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Letter

Understanding the Activation of Air-Stable Ir(COD)(Phen)Cl Precatalyst for C−H Borylation of Aromatics and Heteroaromatics

Eric D. Slack* and Thomas J. Colacot*

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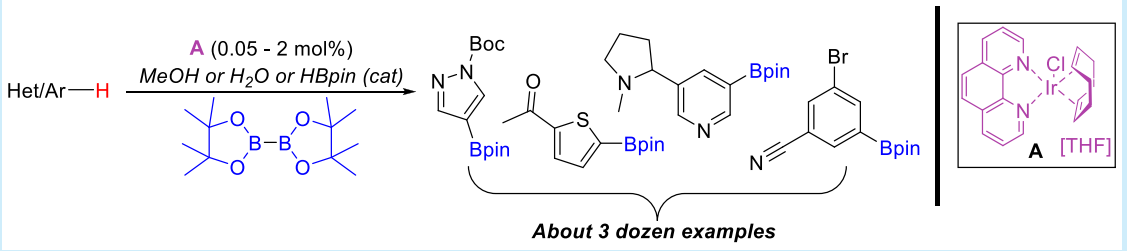
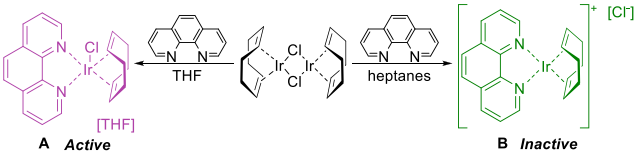


ABSTRACT: A newly developed robust catalyst [Ir(COD)(Phen)Cl] (**A**) was used for the C−H borylation of three dozen aromatics and heteroaromatics with excellent yield and selectivity. Activation of the catalyst was identified by the use of catalytic amounts of water, alcohols, etc., when B_2pin_2 was used in noncoordinating solvents, while for THF catalytic use of HBpin was required. The results were on par with the *in situ* based expensive system $[Ir(OMe)(COD)]_2$/dtbbpy or Me_4Phen.

Introduction. Pioneering reports by Hartwig/Ishiyama[1] and Maleczka/Smith III[2] in the early 2000s propelled the area of iridium-catalyzed borylation to be a viable alternative route to aryl and heteroaryl boronates via C−H borylation for a variety of highly desirable intermediates and products.[3] While the earlier works of Maleczka/Smith III using phosphine based systems[2a−c] have not gained popularity due to lower conversions, both groups eventually identified $[Ir(OMe)(COD)]_2$ as the preferred precatalyst in conjunction with either 4,4′-di-*tert*-butyl-2,2′-bipyridyl (dtbbpy) or 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4Phen) as a ligand for improved activity.[1,3,4] $[Ir(OMe)(COD)]_2$ being employed due to the formation of the innocuous MeOBpin byproduct versus the use of $[Ir(Cl)(COD)]_2$ which generates ClBpin and subsequently reacting with the nitrogen/phosphine based ligands, thereby preventing ligand complexation with Ir.[5−7] Metal-catalyzed borylation technology has allowed for the total synthesis of various natural products such as (±)-thysanone,[8] (+)-complanadine,[9] and drug targets which would be cumbersome to prepare by classical methods.[10,11] Extensive use of the catalyst systems $[Ir(MeO)(COD)]_2$/Me_4Phen or dtbbpy led to the notion that this combination creates the most efficient Ir-based catalyst systems for C−H borylations with the broadest substrate scope.[3,10,11] Although high quality $[Ir(OMe)(COD)]_2$ was originally commercialized by our group on multigram quantities, multikilogram implementation had presented challenges due to shelf-life concerns and batch-to-batch variations, as documented by both academia and industry.[12−14] While our attempts to synthesize a stable [Ir(OMe)(COD)(Phen)] were not successful, we focused our efforts toward identifying methodologies in accessing stable complexes from $[Ir(Cl)(COD)]_2$. From scattered reports on the use of other electronically diverse diamine[15,16] and phosphine ligands[17] for borylations, we saw this as a possible platform to create highly active and selective Ir precatalysts. Recently, the importance of these ligands was exemplified by Baran et al. for the synthesis of the biologically active Verruculogen and Fumitremorgin A where the role of the ligand was crucial for regioselective C−H borylation.[18] Based on reports from other laboratories[19] and from our own lab[20] in developing effective palladium based precatalysts, we hypothesized that a more stable preformed iridium chloride complex like **A**[21] (Scheme 1) with the overlooked ligands, such as phenanthrene (Phen), may improve the catalytic outcome by preventing interactions of the ligand and proposed "off-cycle" formation of ClBpin.[5−7] Recently we were able to briefly

