presence and Absence of Added Olefin. In a glovebox, three screw-capped NMR tubes were prepared containing B_2pin_2 (70 mg, 0.276 mmol), *cis*-COE (10 μL, 0.077 mmol), and tris(trimethylsilyl)benzene (internal standard, 5.0 μL, 0.016 mmol) in cyclohexane-d_{12} (0.60 mL). To each NMR tube was added catalyst **1** (5.0 mg, 0.0053 mmol; 10 mg, 0.0105

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mmol; or 20 mg, 0.0210 mmol). The samples were inserted into a temperature-equilibrated NMR spectrometer at 40 °C for reactions in the presence of COE and 10 °C for reactions in the absence of added COE. An initial ^{1}H NMR spectrum was acquired. The samples were removed from the probe, injected with 1,2-dichlorobenzene (20 μL, 0.198 mmol), mixed, and returned to the probe. The borylation reaction was monitored for more than five half-lives at 40 °C. An exponential decay of arene was observed. The rate constants, as a function of the concentration of **1**, were [**1**] = 0.0088 M, $k_{obs} = 1.9 \times 10^{-4}$ s^{-1}; [**1**] = 0.018 M, $k_{obs} = 4.1 \times 10^{-4}$ s^{-1}; [**1**] = 0.035 M, $k_{obs} = 7.6 \times 10^{-4}$ s^{-1}. A plot of k_{obs} vs [**1**] that included the origin was linear ($R^2 = 0.997$). The same procedure was followed for reactions conducted in the absence of any added COE. The rate constants for these reactions were [**1**] = 0.00841 M, $k_{obs} = 1.7 \times 10^{-4}$ s^{-1}; [**1**] = 0.0168 M, $k_{obs} = 2.6 \times 10^{-4}$ s^{-1}; [**1**] = 0.0336 M, $k_{obs} = 3.7 \times 10^{-4}$ s^{-1}. The plot of k_{obs} vs [**1**]$^{1/2}$ was linear ($R^2 = 0.998$), but the plot of k_{obs} vs [**1**] that included the origin was curved ($R^2 = 0.928$).

Measurement of the Isotope Effect from Separate Reactions of 1,2-Dichlorobenzene and 1,2-Dichlorobenzene-*d*$_4$. NMR samples were prepared with catalyst **1** (100 μL of a 0.0263 M stock solution in C_6D_{12}, 2.63 μmol), B_2pin_2 (50 mg, 0.20 mmol), and the internal standard tris(trimethylsilyl)benzene (20 mL, 0.063 mmol) in 0.625 mL of cyclohexane-d_{12}. 1,2-Dichlorobenzene or 1,2-dichlorobenzene-d_4 (20 μL, 0.18 mmol) was added via microsyringe, and the reaction was monitored by ^{1}H NMR spectroscopy at 25 °C. A first-order decay of arene was observed. The rate constants were 1,2-dichlorobenzene, $k = 7.5 \times 10^{-4}$ s^{-1}; 1,2-dichlorobenzene-d_4, $k = 2.2 \times 10^{-4}$ s^{-1}. These rate constants correspond to a kinetic isotope effect k_h/k_d of 3.3.

Experiments To Determine the Maximum Turnover Number for the Borylation of Benzene-*d*$_6$ with B_2pin_2. In a glovebox, dilute stock solutions of the iridium precursors were prepared by dissolving 10 mg of iridium source ([Ir(COE)$_2$Cl]$_2$, 1.12 mM; [Ir(COD)Cl]$_2$, 1.49 mM; [Ir(COD)(OMe)]$_2$, 1.51 mM) in 10 mL of benzene-d_6 that had been distilled from Na/K alloy. A 3.72 mM stock solution of dtbpy in this rigorously dried solvent was also prepared. Into an NMR sample tube was placed B_2pin_2 that had been dried by refluxing in benzene with a Dean−Stark trap, followed by recrystallization from dry *n*-pentane and sublimation, dodecahydrotriphenylene (internal standard, 25 mg, 0.10 mmol), and benzene-d_6 (0.75 mL).

