# High-Turnover Aromatic C−H Borylation Catalyzed by POCOP-Type Pincer Complexes of Iridium

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S *Supporting Information*

ABSTRACT: The catalytic C−H borylation of arenes with HBpin (pin = pinacolate) using POCOP-type pincer complexes of Ir has been demonstrated, with turnover numbers exceeding 10 000 in some cases. The selectivity of C−H activation was based on steric preferences and largely mirrored that found in other Ir borylation catalysts. Catalysis in the (POCOP)Ir system depends on the presence of stoichiometric quantities of sacrificial olefin, which is hydrogenated to consume the H_2 equivalents generated in the borylation of C−H bonds with HBpin. Smaller olefins such as ethylene or 1-hexene were more advantageous to catalysis than sterically encumbered *tert*-butylethylene (TBE). Olefin hydroboration is a competing side reaction. The synthesis and isolation of multiple complexes potentially relevant to catalysis permitted examination of several key elementary reactions. These experiments indicate that the C−H activation step in catalysis ostensibly involves oxidative addition of an aromatic C−H bond to the three-coordinate (POCOP)Ir species. The olefin is mechanistically critical to gain access to this 14-electron, monovalent Ir intermediate. C−H activation at Ir(I) here is in contrast to the olefin-free catalysis with state-of-the-art Ir complexes supported by neutral bidentate ligands, where the C−H activating step is understood to involve trivalent Ir-boryl intermediates.
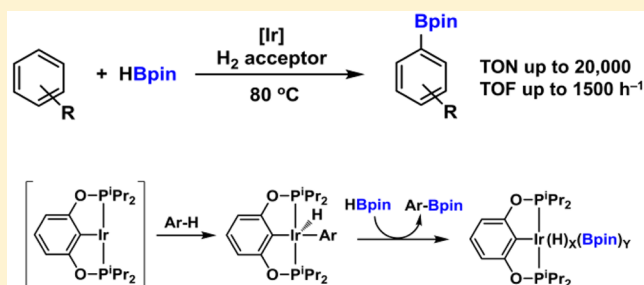
■ INTRODUCTION

In the last 15−20 years, C−H borylation has grown from an offhand observation[1] to a mature synthetic method.[2−7] C−H borylation is attractive, as it directly converts typically unreactive C−H bonds into organoboronate esters, whose use in a large number of synthetic transformations has been well documented.[8] The history and scope of C−H borylation has been thoroughly reviewed.[4−7] Early examples of transition metal-catalyzed C−H borylation utilized Ru, Rh, and Re, but the most impressive reactivity thus far has been achieved with Ir catalysts. Recent successes with Fe/Cu,[9] Co,[10,11] Pt,[12] and even main group[13] catalysts indicate that catalytic aromatic C−H borylation is not limited to the heavier group 9 metals. Nonetheless, Ir catalysts have proven especially effective in the borylation of aromatic C−H bonds where bidentate bis-(phosphine), 2,2′-bipyridine-type, or 1,10-phenanthroline ligands[14] have given rise to remarkable turnover numbers with sterically controlled selectivity. In these systems, the mechanism of Ir-catalyzed C−H borylation is believed to proceed via a 16-electron triboryl intermediate $L_2Ir(Bpin)_3$ (**I**, Scheme 1), which activates the arene C−H bond via oxidative addition (as shown in Scheme 1) or the closely related oxidative, hydrogen migration pathway.[14−17] Some of the most recent advances in Ir-catalyzed C−H borylation rely on access to intermediates that could be viewed as modified $L_2Ir(Bpin)_3$. Hartwig and co-workers used pendant Si−H groups in substrates and propose the intermediacy of a silyl/diboryl Ir(III) complex (**IV**, Scheme 1).[18] Krska, Maleczka, Smith et al.
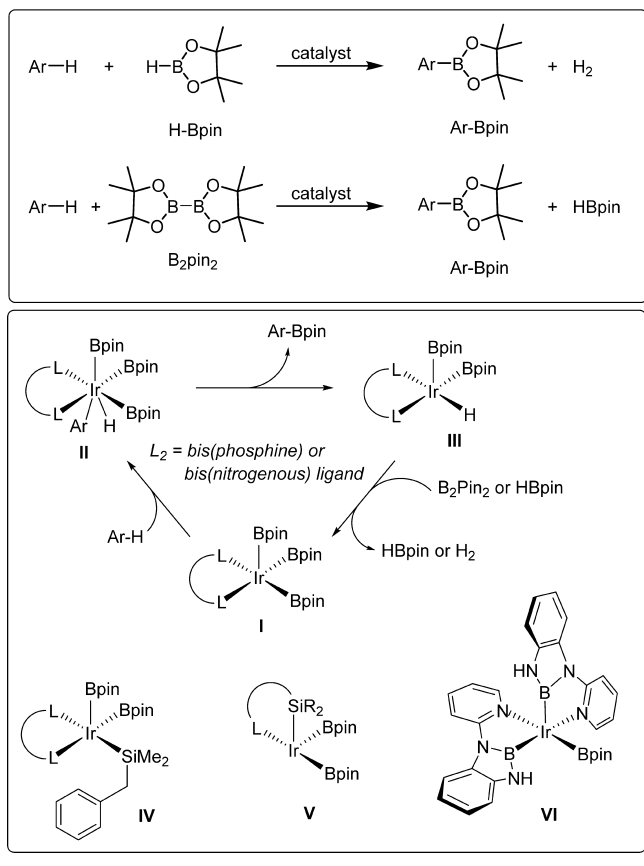
also proposed the intermediacy of a silyl/diboryl Ir(III) complex (**V**) in a study demonstrating the efficacy of phosphine/silyl or quinoline/silyl bidentate ligands.[19] Li et al. demonstrated that a combination of two pyridine/boryl bidentate ligands on Ir gave rise to a potent catalyst, again with an implied Ir(III) triboryl intermediate (**VI**).[20]

Examples **V** and **VI** illustrate that the boryls in intermediate **I** do not all have to be Bpin reagent-derived boryls and may be replaced by similar, strongly donating anionic donors as part of a bidentate ligand. With this in mind, the notion of borylation catalysis with Ir supported by a tridentate, monoanionic pincer ligand appears plausible, as well. Some efforts in pincer-ligated Ir-catalyzed arene borylation have been reported. Shimada et al.[21] determined that (PSiP)Ir catalysts gave 5−80 turnovers in the borylation of benzene with B_2pin_2 after 1 d at 120 °C. Driess and Hartwig tested iridium complexes supported by the sterically bulky SiCSi (silylene-aryl-silylene) and POCOP^{tBu} pincers, finding that they gave low TON (<20) under similar conditions. Importantly, they noted a modest increase in the yield of C−H borylated product upon addition of cyclooctene as a sacrificial hydrogen acceptor.[22] It was remarked that the sterically imposing pincers used in their study may have been detrimental to catalysis. Chirik's group has successfully used cobalt pincer complexes in the catalytic borylation of arenes and heteroarenes,[10,11] but those examples utilize neutral,

Scheme 1. Top: Net Reactions of Catalytic Borylation of Arenes with HBpin or B$_2$pin$_2$. Bottom: Catalytic Cycle Commonly Invoked in Ir-Catalyzed Aromatic Borylation and Recent Analogues (IV, V, VI)[18−20] to the Triboryl Intermediate I