Scheme 1. Divergent Synthesis of Catalytically Active, A, and Inactive, B, from 1,10-Phenanthroline and $[Ir(Cl)(COD)]_2$[21]



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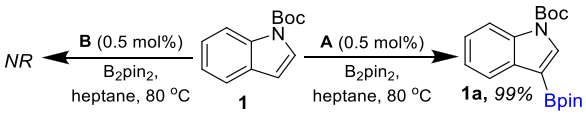
demonstrate the merits of **A** as precatalyst versus the respective *in situ* formed catalyst for the borylation of **1** as a model system (Scheme 2).[21] We found that the formation of the competent

Scheme 2. Activity Comparison of Complexe A and B[21]

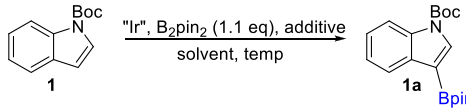


precatalyst was highly dependent on the reaction conditions employed (Scheme 1). We exemplified this by mixing $[Ir(Cl)(COD)]_2$ with Phen using the solvent of choice (hexanes) for borylation forming an inactive green cationic complex **B** as shown in Scheme 1. While the same combination of ligand with $[Ir(Cl)(COD)]_2$ in THF led to a purple colored precatalyst **A**, which after isolation could be activated, leading to high conversion of **1** to **1a** at low, 0.5 mol %, Ir loading (Scheme 2).[21]

The formation of **B** under the *in situ* conditions had contributed to the poor performance of the *in situ* $[Ir(Cl)(COD)]_2$/Phen system and hence was overlooked previously. Although THF was required to make the active precatalyst **A**, our recent deliberate efforts to utilize THF as a solvent for broadening the scope of the reaction using **A** often gave erratic or poor results. This prompted us to systematically investigate the activation of **A** to create a robust precatalyst system. Herein, we report our results of this study, which will hopefully promote the borylation technology widely for both academia and industry.

Results and Discussion. Since THF gave erratic results, we decided to reinvestigate the reaction with heptane as the solvent (Scheme 2). Surprisingly, erratic results were also obtained from borylations in heptanes even when using **A**. We initially suspected that trace moisture in purchased anhydrous solvent might be altering the activity of **A**, which prompted us to conduct the study by mixing a catalytic amount of **A** with model substrate **1** and bis(pinacolato)diboron (B_2pin_2) using rigorously dried heptanes at 80 °C using our conditions.[21] Surprisingly, it gave only trace conversion (ca. 10% by GC) of starting material, **1** to **1a** (Table 1, entry 1). To account for the possibility that **A** might be deactivated by one of the reactants in our reaction mixture, we varied the order of addition of substrate, catalyst, reagent, and solvent. All perturbations[14] led to the same outcome: no reaction! Aware of Hartwig's proposed active Ir borylation catalyst (dtbbpy)Ir(Bpin)$_3$(COE) (**C**)[5] we sought to determine how complex **A** might transform to a similar species under our reaction conditions. However, our efforts to isolate the phenanthroline analogue of **C** following methodology developed for dtbbpy[5] and Me_4Phen[14] was not successful. Previous work from Hartwig's group had shown that similar to the activity of the $[Ir(OMe)(COD)]_2$ complex, $[Ir(OH)(COD)]_2$ was also catalytically competent in the presence of either Me_4Phen or dtbbpy ligand.[1b] This suggests that a similar pathway to Hartwig's proposed mechanism might be occurring in our system.[5] To test whether adventitious water was causing erratic results in our studies, we deliberately added a catalytic amount of H_2O (1:1/Ir:H_2O) to rigorously dried heptanes. Notably, this led to quantitative conversion of our model substrate **1** (Table 1, entry 2) to **1a** consistently. In addition, MeOH, *i*PrOH, and NaOMe also gave good results. From the reported mechanisms and experiments described in 1d from the