One sample was prepared by adding a 20-μL aliquot of the [Ir(COE)$_2$Cl]$_2$ stock solution (2.23×10^{-5} mmol) and a 20-μL aliquot of the dtbpy stock solution (7.45×10^{-5} mmol) to the NMR tube containing the B_2pin_2 (500 mg, 1.97 mmol), dodecahydrotriphenylene (25 mg, 0.10 mmol), and benzene-d_6 (0.75 mL). A second sample was prepared by adding a 20-μL aliquot of the [Ir(COD)Cl]$_2$ stock solution (2.98×10^{-5} mmol) and a 20-μL aliquot of the dtbpy stock solution to the NMR tube containing the B_2pin_2, dodecahydrotriphenylene, and benzene-d_6. A third sample was prepared by adding 25 μL (1.72×10^{-5} mmol) of pinacolborane to the reaction solution before adding the stock solutions of [Ir(COD)Cl]$_2$ and dtbpy. The fourth solution containing a 3-fold greater amount of catalyst was prepared by adding a 60-μL aliquot of the [Ir(COD)Cl]$_2$ stock solution (8.94×10^{-5} mmol) and a 60-μL aliquot of the dtbpy stock solution (2.24×10^{-4} mmol) to the NMR tube with the same amounts of the other reaction components. The fifth sample was prepared by adding a 20-μL aliquot of the [Ir(COD)OMe]$_2$ stock solution (3.02×10^{-5} mmol) and a 20-μL aliquot of the dtbpy stock solution to the NMR tube containing the B_2pin_2, dodecahydrotriphenylene, and benzene-d_6. The sixth solution with a 3-fold greater amount of catalyst was prepared by adding a 60-μL aliquot of the [Ir(COD)OMe]$_2$ stock solution (9.06×10^{-5} mmol) and a 60-μL aliquot of the dtbpy stock solution to the NMR tube containing the B_2pin_2, dodecahydrotriphenylene, and benzene-d_6 together. The seventh sample was prepared by dissolving 10.2 mg of isolated **1** in rigorously dried cyclohexane ([**1**] = 5.36 mM). A 10-μL aliquot of this solution was added to an NMR tube containing B_2pin_2 (498 mg, 1.96 mmol) and dodecahydrotriphenylene (internal standard, 20.9 mg, 0.0871 mmol) dissolved in benzene-d_6 (0.75 mL). Each sample was flame-sealed under vacuum and heated in an oil bath at 100 °C for 24 h. Yields were determined by integrating the pinacol methyl groups of the product vs the resonances of the internal standard in the ^{1}H NMR spectrum. The yields and corresponding turnover numbers are provided in Table 1 of the text.

Catalytic Reaction with Added 9-BBN. Two NMR samples were prepared with catalyst **1** (5.0 mg, 5.2 μmol), B_2pin_2 (60 mg, 0.24 mmol), and the internal standard dodecahydrotriphenylene (11 mg, 0.046 mmol) in cyclohexane-d_{12} (0.5 mL). To one sample was added 9-borabicyclo[3.3.1]nonane dimer (9-BBN, 6.0 mg, 0.024 mmol), followed by *m*-xylene (60 μL, 0.49 mmol). To the other sample was added only *m*-xylene (60 μL, 0.49 mmol). Initial ^{1}H and ^{11}B NMR spectra were acquired, and the samples were allowed to stand at room temperature. The yield of arylboronate ester was periodically measured by integration of the pinacol methyl groups of the product vs the resonances of the internal standard. The yields are based on the formation of ArBpin and HBpin from B_2pin_2. The reaction without added 9-BBN had proceeded to 15% yield after 8 h, and to 25% yield after 20 h; the reaction with added 9-BBN had proceeded to 44% yield after 8 h, and to 80% yield after 20 h. A resonance at δ 85 in the ^{11}B NMR spectrum indicated the formation of the *cis*-COE hydroboration product 9-cyclooctyl-9-bora-bicyclo[3.3.1]nonane.

Derivation of Rate Equations. The full rate equation for the catalytic cycle of Scheme 3 was derived by the schematic method developed for deriving the steady-state concentrations of enzyme-containing species based on the determinant method.[63,64] This equation and the assumptions made to simplify this equation are shown below:

$$\text{rate} = k_1k_2k_3k_4[\text{Ar-H}][B_2pin_2][\text{lr}]_{total}/\{k_1k_3k_4[\text{COE}][B_2pin_2] + k_1k_3k_4[B_2pin_2] + [\text{Ar-H}][B_2pin_2] + k_1k_2k_4[\text{Ar-H}][B_2pin_2] + k_1k_2k_3[\text{Ar-H}]\}$$

Because k_2[Ar−H] ≪ k_3 or k_4, the third and fourth term of the denominators are much smaller than the second. Because k_{-1}[COE] ≫ k_1, the second term in the denominator is much smaller than the first. Because NMR spectroscopy detects only **1**, $[\text{Ir}]_{total} \sim [\mathbf{1}]$. Therefore, this complex equation simplifies to

$$\text{rate} = \frac{k_1k_2[\text{Ar-H}][\mathbf{1}]}{k_{-1}[\text{COE}]}$$

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