■ RESULTS AND DISCUSSION

Synthesis of (POCOP)Ir(H)(Cl) and (POCOP)Ir(olefin) Precatalysts. Introduction of monoanionic L$_2$X type pincer ligands into the coordination sphere of Ir is commonly accomplished by metalation of the proligand with [(COD)-IrCl]$_2$ or [(COE)$_2$IrCl]$_2$, whereby oxidative addition of the central element-hydrogen bond leads to compounds of the general formula: (pincer)Ir(H)(Cl). For POCOP^{iPr} (1a, Figure 1), the corresponding synthesis has been described by
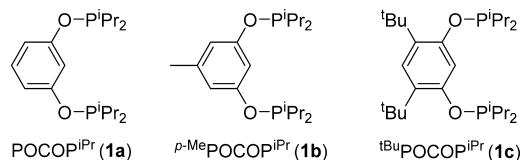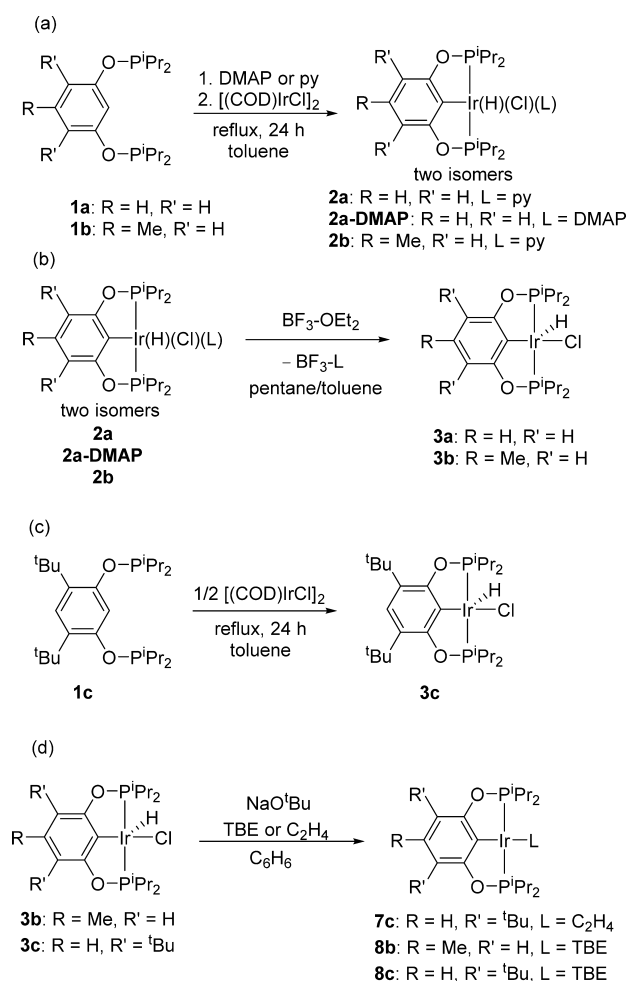

Figure 1. POCOP (pro)ligands used in this study.

Morales−Morales,[32] but in our hands, reaction of 1a with [(COD)IrCl]$_2$ or [(COE)$_2$IrCl]$_2$ in toluene at reflux for 24 h led only to complex mixtures. Instead, we were able to access pure 3a and 3b via a procedure analogous to the one utilized in the synthesis of (POCOP^{iPr})Rh compounds.[33,34] Reacting [(COD)IrCl]$_2$ with pyridine or DMAP,[35] followed by the addition of 1a and $^{p-Me}$POCOP^{iPr} (1b, Figure 1), gave adducts 2a-DMAP and 2b (Scheme 2a). The pyridine ligand was then

Scheme 2. Synthesis of (POCOP)Ir Complexes

tridentate pincers and must function via a different mechanism. Successful catalytic C−H borylation of alkenes with pincer complexes of Pd has also been reported by Szabo et al.[23] and by Iwasawa et al.[24]

Our group has recently discovered and developed the catalytic dehydrogenative borylation of terminal alkynes (DHBTA) by pincer complexes of Ir and Pd.[25−27] DHBTA appears to be orthogonal to the C−H borylation of aromatic C−H bonds in that our Ir DHBTA catalysts based on amido-containing pincers showed no propensity toward the borylation of arenes,[28] while the bipyridine-based Ir catalysts for aromatic C−H borylation were incapable of DHBTA.[24] However, in the course of exploring the potential of pincer-based Ir complexes for borylation, we came across a catalytic system for the C−H borylation of arenes whose activity and longevity rivals that of the state-of-the-art Ir catalysts supported by neutral bidentate ligands. The key to our findings lies in the use of smaller POCOP-type pincers vs the study of Driess and Hartwig, as well as in the use of smaller olefins as hydrogen acceptors. In contrast to the systems summarized in Scheme 1, the evidence in our case points to C−H activation not at an Ir(III) boryl intermediate but rather at an Ir(I) center devoid of boryl ligands, in a step reminiscent of the C−H activation in studies of catalytic alkane dehydrogenation and many other reactions by POCOP and PCP-type pincer complexes of iridium.[29−31]

abstracted from **2a**-DMAP (two isomers) or **2b** (two isomers) with $BF_3 \cdot Et_2O$ to give moderate yields of pure **3a** and **3b** (Scheme 2b). A recent report by Waterman and co-workers showed that a direct reaction of **1a** with $[(COE)_2IrCl]_2$ at 120 °C for 24 h in toluene under an atmosphere of H_2 gave **3a** in excellent yields.[36] The more strictly rigid $^{tBu}POCOP^{iPr}$ (**1c**, Figure 1), carrying two *tert*-butyl substituents on its central aromatic ring, did not require the pyridine addition/abstraction protocol, and pure **3c** was isolated from direct metalation in excellent yield (Scheme 2c). Dehydrochlorination of **3b** or **3c** with NaO^{t}Bu in the presence of ethylene or 3,3-dimethyl-1-butene (*tert*-butylethylene or TBE) provided the corresponding olefin adducts **7c**, **8b**, and **8c** (Scheme 2d).

Complexes **3a**−**c** display a triplet hydride resonance at ca. −37 ppm in their ^1H NMR spectra. This is somewhat downfield from the hydride signals for the analogous ($^{tBu}POCOP^{tBu}$)Ir(H)(Cl) complex (ca. −42 ppm).[22] The structures of **3a** (reported by Waterman et al.)[33] and **3c** (this work, Figure 2, vide infra) in the solid state present as chloride-
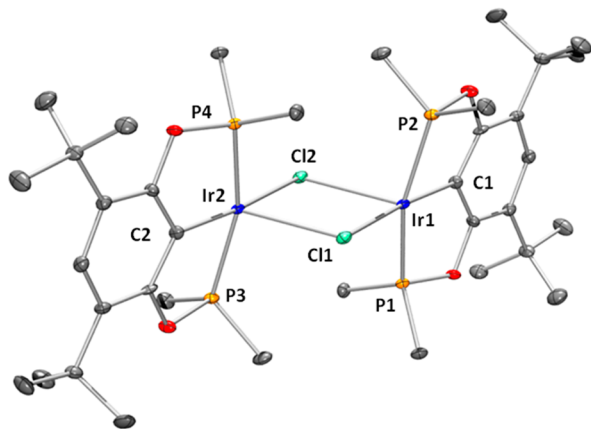

Figure 2. ORTEP[38] drawings (50% probability ellipsoids) of **3c**. Omitted for clarity: H atoms and methyl groups of isopropyl arms. Selected distance (Å) and angles (deg) follow: Ir1−Ir2, 4.040(1); Ir1−Cl1, 2.5169(9); Ir1−Cl2, 2.594(1); Ir1−C1, 2.042(2); P1−Ir1−P2, 158.09(3); C1−Ir1−Cl1, 173.6(1).

bridged dimers, in contrast to the monomeric solid-state structures determined for the ($POCOP^{tBu}$)Ir(H)(Cl) analogues.[22,37] In solution, **3a**−**c** likely exist in rapid equilibrium between dimeric and monomeric forms, resulting in the observation of an ^1H NMR chemical shift that is a weighted average of the two.