Table 1. Activation Studies of A for the Borylation of 1

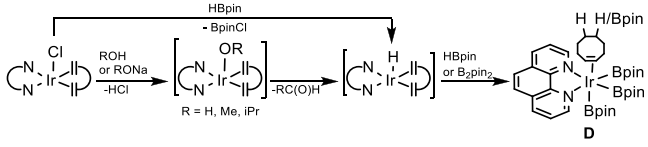


no.	"Ir" (0.5 mol % Ir)	additive (0.5 mol %)	solvent	conv[a]	time (h)
1[c]	A	none	heptane[b]	0–20%	18
2[c]	A	H_2O	heptane[b]	100%	8
3[c]	$[Ir(OMe)(COD)]_2$	none	heptane[b]	90%	7
4[d]	A	*i*PrOH	heptane[b]	100%	2
5[d]	A	NaO*t*Bu	heptane[b]	5%	18
6[d]	A	HO*t*Bu	heptane[b]	15%	18
7[d]	A	*i*PrOH	THF[e]	0%	1
8[d]	A	H_2O	THF[e]	72%	4
9[d]	A	NaOMe	THF[e]	69%	4
10[d]	A	HBpin	THF[e]	99%	4

[a]Determined by GC analysis. [b]0.33 M. [c]Reaction conditions: "Ir" (0.5 mol %), additive (0.5 mol %), B_2pin_2 (1.1 equiv), solvent, 80 °C, **1** (1 equiv), 80 °C. [d]Reaction conditions: (1) **A** (0.5 mol %), B_2pin_2 (1.1 equiv), additive (0.5 mol %), solvent, 80 °C, 1 h. (2) **1** (1 equiv), 80 °C. [e]1.4 M.

Supporting Information, we proposed a similar intermediate **D** (Scheme 3), analogous to the reported intermediate **C**.[5] Our

Scheme 3. Plausible Activation of A with Additives



efforts to isolate **D**, or $[Ir(OH)(Phen)(COD)]$, or the corresponding −OMe complex were not successful; however, aldehydes were observed when higher boiling alcohols (i.e. 1-octanol and 1-hexanol). Although we propose the formation of $[Ir(OH)Phen(COD)]$ in analogy with Hartwig's observation, the corresponding pathway from this catalyst to **D** has not yet been studied. Hartwig had shown the effectiveness of the methoxide addition to $[Ir(Cl)(COD)]_2$/dtbbpy; however, it produced decreased yields.[1b] In addition, previous methods using $[Ir(OMe)(COD)]_2$/Me_4Phen or dtbbpy showed improved activity while premixing the ligand with HBpin/B_2pin_2 prior to the addition of substrate, with the observation of a dark red solution at rt.[14] When we attempted the same process using **A** mixed with B_2pin_2 followed by the addition of water or isopropanol at room temperature (25–27 °C), a heterogeneous mixture was observed, which upon heating at 80 °C for 1 h changed to a homogeneous red solution. Addition of the substrate to the above solution with continued heating for 2 h gave complete conversion (Table 1, entry 4), versus 8 h when **1** was added prior to heating (Table 1, entry 2). Similar results were obtained for NaOMe, MeOH, *i*PrOH, and H_2O respectively, while negative results were obtained for both NaO*t*Bu and *t*BuOH (Table 1, entries 5 and 6). Although catalyst **A** was synthesized using THF as a solvent, the conditions employed above for heptanes gave complications due to borylation of THF.[22] While *i*PrOH could be used for full conversion of **1** in heptanes, its use in THF was unsuccessful, giving only trace conversion (Table 1, entry 7). Interestingly, 1 equiv of HBpin w.r.t. **A** gave complete conversion (Table 1,

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entry 10) versus the use of water or sodium methoxide (Table 1, entries 8 and 9).

Ozerov et al. performed a thorough analysis of turnover numbers (TON) for several substrates and catalyst along with their recently developed catalyst [(5-methyl-1,3-phenylene)bis(oxy))bis(diisopropylphosphane)], (Ir(POCOP)).[23] We selected **4** as a model substrate considering its regioselectivity in lieu of benzene. Under our optimized procedure, we obtained a TON of 1940 within 24 h for **4a** with a yield of 97%, in comparison their TONs of 1720 (Scheme 4 and Table 2, **4a**).[5,24]

Scheme 4. Comparison of Ir(POCOP) Catalyst and Catalyst A TON for the Borylation of 1,2-Dichlorobenzene[24]

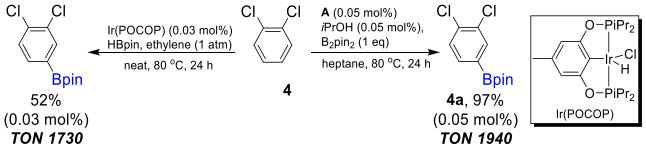
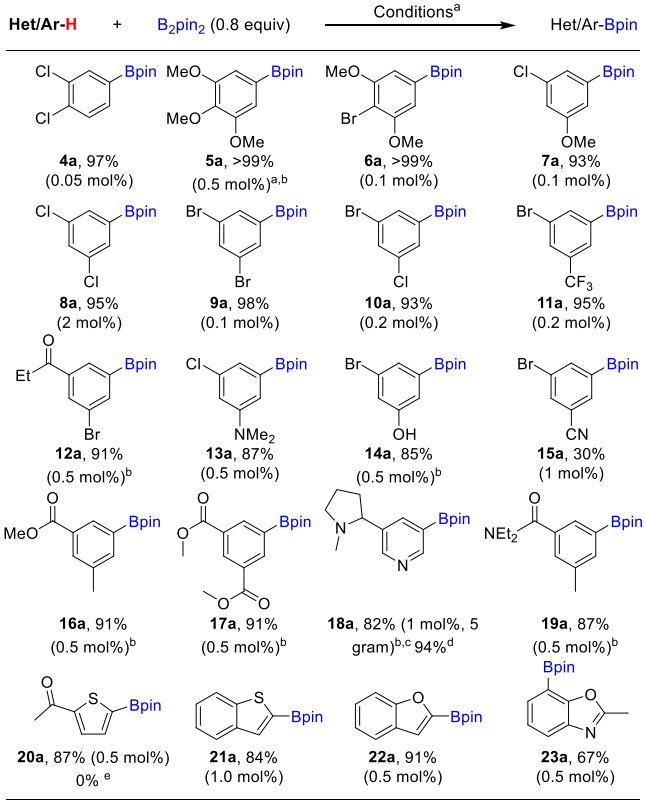


Table 2. Borylation of Aromatic Substrates



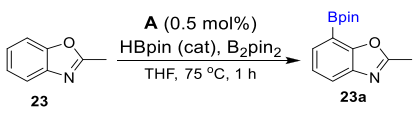
[a]**A**, B_2pin_2, *i*PrOH,substrate, and heptanes. 80 °C. [b](1) **A**, B_2pin_2,and *i*PrOH were loaded in heptanes and heated at 80 °C for 1 h. (2) Substrate. [c]Run at 5 and 10 g scale. [d]Run at 1 mmol. [e]Substrate added before induction/activation.

Using the same methodology we saw similar trends for other substrates, giving complete conversion (high yields) with low Ir loadings (Table 2, entries **4a**−**11a**), except for substrate **8**, where the loading had to be increased to 2 mol % (Table 2, **8a**).

Mildly coordinating carbonyl groups and tertiary amines also showed good reactivity at 0.5 mol % loading of Ir (Table 2, entries **12a**, **16a**, and **17a**). Substrates with stronger coordinating groups such as nitriles and pyridines, in heptanes, were more challenging and hence required higher catalyst loadings (Table 2, **15a**, **18a**). However, this was in very good agreement with previously disclosed methods using both dtbbpy and Me_4Phen in conjunction with $[Ir(OMe)(COD)]_2$.[3,11] The borylation of (−)-nicotine, **18**, was of particular interest due to its pharmaceutical applications. We were able to reduce the Ir loading by half using **A** versus the reported 1 mol % $[Ir(Cl)(COD)]_2$/Me_4Phen *in situ* system for nearly the same yield up to a 10 g scale.[12] The order of addition and activation of the catalyst was important with respect to substrate **20**. Addition of substrate **20** prior to the activation of the catalyst gave no yield of **20a**, presumably due to coordination of **20** to Ir. With our protocol **20a** was isolated in 87% yield even at 0.5 mol % catalyst loading (Table 2).