Catalytic Arene Borylation Studies with (POCOP)Ir Precatalysts. Initial experiments using 5 mol % **3a/b/c** or **8c** as precatalysts for the borylation of C_6D_6 with HBpin or B_2pin_2 at temperatures up to 100 °C for 72 h resulted in only stoichiometric formation (1 turnover) of C_6D_5Bpin (**A**) (Table 1, entries 1−3, 7, 11). Repeating the HBpin experiments using 1-hexene as a hydrogen acceptor (Table 1, entries 4−6, 8) yielded 75−88% of C_6D_5Bpin and 11−24% of hexylBpin (Table 1, entry 5) after 30 min at 80 °C. The use of TBE as H_2 acceptor (Table 1, entry 10) diminished the rate of C_6D_6 borylation relative to the rates with ethylene (Table 1, entry 13) or 1-hexene (Table 1, entry 6). The reaction of C_6D_6 and HBpin with 5 mol % of **3c** and ethylene at 80 °C (Table 1, entry 13) was complete within minutes of heating, while an analogous reaction using 1-hexene took 0.5 h to reach completion (Table 1, entry 6). We surmised the order of

increased rate of C_6D_5Bpin formation (ethylene > 1-hexene > TBE) could be explained by the smaller ethylene ligand having an increased rate of coordination and subsequent olefin insertion into the Ir−H or Ir−B bonds. Ethylene has previously been demonstrated to be a capable hydrogen acceptor in other dehydrogenative transformations catalyzed by POCOP−iridium systems.[39] Remarkably, we found that borylation of C_6D_6 with ethylene as the hydrogen acceptor could use as little as 0.1 or even just 0.004 mol % precatalyst **3c** (Table 1, entries 14 and 15), resulting in 83% yield of C_6D_5Bpin after 14 h at 80 °C. This translates to a turnover number (TON) of over 20 000 and turnover frequency (TOF) of 1480 h^{-1}.

An attempt at borylation with B_2pin_2 was unaffected by addition of 1-hexene (Table 1, entry 12); only 1 equiv of C_6D_5Bpin was produced. Performing the reaction with HBpin under argon flow in an open vessel (to potentially allow evolution of H_2 byproduct) also resulted in only 1 equiv of C_6D_5Bpin (Table 1, entry 9).

We performed a series of benzene borylation experiments using 0.1 mol % **3b** as precatalyst and varied the concentrations of benzene and 1-hexene relative to the constant (0.4 M) concentration of HBpin (see Supporting Information). It was clear that the degree of consumption of HBpin increased with increased benzene concentration, but there was no consistent trend with respect to the effect of 1-hexene concentration. We also investigated the apparent effect of catalyst concentration on the apparent rate of conversion by monitoring borylation of benzene with 8.0, 0.8, and 0.4 mM concentrations of **3b** (see Supporting Information). The conversions were highest at 8.0 mM [Ir] (e.g., 45% after 2 h vs 4% with 0.8 mM [Ir]) but were slightly higher for the 0.4 mM [Ir] experiment than the 0.8 mM [Ir]. All in all, the influence of concentration or reaction participants on the rate cannot be rationalized in simple terms.

In catalytic reactions utilizing precatalyst **3**, the fate of the Ir complex after all HBpin had been consumed was either the respective olefin complex (POCOP)Ir(olefin) or the chloro boryl complex (POCOP)Ir(Cl)(Bpin) (**10**). For example, utilizing **3c** with ethylene (Table 1, entry 13), **10c** and **7c** were observed as the main products among several other compounds by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The catalytic reaction utilizing **3c** with 1-hexene (Table 1, entry 6) contained **10c** as well as ($^{tBu}POCOP^{iPr}$)Ir(1-hexene) (**12c**) after catalysis, while experiments using **8c** with 1-hexene (Table 1, entry 8) gave almost exclusively **12c** as the final organometallic product.

Preparative Scale Catalytic Arene Borylation Using (POCOP)Ir Precatalysts. In a series of 0.20 to 0.35 g scale reactions, the high activity of the (POCOP)Ir system was demonstrated in experiments utilizing 0.005 mol % of **3c** in the reaction of HBpin with benzene and ethylene (3:1 to HBpin) (Table 2, entry B). C_6H_5Bpin (**B**) was isolated in a 75% yield which translates to TON = 15 000 with a TOF = 625 h^{-1}. Expanding the substrate scope to various substituted arenes (Table 2) including toluene, *m*-xylene, mesitylene, chlorobenzene, *o*-dichlorobenzene, *m*-chorotoluene, anisole, *N,N*-dimethyl-*m*-toluidine, benzotrifluoride, fluorobenzene, *m*-bromotoluene, and methyl benzoate, we found high turnovers with moderate yields of ArBpin after 24 h at 80 °C using precatalysts **3b** and **3c**. The selectivity of the borylated products was decidedly under steric control which is typical of most iridium-catalyzed C−H borylations.[4] Monosubstituted arenes gave nearly statistical mixtures of meta- and para-borylated products while 1,2-disubstituted or 1,3-disubstituted arenes were

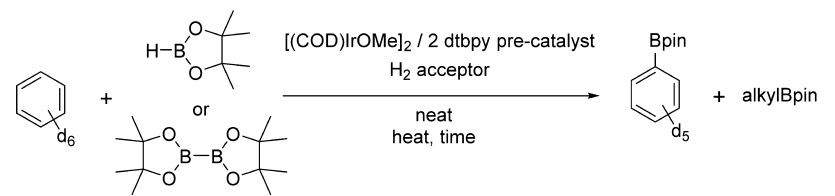## Table 1. C−H Borylation Experiments Using (POCOP)Ir Precatalysts[a]

entry	precat	mol %	boryl reagent	H$_2$ acceptor	temp (°C)	time (h)	TON	TOF (h^{-1})	yield (%) C$_6$D$_5$Bpin	yield (%) alkylBpin
1	3a	5.0	HBpin	none	100	36	1	<1	6	−
2	3b	5.0	HBpin	none	100	36	1	<1	4	−
3	3c	5.0	HBpin	none	100	36	1	<1	6	−
4	3a	5.0	HBpin	1-hexene	80	0.5	16	32	77	22
5	3b	5.0	HBpin	1-hexene	80	0.5	17	34	85	14
6	3c	5.0	HBpin	1-hexene	80	0.5	15	30	75	24
7	8c	5.0	HBpin	none	80	1	1	<1	6	−
8	8c	5.0	HBpin	1-hexene	80	0.5	18	36	88	11
9	8c	5.0	HBpin	none	80	0.5	1	<1	5	−
10	8c	5.0	HBpin	TBE	80	1	13	13	66	33
11	8c	5.0	B$_2$pin$_2$	none	100	72	1	<1	5	−
12	8c	5.0	B$_2$pin$_2$	1-hexene	100	72	1	<1	5	<1
13	3c	5.0	HBpin	ethylene	80	<0.2	16	80	80	19
14	3c	0.1	HBpin	ethylene	80	0.5	760	1520	76	24
15	3c	0.004	HBpin	ethylene	80	14	20750	1480	83	17

[a]All entries used a 1:25 HBpin (0.28 mmol):C$_6$D$_6$ (7 mmol) ratio and a 1:3 HBpin (0.28 mmol):olefin (0.84 mmol) ratio. Entries 1−12 used cyclohexane internal standard (0.19 mmol). Entries 13−15 used mesitylene internal standard (0.072 mmol). Yields of C$_6$D$_5$Bpin and RBpin are spectroscopic yields. In entries where the sum of C$_6$D$_5$Bpin and RBpin yield is <100% the remaining percent was unadulterated HBpin.

Table 2. Catalytic Arene Borylation Using (POCOP)Ir Precatalysts[a]

[a]Entries **B** and **C** utilized 0.005 mol % of **3c**. Entries **D−L** utilized 0.03 mol % of **3b** except entry **E** which used 0.5 mol % of **3b**. All reactions were run in neat arene for 24 h at 80 °C with 1 atm of ethylene (4 mmol total) added to the reactor headspace. Isolated yields (%) of ArBpin are calculated based on HBpin. Catalyst loading is expressed by [(mol of precatalyst/mol of HBpin) × 100]. TONs were calculated by [(mol of HBpin added) × (isolated yield of ArBpin)/(mol of precatalyst)].

Table 3. C−H Borylation Experiments Using ITHM Precatalysts[a]

entry	precat	mol %	boryl reagent	H$_2$ acceptor	temp (°C)	time (h)	TON	yield (%) C$_6$D$_5$Bpin	yield (%) alkylBpin
1	[(cod)IrOMe]$_2$/2 dtbpy	2.5/5.0	HBpin	none	80	1.5		72	−
2	[(cod)IrOMe]$_2$/2dtbpy	2.5/5.0	HBpin	1-hexene	80	0.5		21	74
3	[(cod)IrOMe]$_2$/2 dtbpy	2.5/5.0	B$_2$pin$_2$	none	80	1		87	−
4	[(cod)IrOMe]$_2$/2 dtbpy	2.5/5.0	B$_2$pin$_2$	1-hexene	80	0.5		57	37
5	[(cod)IrCl]$_2$/2 dtbpy	0.0015/0.003	B$_2$pin$_2$	none	100	24	7000	21	−
6	[(cod)IrCl]$_2$/2 dtbpy	0.0015/0.003	B$_2$pin$_2$	ethylene	100	24	<1	<1	2
7	[(cod)IrOMe]$_2$	2.5	HBpin	none	80	18		17	−
8	[(cod)IrOMe]$_2$	2.5	HBpin	1-hexene	80	0.5		<1	91

[a]Entries with HBpin used a 1:25 HBpin (0.28 mmol):C$_6$D$_6$ (7 mmol) ratio. Entries 3 and 4 used a 1:25 B$_2$pin$_2$(0.28 mmol):C$_6$D$_6$ (7 mmol) ratio. Entries with added olefin used a 1:3 HBpin (0.28 mmol):olefin (0.84 mmol) ratio. Entries 1−8 used cyclohexane internal standard (0.19 mmol). Yields of C$_6$D$_5$Bpin and RBpin are spectroscopic yields. In entries where the sum of C$_6$D$_5$Bpin and RBpin yield is <100% the remaining percent was unadulterated HBpin and/or B$_2$pin$_2$.

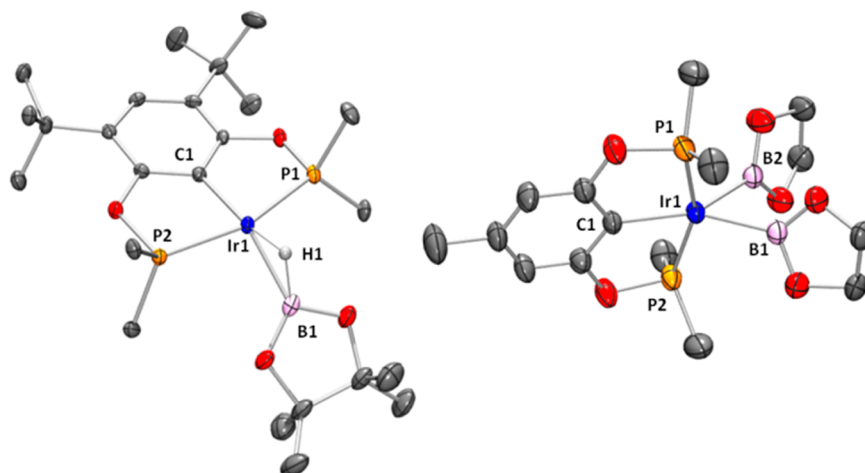## Scheme 3. Synthesis of Various (POCOP)Ir Compounds
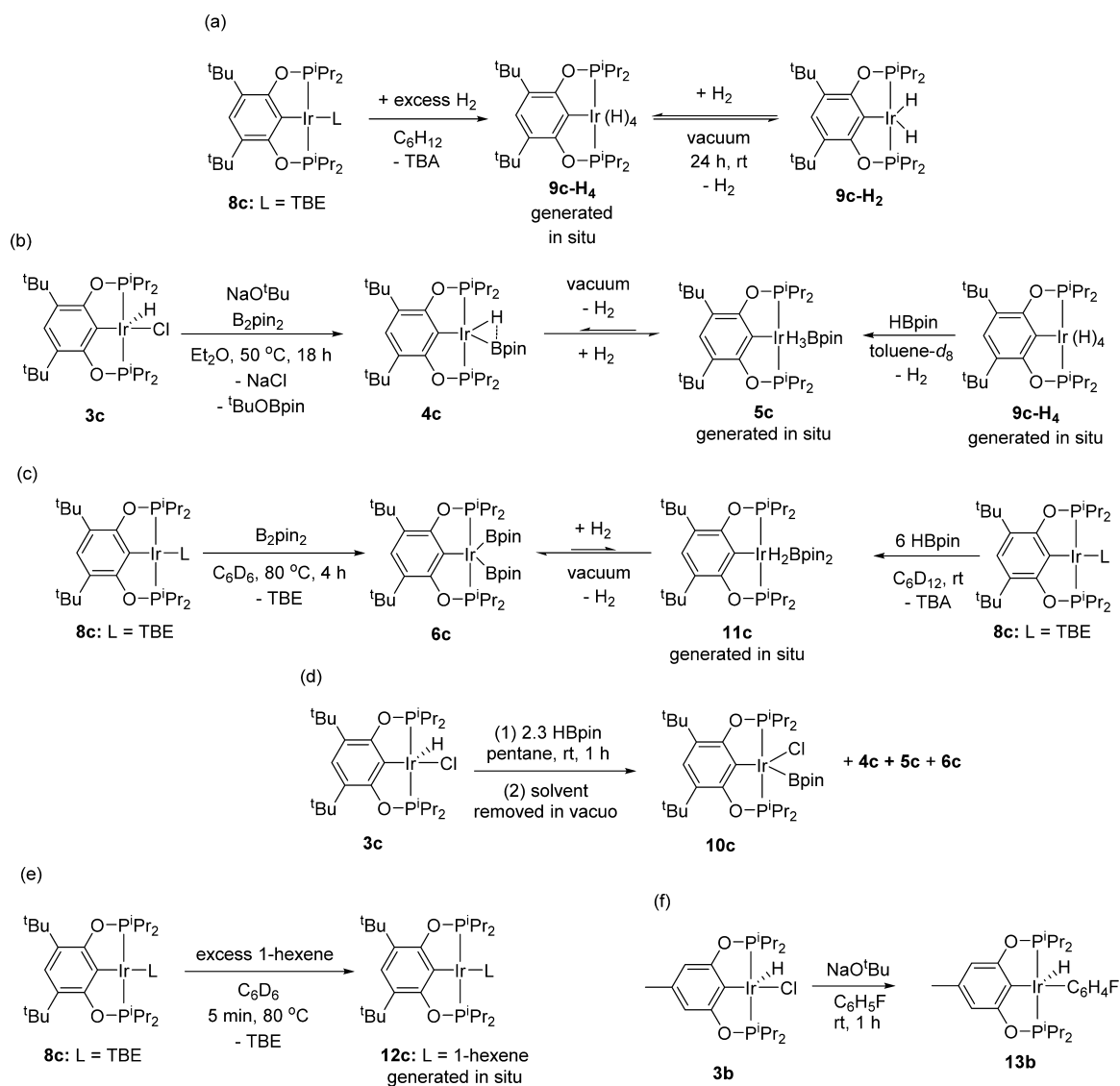
Figure 3. ORTEP[35] drawings (50% probability ellipsoids) of **4c** (left) and **6b** (right). Omitted for clarity: H atoms, methyl groups of isopropyl arms. Selected distance (Å) and angles (deg) follow: For **4c**: Ir1−B1, 2.069(4); Ir1−H1, 1.56(3); B1−H1, 1.42(3); P1−Ir1−P2, 159.39(3); B1−Ir1−H1, 43.0(1); C1−Ir1−B1, 149.0(1); C1−Ir1−H1, 168.0(2). For **6b**, the asymmetric unit contains two independent molecules, only values for one fragment are represented here: Ir1−B1, 2.065(4); Ir1−B2, 2.065(4); B1−B2, 2.251(8); P1−Ir1−P2, 156.92(5); C1−Ir1−B1, 146.98(11); B1−Ir−B2, 66.0(2).