While THF is considered to be an inferior solvent, likely due to byproduct formation,[22] its use was required for substrates insoluble in heptanes and MTBE.[24] Efforts to apply the same methodology used with heptanes gave inferior results in accordance with the literature results.[22,25] Through optimization using substrate **23**, we found that the ideal concentration of substrate was ca. 1.4 M, which gave similar conversions as those obtained in heptanes (Table 3, **23a**). With optimized conditions

Table 3. Optimization of Conditions Using THF as a Solvent[a]

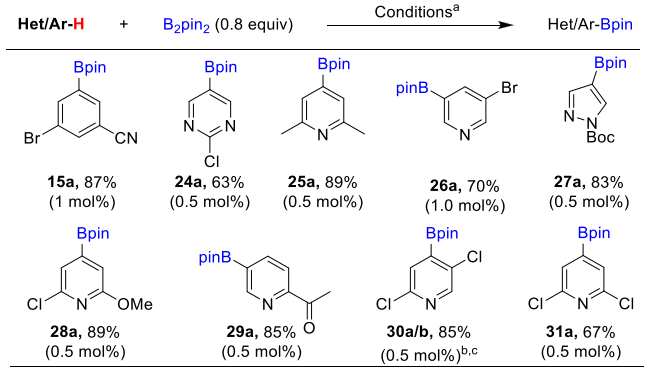


concentration (M)	conv. to **23**
0.3	0
0.5	10
1.0	53
1.4	73

[a]Conditions: (1) **A** (0.5 mol %), "HBpin$^-$" (0.5 mol %), B_2pin_2 (1.1 equiv), solvent, 80 °C, 1 h. (2) **1** (1 equiv), 80 °C.

in THF for **23**, we explored the scope for an array of substrates, including pyridines and diazole-based substrates. Pyridines substituted ortho to the heteroatom gave good conversion at 0.5 mol % Ir loading (Table 4, **25a**, **28a**, **29a**, **30a**, and **31a**).

Table 4. Borylation of Heteroaromatic Substrates



[a]Reaction conditions: (1) **A**, B_2pin_2, and HBpin were loaded, diluted with THF, and heated at 75 °C for 1 h. (2) Substrate added. [b]NMR yield of all isomers. [c]Mixture of of isomers (1:4 ratio) at 80 °C.

Counter to expectations, optimized conditions in THF improved the borylation yield of **15a** to 87% from 30% in heptanes (Table 2 and 4, **15a**), demonstrating the importance of the conditions. Curiously when this methodology was applied to produce **30a** and **30b**, we obtained a 1:4.5 isomer ratio with 84% conversion by ^{1}HNMR, a result similar to what was previously disclosed with the $[Ir(OMe)(COD)]_2$/dtbbpy system at rt.[1b]

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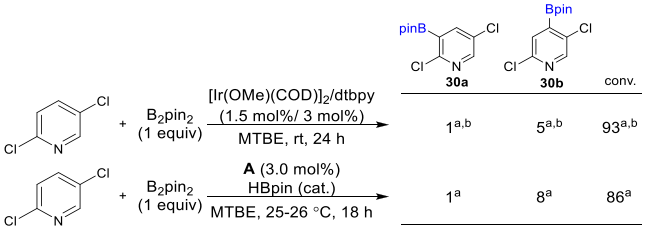
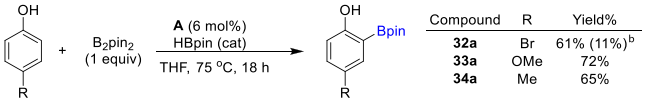
Transition to MTBE, often used to avoid difficulties with THF, at 80 °C as well gave the same isomer ratio. However, activating **A** (3 mol %), followed by cooling to 25−26 °C, followed by the addition of 2,5-dichloropyridine (**30**) while stirring for 18 h gave an improved 1:8 isomer ratio of borylated products with 86% conversion (Table 5). We applied this methodology (Table 6)

Table 5. Selectivity Improvement of A for the Borylation of 2,5-Dichloropyridine[24a]



[a]Reaction conditions: Ir source, B_2pin_2, solvent, 1 h at temperature. Then substrate was added. Determined by ^1H NMR. [b]From ref 27.

Table 6. Ortho Borylation Using Traceless Directing Phenols Applying Catalyst A[a]



Compound	R	Yield%
32a	Br	61% (11%)[b]
33a	OMe	72%
34a	Me	65%

[a]Reaction conditions: (1) **A**, HBpin, B_2pin_2, THF 75 °C, 1 h. (2) ROBpin, 75 °C 16 h. [b]Substrate added before induction/activation.

to more challenging substrates that offered access to unique regioselectivity through traceless directing groups, disclosed by Smith and Maleczka for the ortho-borylation of protected phenols.[26] A very recent work showing the applicability of this strategy using nickel catalysis has also been disclosed.[27] We found parity in catalyst loading and yield from their original work using $[Ir(OMe)(COD)]_2$/dtbbpy, with our Phen ligand based system offering a slight increase of yield for the *para*-methoxy phenol (Table 6, **34a**), suggesting the true merits of the Phen system.

Summary. This study shows that the precise formation and activation of iridium precatalysts of the type **A** are important for the efficient borylation of aromatics and heteroaromatics for practical applications. The performance of **A** based on our studies in the context of sourcing high purity $[Ir(OMe)(COD)]_2$ in bulk quantities for *in situ* borylation with relatively expensive Me_4Phen or dtbbpy shows that the current technology can be a breakthrough in overcoming the process challenges. Therefore, we hope that this study will prompt others to look into the activity of the more stable iridium chloride precatalysts with newer ligands as a platform to avoid many of the pitfalls of the *in situ* formed catalyst systems, in analogy with the Pd precatalysts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c04210.

Experimental details and spectral data of all compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Eric D. Slack − *Johnson Matthey, West Deptford, New Jersey 08066, United States*; Email: eric.slack@jmusa.com

Thomas J. Colacot − *Johnson Matthey, West Deptford, New Jersey 08066, United States*; orcid.org/0000-0001-9976-1376; Email: thomas.colacot@milliporesigma.com, tcolacot@yahoo.com

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c04210

Notes

The authors declare the following competing financial interest(s): Johnson Matthey has a financial interest in Compound A.

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■ REFERENCES

(1) (a) Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 390. (b) Ishiyama, T.; Takagi, J.; Hartwig, J. F.; Miyaura, N. *Angew. Chem., Int. Ed.* **2002**, *41*, 3056. (c) Ishiyama, T.; Nobuta, Y.; Hartwig, J. F.; Miyaura, N. *Chem. Commun.* **2003**, *23*, 2924.

(2) (a) Cho, J.; Tse, M. K.; Holmes, D.; Maleczka, R. E., Jr.; Smith, M. R., III *Science* **2002**, *295*, 305. (b) Chotana, G. A.; Vanchura, B. A.; Tse, M. K.; Staples, R. J.; Maleczka, R. E., Jr.; Smith, M. R., III *Chem. Commun.* **2009**, 5731. (c) Maleczka, R. E.; Shi, F.; Holmes, D.; Smith, M. R. *J. Am. Chem. Soc.* **2003**, *125*, 7792.

(3) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890.

(4) Oeschger, R. J.; Larsen, M. A.; Bismuto, A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2019**, *141*, 16479.

(5) Boller, T. M.; Murphy, J. M.; Hapke, M.; Ishiyama, T.; Miyaura, N.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 14263.

(6) Tamura, H.; Yamazaki, H.; Sato, H.; Sakaki, S. *J. Am. Chem. Soc.* **2003**, *125*, 16114.

(7) Coapes, R. B.; Souza, F. E. S.; Fox, M. A.; Batsanov, A. S.; Goeta, A. E.; Yufit, D. S.; Leech, M. A.; Howard, J. A. K.; Scott, A. J.; Clegg, W.; Marder, T. B. *J. Chem. Soc., Dalt. Trans.* **2001**, 1201.

(8) Schünemann, K.; Furkert, D. P.; Connelly, S.; Fraser, J. D.; Sperry, J.; Brimble, M. A. *Synlett* **2014**, *25*, 556.

(9) Fischer, D. F.; Sarpong, R. *J. Am. Chem. Soc.* **2010**, *132*, 5926.

(10) Hiroto, S.; Miyake, Y.; Shinokubo, H. *Chem. Rev.* **2017**, *117*, 2910.