borylated exclusively in the 4 or 5 position, respectively. Exceptions to the ortho-blocking were fluorobenzene which was borylated at the ortho, meta, and para positions in a 40:46:14 ratio (Table 2, entry L) and anisole, with 5% ortho-borylation. In addition, we observed up to 27% sp^3 C−H borylation in methyl benzoate, m-xylene, m-chlorotoluene, m-bromotoluene, and anisole. Metal-catalyzed borylation of benzylic CH bonds has been demonstrated with various systems including Rh,[40] Pd,[41] Ir,[42] and more recently Co.[43] When mesitylene was used, we observed exclusive borylation at the sp^3 C−H bond that proceeded much more slowly than the borylation of aromatic C−H bonds in other substrates.

Comparison with the ITHM Arene Borylation System. We investigated one variation of the ITHM (Ishiyama, Takagi, Hartwig, and Miyaura)[44] arene borylation catalyst system[14] (i.e., [(COD)IrOMe]$_2$ with 4,4′-di-tert-butyl-2,2′-bipyridine or dtbpy) and the effects of adding excess olefin (Table 3). Reacting HBpin or B$_2$pin$_2$ with neat C$_6$D$_6$ utilizing [(COD)-IrOMe]$_2$/2 dtbpy as precatalyst gave high yields of C$_6$D$_5$Bpin (Table 3, entries 1 and 3) while an identical reaction setup in parallel where 1-hexene was added resulted in a large amount of olefin hydroboration product (Table 3, entries 2 and 4). Repeating the high TON experiments reported in the literature,[15] we found [(COD)IrCl]$_2$/2 dtbpy precatalyst with B$_2$pin$_2$ in benzene indeed gave a high TON (7000) after 24 h at 100 °C (Table 3, entry 5). However, catalysis was totally inhibited by addition of ethylene (Table 3, entry 6). We also found that [(COD)IrOMe]$_2$ in the absence of added ligand catalyzed the reaction of HBpin with neat C$_6$D$_6$, giving C$_6$D$_5$Bpin in 17% yield (Table 3, entry 7) after 18 h at 80 °C, but addition of 1-hexene resulted predominantly in hydroboration (91% yield of hexylBpin, Table 3, entry 8). All in all, it appears that the ITHM catalyst system is inhibited by the addition of small, sacrificial olefins.
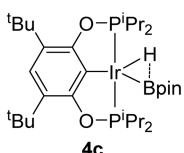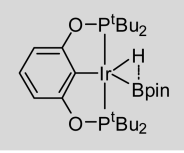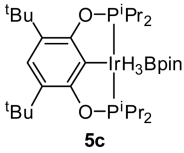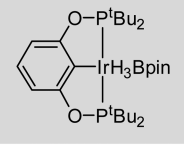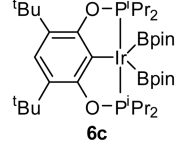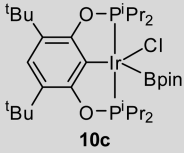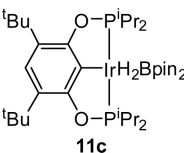
Synthesis of Relevant (POCOP)Ir Compounds. We sought to prepare Ir complexes that may be plausibly relevant to borylation, and also to examine the reactions of precatalysts **3** and **8** with HBpin. Considering the similar activity engendered by the three POCOP-type ligands discussed, we

selected Ir complexes of ligand **1c** and **1b** for these studies out of synthetic convenience.

Treatment of the TBE complex **8c** with excess H$_2$ generated the polyhydride compound **9c-H$_4$** in situ (Scheme 3a). Similar to (POCOP^{tBu})Ir(H)$_4$,[45] attempts to isolate **9c-H$_4$** by removal of solvent in vacuo (24 h of dynamic vacuum at ambient temperature) resulted in loss of H$_2$ to give **9c-H$_2$** (Scheme 3a). The HBpin complex **4c** was synthesized and isolated by treatment of **3c** with B$_2$pin$_2$ and NaO^{t}Bu in diethyl ether at 50 °C for 18 h (Scheme 3b). Complex **5c** exists in equilibrium with **4c** and H$_2$ and was observed as the dominant product in situ upon exposure of **4c** to an H$_2$ atmosphere or by adding HBpin to **9c-H$_4$** (Scheme 3b). Facile loss of H$_2$ precluded isolation of **5c** in a pure form. The diboryl complex (**6c**) was independently prepared and isolated via thermolysis of **8c** with B$_2$pin$_2$ in benzene (Scheme 3c). Compounds **5c** and/or **6c** were occasionally observed as impurities in varying amounts (up to 20%) during the synthesis of **4c**. Reacting **8c** with excess HBpin (20 equiv) in C$_6$D$_6$, then heating to reflux under argon flow for 0.5 h gave a mixture of **6c** and a second C_{2v} symmetric compound, tentatively assigned as **11c**. Similar to compound **5c**, loss of H$_2$ precluded the isolation of **11c**. When **8c** was reacted with HBpin (6 equiv) in cyclohexane-d_{12} at ambient temperature, **11c** was observed as the major product in situ (Scheme 3c). Subjecting the resultant mixture to high vacuum gave a mixture comprised of mostly **6c**. We attempted to prepare pure **5c** by treating **3c** with 2.3 equiv of HBpin in pentane at ambient temperature. We anticipated the reaction would generate **5c** and ClBpin, whereupon the volatile ClBpin could be easily removed in vacuo. Unexpectedly, the reaction resulted in a mixture of four compounds including **4c** (9%), **5c** (5%), **6c** (33%), and **10c** (52%) (Scheme 3d). Using column chromatography, compound **10c** was isolated out of this mixture in 42% yield. The TBE ligand of **8c** was readily displaced, as heating a C$_6$D$_6$ solution of **8c** containing excess 1-hexene at 80 °C gave **12c** within minutes (Scheme 3e).

We investigated various routes to synthesize pure hydrido/phenyl complexes of (POCOP)Ir but were only able to obtain complex mixtures.[46] Dehydrochlorination of **3c** with NaO^{t}Bu in neat C$_6$H$_6$ prepared free of ethers and halocarbons did give one
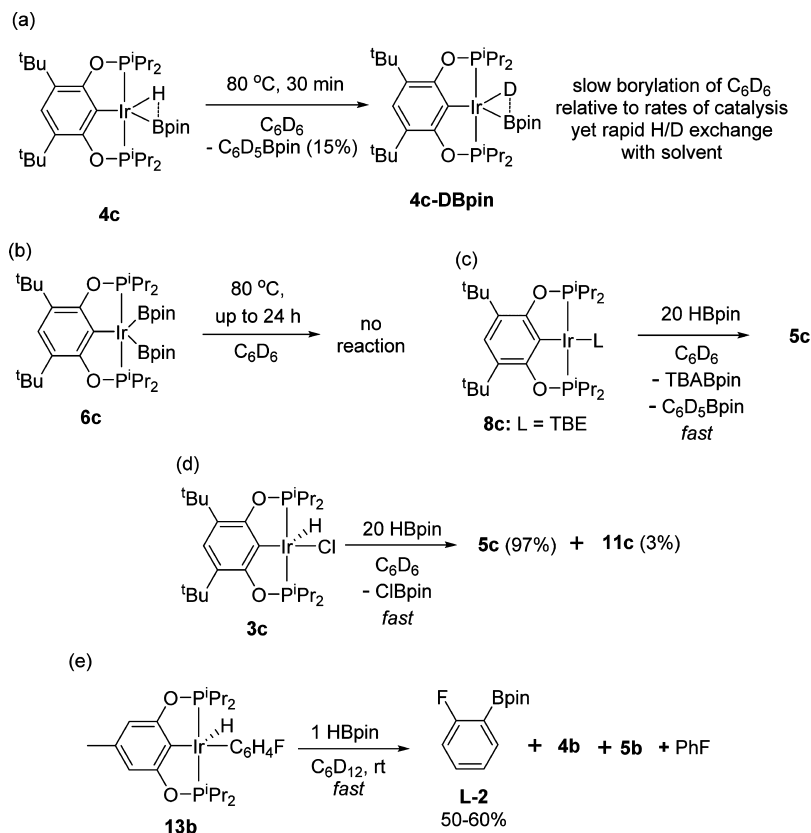
Table 4. Selected NMR Data for Bpin-Containing Ir Pincer Complexes

compound	^{1}H NMR hydride δ	^{11}B NMR δ	solvent
4c	−10.64, br s	27.6	toluene-d_8
(O–P^{t}Bu$_2$)$_2$ Ir(H)(Bpin)	−13.15, br s	29.0	THF-d_8
5c	−8.10, 1H br s −10.09, 2H br s	37.0	toluene-d_8
(O–P^{t}Bu$_2$)$_2$ IrH$_3$Bpin	−8.00, 1H br s −10.00, 2H br s	37.0	THF-d_8
6c	n/a	33.6	C$_6$D$_6$
10c	n/a	12.0	C$_6$D$_6$
11c	−8.30, 2H, t	unknown	C$_6$D$_6$

major product in the ^{31}P{^{1}H} NMR spectrum (δ = 177.5 ppm) as well as a broad hydride signal (ca. −42 ppm, C$_6$H$_6$) in the ^{1}H NMR spectrum. Brown solids were obtained by filtering the solution through Celite followed by lyophilization. NMR analysis at ambient temperature in cyclohexane-d_{12} revealed no hydride resonances in the ^{1}H NMR spectrum, while the ^{31}P{^{1}H} NMR spectrum contained multiple products. These results are consistent with the behavior of POCOP and PCP-supported hydrido-aryl complexes reported in the literature, as Goldman et al. found that (PCP^{tBu})Ir(Ph)(H) displayed only PCP ligand resonances at room temperature, and low temperature VT NMR studies were required to observe the hydride resonance.[47] Brookhart et al.[42] reported difficulty observing the hydride resonances for the isomers of (POCOP^{tBu})Ir(tolyl)(H) at temperatures above 10 °C. Previous work in the Ozerov group found that (PNP)Rh-(C$_6$H$_4$F)(H) existed as multiple isomers in solution, with broad

hydride resonances that were unobservable without the assistance of low temperature NMR studies.[48] Fluorobenzene is expected to give a more favorable C−H oxidative addition compared to benzene.[49] Indeed, use of fluorobenzene gave more promising results as dehydrochlorination of 3c with NaO^{t}Bu in neat C$_6$H$_5$F gave (^{tBu}POCOP^{iPr})Ir(C$_6$H$_4$F)(H) as the major product, though several other compounds were observed. Alternatively, we found that dehydrochlorination of 3b with NaO^{t}Bu in neat fluorobenzene gave ($^{p\text{-}Me}$POCOP^{iPr})-Ir(C$_6$H$_4$F)(H) (13b) in excellent yield and purity (Scheme 3f). The broad hydride signal of 13b observed at room temperature (−42.5 ppm, cyclohexane-d_{12}) is comparable to the hydride resonance observed for (POCOP^{tBu})Ir(tolyl)(H).[47] The chemical shift is indicative of a five-coordinate, square pyramidal complex with the hydride trans to an empty site while the broad nature of the hydride resonance likely indicates some fluxional process, including the possibility that 13b may

Scheme 4. Reactions Examining Possible Pathways for ArBpin Formation

(a)

80 °C, 30 min
C_6D_6
- C_6D_5Bpin (15%)

slow borylation of C_6D_6 relative to rates of catalysis yet rapid H/D exchange with solvent

4c

4c-DBpin

(b)

80 °C, up to 24 h
C_6D_6

no reaction

6c

(c)

20 HBpin
C_6D_6
- TBABpin
- C_6D_5Bpin
fast

5c

8c: L = TBE

(d)

20 HBpin
C_6D_6
- ClBpin
fast

5c (97%) + **11c** (3%)

3c

(e)

1 HBpin
C_6D_{12}, rt
fast

L-2
50-60%

+ **4b** + **5b** + PhF

13b

exist as multiple isomers of $(^{p\text{-Me}}POCOP^{iPr})Ir(C_6H_4F)(H)$ in solution.