(11) Yuan, C.; Liu, B. *Org. Chem. Front.* **2018**, *5*, 106.

(12) Sieser, J. E.; Maloney, M. T.; Chisowa, E.; Brenek, S. J.; Monfette, S.; Salisbury, J. J.; Do, N. M.; Singer, R. A. *Org. Process Res. Dev.* **2018**, *22*, 527.

(13) Arrington, K.; Barcan, G. A.; Calandra, N. A.; Erickson, G. A.; Li, L.; Liu, L.; Nilson, M. G.; Strambeanu, I. I.; VanGelder, K. F.; Woodard, J. L.; Xie, S.; Allen, C. L.; Kowalski, J. A.; Leitch, D. C. *J. Org. Chem.* **2019**, *84*, 4680.

(14) Preshlock, S. M.; Ghaffari, B.; Maligres, P. E.; Krska, S. W.; Maleczka, R. E., Jr.; Smith, M. R., III *J. Am. Chem. Soc.* **2013**, *135*, 7572.

(15) Larsen, M. A. Frontiers in Iridium-Catalyzed C-H Borylation: Attaining Novel Reactivity and Selectivity. Ph.D. Dissertation, University of California, Berkley, CA, 2016.

(16) Miller, S. L.; Chotana, G. A.; Fritz, J. A.; Chattopadhyay, B.; Maleczka, R. E., Jr.; Smith, M. R., III *Org. Lett.* **2019**, *21*, 6388.
(17) Ros, A.; Fernández, R.; Lassaletta, J. M. *Chem. Soc. Rev.* **2014**, *43*, 3229.
(18) Feng, Y.; Holte, D.; Zoller, J.; Umemiya, S.; Simke, L. R.; Baran, P. R. *J. Am. Chem. Soc.* **2015**, *137*, 10160.
(19) Ingoglia, B. T.; Wagen, C. C.; Buchwald, S. L. *Tetrahedron* **2019**, *75*, 4199 (see references therein).
(20) Gildner, P. G.; Colacot, T. J. *Organometallics* **2015**, *34* (23), 5497 (see references therein).
(21) Seechurn, C. C. C. J.; Sivakumar, V.; Satoskar, D.; Colacot, T. J. *Organometallics* **2014**, *33*, 3514.
(22) Zhong, R.; Sakaki, S. *J. Am. Chem. Soc.* **2019**, *141*, 9854.
(23) Press, L. P.; Kosanovich, A. J.; McCulloch, B. J.; Ozerov, O. V. *J. Am. Chem. Soc.* **2016**, *138*, 9487.
(24) (a) Sadler, S. A.; Tajuddin, H.; Mkhalid, I. A. I.; Batsanov, A. S.; Albesa-Jove, D.; Cheung, M. S.; Maxwell, A. C.; Shukla, L.; Roberts, B.; Blakemore, D. C.; Lin, Z.; Marder, T. B.; Steel, P. G. *Org. Biomol. Chem.* **2014**, *12*, 7318. (b) Harrisson, P.; Morris, J.; Steel, P. G.; Marder, T. B. *Synlett* **2009**, *2009*, 147. (c) Tajuddin, H.; Harrisson, P.; Bitterlich, B.; Collings, J. C.; Sim, N.; Batsanov, A. S.; Cheung, M. S.; Kawamorita, S.; Maxwell, A. C.; Shukla, L.; Morris, J.; Lin, Z.; Marder, T. B.; Steel, P. G. *Chem. Sci.* **2012**, *3*, 3505.
(25) Larsen, M. A.; Oeschger, R. J.; Hartwig, J. F. *ACS Catal.* **2020**, *10*, 3415.
(26) Chattopadhyay, B.; Dannatt, J. E.; Andujar-De Sanctis, I. L.; Gore, K. A.; Maleczka, R. E., Jr.; Singleton, D. A.; Smith, M. R., III *J. Am. Chem. Soc.* **2017**, *139*, 7864.
(27) Tian, Y. M.; Guo, X. N.; Wu, Z.; Friedrich, A.; Westcott, S. A.; Braunschweig, H.; Radius, U.; Marder, T. B. *J. Am. Chem. Soc.* **2020**, *142*, 13136.

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