XRD and NMR Characterization of Complexes 4c and 6b. The metrics in the X-ray structure of **4c** (Figure 3, left) as well as the ^1H and ^{11}B NMR data (Table 4) indicate that the compound is a B−H σ-complex, comparable to (POCOP^{tBu})-Ir(HBpin) reported by Heinekey and co-workers.[50] In that study, Heinekey and co-workers also characterized (POCOP^{tBu})IrH$_3$Bpin. They report ^1H and ^{11}B NMR data similar to what we observe for **5c** (Table 4). An XRD study of **6b** (Figure 3, right) supports its assignment as an Ir(III) diboryl complex, as the B1−B2 distance in **6b** (2.251(8) Å) is ca. 1/3 longer than the B−B bond distance in free B$_2$pin$_2$ (1.7040(9) Å).[51]

Mechanistic Analysis. We were interested in exploring the nature of the C−H (or C−D) activation step that leads to the formation of the C−B bond in the arylboronate product, and in the nature of the step(s) that are involved in hydrogenation of the olefin. The design of our pincer-based catalysts was inspired by the ITHM/Smith−Maleczka catalysts.[2,3,14] By analogy,[14−17] we initially anticipated that C−H bond activation of the arene should be taking place at an unsaturated Ir(III) center carrying an Ir-Bpin functionality. The three compounds fitting this bill that are plausibly accessible in the catalytic mixture are **4**, **6**, and **10**. The ground state of **4** is an Ir(I) σ−B-H complex, but the Ir(III) boryl/hydride form may be thermally accessible. Compound **10** could only be involved if **3** is used as a precatalyst; if **8** is used as a precatalyst, there is no chlorine in the system. From the fact that **3** and **8** both work comparably as precursors, the necessity of **10** as an intermediate in catalysis can be ruled out. Indeed, thermolysis of **10c** in C_6D_6 at 80 °C for 30 min generated no C_6D_5Bpin while heating **10c** for up to

24 h at 80 °C gave a small quantity of Bpin decomposition products (ca. 21.5 ppm) in the ^{11}B NMR spectra, but C_6D_5Bpin was still not observed.

Compounds **4c** and **6b/6c** are stable (excluding H/D exchange observed between **4c** and solvent) in C_6D_6 or toluene-d_8 at ambient temperature for at least 48 h within NMR detection limits. Heating a C_6D_6 solution of **4c** at 80 °C for 30 min revealed only 15% of C_6D_5Bpin in the ^1H NMR spectrum (Scheme 4a). At the same time, we observed a rapid disappearance of the hydride signal for **4c** during the thermolysis experiment, while all other resonances of **4c** remained unchanged in the ^1H NMR spectrum (Scheme 4a), indicating rapid H/D exchange with benzene solvent. Compound **4c** was distinguishable in the corresponding $^{31}P\{^1H\}$ NMR spectrum from its deuterated isotopologue, **4c-DBpin**. As the resonance for **4c** (190.7 ppm, C_6D_6) rapidly disappeared, a resonance for **4c-DBpin** (190.6 ppm, C_6D_6) concurrently increased in intensity. Although C_6D_5Bpin can be produced from the reaction of **4** with C_6D_6, the rate of stoichiometric borylation is too slow to correspond to the relevant C−H activation step in catalytic borylation. Compound **6c** was stable in C_6D_6 at 80 °C for up to 24 h, and no C_6D_5Bpin was observed (Scheme 4b).[52] These experiments show that reactions of benzene with **4**, **6**, or **10** cannot be part of the catalytic cycle producing PhBpin.

With these results in mind, we considered alternative species that may be responsible for the C−H activation step in borylation catalysis. One natural candidate is the three-coordinate, 14-electron species (POCOP)Ir (**14**) (Scheme 5), whose propensity for oxidative addition of various C−H bonds is well documented.[27] This is not an observable species but can be accessed by reductive elimination from five-coordinate

Scheme 5. Net Catalytic Reaction (top), the Proposed Catalytic Cycle Invoking the Three-Coordinate Ir(I) Species 14, and the Auxiliary Hydride/Boryl Redistribution Equilibria
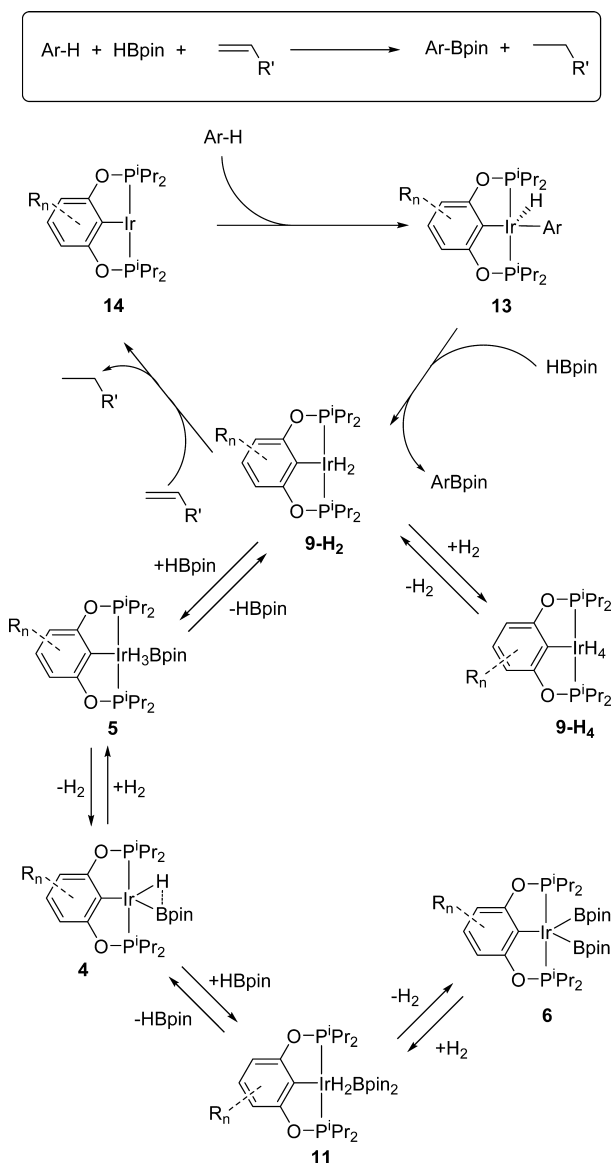
Ir(III) complexes or by dissociation of a neutral ligand from four-coordinate Ir(I) complexes such as **7** or **8**.

When **8c** was treated with HBpin (20 equiv) in C_6D_6 at ambient temperature, we immediately observed only **5c** in the $^{31}P\{^1H\}$ NMR spectrum, while the ^1H and ^{11}B NMR spectra contained resonances for **5c**, 1 equiv of TBABpin, 1 equiv of C_6D_5Bpin, and the remaining HBpin (Scheme 4c). While this reaction does produce C_6D_5Bpin, it cannot be responsible for all of the C_6D_5Bpin produced in catalysis because only a minor fraction of the hydroboration product (e.g., TBABpin) is produced in a catalytic reaction. In other words, access to intermediate **14** in catalysis cannot rely on olefin hydroboration because hydroboration products are not generated in amounts equal to the arene borylation products. Reacting the other precatalyst, **3c**, with HBpin (20 equiv) in C_6D_6 at ambient temperature immediately generated complexes **5c** and **11c** in a 97:3 ratio (Scheme 4d), but C_6D_5Bpin was not observed. Removal of the two Bpin groups from **6c** via diboration of an

olefin is apparently inaccessible, as no diboration products were observed in catalytic experiments reacting B_2pin_2 with C_6D_6, utilizing precatalyst **8c** and 1-hexene (Table 1, entry 12).

On the other hand, when compound **13b** was allowed to react with 1 equiv of HBpin in thawing C_6D_{12}, the ortho-borylated product 2-Bpin-C_6H_4F (**L-2**) was obtained (Scheme 4e).[53] On the basis of ^{19}F and ^{11}B NMR evidence, roughly half of **13b** and half of HBpin was converted to **L-2**. Most of the rest of the ^{19}F NMR intensity belonged to free fluorobenzene and most of the rest of the boron-containing products were **4b** and **5b**. **9b-H_2** was also detected by ^{31}P NMR spectroscopy, along with <20% of unidentified products. An analogous experiment reacting **13b** with 1 equiv of HBpin using C_6H_5F as solvent (in order to ensure the solubility of **13b**) gave comparable results in terms of **L-2** yield (69% of the ^{11}B NMR intensity), as well as the organometallic products observed: **4b** (8% of observed ^{31}P NMR intensity), **5b** (54%), **9b-H_2** (3%), and **13b** (30%). The higher preference for the ortho-borylated product in these reactions compared against the catalytic borylation of fluorobenzene (40% ortho, Table 2) stems from the use of pure **13b**, isolated under conditions differing from that in catalytic experiments.

The rapid formation of the arylboronate in the reaction of **13** with HBpin is consistent with it being part of a catalytic cycle that involves **14** (Scheme 5). Generation of (POCOP)Ir (**14**) permits oxidative addition of Ar−H to Ir to produce **13**, which then reacts with HBpin to generate the Ar-Bpin product. It is important to note that **13** cannot be producing ArBpin by reductively eliminating an Ar−H molecule and adding HBpin to the resultant (POCOP)Ir to give **4**, because **4** does not react with free Ar−H fast enough.[54] The net catalytic reaction (Scheme 5) does not produce free H_2, and so the equilibria between **4−6**, **9-H_2**, **9-H_4**, **11**, H_2, and HBpin (Scheme 5) are important as a way to access **9-H_2** by the redistribution of H and Bpin groups.

In the catalytic experiments reacting HBpin with C_6D_6, compound **5** is the initial resting state of the system at room temperature. As mentioned, reacting **8c** with HBpin (20 equiv) in C_6D_6 gives **5c** at ambient temperature. After heating the solution to 80 °C for 1 h (Table 1, entry 7), we observed compound **5c** and compound **11c** in an 86:14 ratio with trace quantities of compounds **4c**, **6c**, and **9c-H_4** (Figure 4, bottom).[55] A variable temperature $^{31}P\{^1H\}$ NMR study (Figure 4) of the sample found that upon heating the solution from ambient temperature to 80 °C, the mixture of compounds **5** and **11** were found to be in equilibrium with compounds **4c**, **6c**, and **9c-H_4**. This observation is in agreement with our previous experiments that established relationships between **5c**, **4c**, and H_2; **11c**, **6c**, and H_2; **9c-H_4**, **9c-H_2**, and H_2. Notably, the complex (POCOP^{iPr})Ir(Ar)(H) which we would anticipate at ca. 178 ppm in the $^{31}P\{^1H\}$ NMR spectrum is not observed. Compound **9c-H_2** is also not observed, but the presence of **9c-H_4** implies accessibility of **9-H_2** at 80 °C. Sacrificial olefin therefore removes H_2 from **9c-H_2** to provide the resultant 14 e⁻ (^{tBu}POCOP^{iPr})Ir fragment the opportunity to react with arene.

■ CONCLUSION

This work demonstrates that high activity and high turnover number in aromatic C−H borylation is possible with POCOP-type pincer-based Ir catalysts. The use of hydrogen acceptors and their involvement in hydroboration as a minor side reaction places some limits on the applicability of this system. But, it is important to note that the presented system uses the simplest,
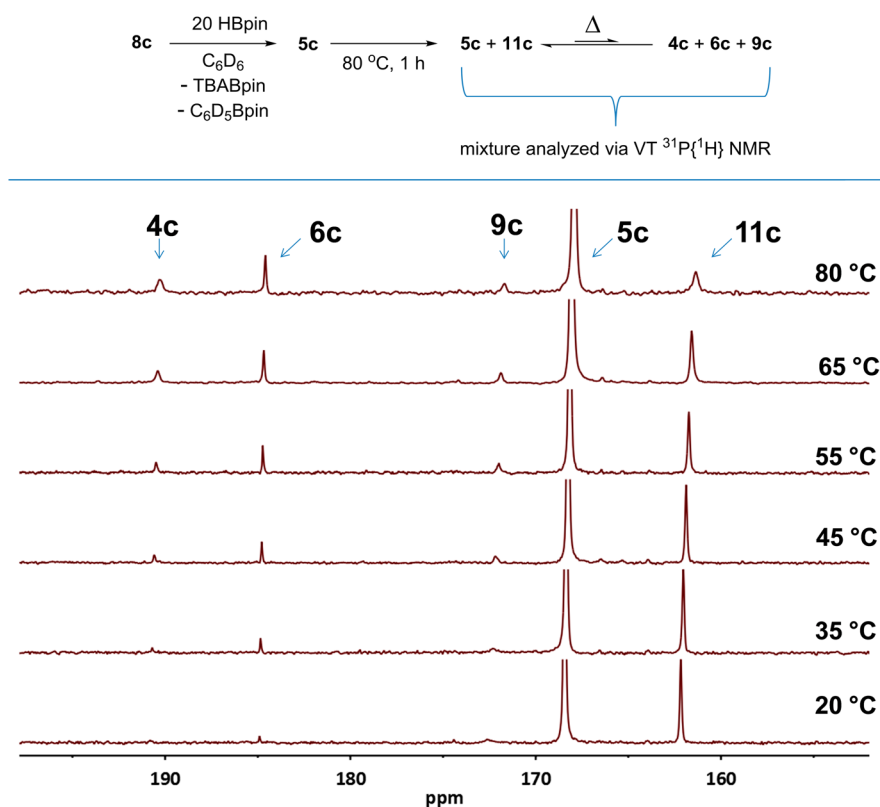
Figure 4. $^{31}P\{^{1}H\}$ VT NMR (C_6D_6, 202 MHz) spectra from 20 °C to 80 °C showing the reaction of HBpin and C_6D_6 with 5 mol % **8c** (Table 1, entry 7). As the temperature increased, resonances for compounds **4c**, **6c**, and **9c** increased in intensity.

least expensive olefins as hydrogen acceptors, whose cost is a small fraction of the borylating agent (HBpin) and is considerably lower than that of many simple arene substrates. (POCOP)Ir catalysts were found to be compatible with arene substrates containing C−O, C−N, and C-Hal bonds and, in general, display similar, sterically governed regioselectivity compared with that of the nonpincer Ir catalysts reported in the literature. An array of relevant Ir complexes were independently synthesized and characterized and their role in catalysis examined. Analysis of plausible mechanistic pathways led to the rather unexpected conclusion that, in contrast to Ir catalysts supported by neutral bidentate ligands, the C−H activation step in the borylation catalysis described here appears to take place not at an Ir(III) boryl center but at an Ir(I) center devoid of boryl ligands. This is connected to the perceived role of olefin. Olefin hydrogenation is part of the net stoichiometry of the catalytic reaction, but the role of olefin hydrogenation is not merely to consume H_2 equivalents released in C−H borylation but rather to provide access to a specific reactive species instrumental to the C−H activation step: the 14-electron (POCOP)Ir. It may be speculatively proffered here that analogous pathways may need to be considered in the analysis of other Ir-based borylation catalysts.

ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b03656.

> Additional experimental details and details of spectroscopic characterization (PDF)
> Crystallographic information in the form of CIF files. The CIF files are also available free of charge from the

Cambridge Crystallographic Data Centre (CCDC 1471756−1471758) (CIF)

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Notes

The authors declare no competing financial interest.

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(52) We have also prepared **6b** via analogous reaction of **8b** with B_2pin_2, and it displayed similar stability in C_6D_6 at room temperature and 80 °C over 24 h.

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(54) It is possible that the reactions of **4** with Ar-H also proceed via (POCOP)Ir, by elimination of HBpin, which would nonetheless be a slow process.

(55) While heating the solution, we observed a color change from colorless to yellow with a transition back to colorless upon cooling.