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Letter

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Iron-Catalyzed *E*-Selective Dehydrogenative Borylation of Vinylarenes with Pinacolborane

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KEYWORDS: iron, borylation, dehydrogenative, vinylarenes, homogenous catalysis

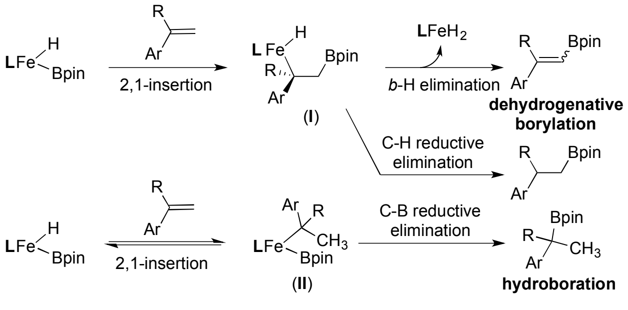
ABSTRACT: We report the dehydrogenative borylation of vinylarenes with pinacolborane (HBpin) catalyzed by an iron(0) complex “$(PMe_3)_4Fe$”. A variety of mono- and di-substituted vinylarenes underwent this iron-catalyzed transformation, affording *E*-vinyl boronate esters (VBEs) selectively in high yields. In addition, we coupled this iron-catalyzed dehydrogenative borylation with further transformations of the resulting vinyl boronate esters and developed various one-pot procedures for the functionalization of the vinylic C-H bonds in vinylarenes. Mechanistic studies reveal that this Fe-catalyzed reaction proceeds through *syn*-insertion of vinylarenes into a Fe-boryl species followed by β-hydrogen elimination from a *syn* coplanar conformation of the borylalkyl iron intermediate.

Vinyl boronate esters (VBEs) are useful building blocks in organic synthesis. They have been employed as synthetic precursors to alkenyl halides and aldehydes and undergo a range of metal-catalyzed cross-coupling reactions.[1] More interestingly, β-aryl VBEs are important intermediates to prepare stilbenoid compounds, which are ubiquitous in biologically active molecules[2] and material sciences.[3] In general, VBEs can be prepared by hydroboration of alkynes,[4] lithiation of alkenyl halides followed by reactions with trialkoxyborates,[5] metal-catalyzed borylation of alkenyl halides or pseudohalides,[6] cross-metathesis of alkenes with pinacolvinylboronates,[7] or a boryl-Heck reaction of alkenes with chloroborane.[8] However, these methods require the pre-activation of the vinyl group or are not suitable to prepare β,β-di-substituted VBEs.

Catalytic dehydrogenative borylation of alkenes is an attractive alternative to prepare vinyl boronate esters. However, this dehydrogenative borylation reaction is not well studied as it has been viewed as a “deleterious” side reaction for metal-catalyzed hydroboration of alkenes.[9] There are a few reports on this catalytic dehydrogenative borylation process, but the catalysts for this reaction are limited to noble metals, such as Rh,[10] Pd,[11] Ir,[12] and Pt[13]. In addition, the scope of alkenes that undergo this catalytic reaction is mainly tested with mono-substituted alkenes and cyclic alkenes.[10-12] The dehydrogenative borylation of 1,1-disubstituted alkenes (with three examples) has been achieved with a palladium catalyst by reactions with a diboron(4) compound B_2pin_2.[11b] The dehydrogenative borylation of 1,1-disubstituted alkenes suffers from either low reactivity or low selectivity.[10c, f] Effective and selective dehydrogenative borylation of disubstituted terminal alkenes is particularly important because products from this process, β,β-di-substituted vinyl boronate esters, are not accessible from catalytic hydroboration of alkynes.[14]

Recently, phosphine/iron complexes have been reported to catalyze the C-H borylation of arenes.[15] The low-valent iron(0) species, generated in situ by irradiation of well-defined iron complexes $(dmpe)FeR_2$ (R = Me or H), adds to pinacolborane (HBpin) to form a hydrido iron boryl species.[15] We envision that vinylarenes can undergo 2,1-migratory insertion into the Fe-B or Fe-H bond (scheme 1) to give the iron species **I** or **II**, respectively. The subsequent C-H or C-B reductive elimination from intermediates **I** or **II** can take place to afford alkyl boronate esters (hydroboration selectivity). Indeed, iron complexes have recently been emerging as highly active catalysts for hydroboration of alkenes with HBpin.[16] Alternatively, species **I** can undergo β-hydrogen elimination to produce vinyl boronate esters (dehydrogenative borylation selectivity). This dehydrogenative process was identified as a minor pathway and gave vinyl boronate esters as byproducts for the iron-catalyzed alkene hydroboration.[16d] In view of broad synthetic applications of vinyl boronate esters (VBEs), we are interested in developing an effective and selective iron-catalyzed dehydrogenative borylation of alkenes to prepare VBEs.

Scheme 1. Expected pathways for Iron-Catalyzed Reactions of Alkenes with Pinacolborane

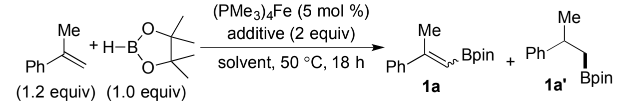


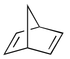
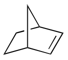
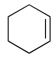
To develop an iron-catalyzed dehydrogenative borylation reaction, we need to identify an iron catalyst that favors β-hydrogen elimination. As an increase in electron-donating ability and a decrease in steric hindrance of ancillary ligands increase the rate of β-hydrogen elimination,[17] we targeted iron complexes with a small and electron-rich trimethylphosphine

(PMe$_3$) as catalysts for the dehydrogenative borylation reaction. We chose an iron complex (PMe$_3$)$_4$Fe as a single-component catalyst precursor, as this iron compound can be readily accessible through the reduction of FeCl$_2$ with magnesium in the presence of PMe$_3$ in THF.[18]

We initiated this study by evaluating the conditions for the (PMe$_3$)$_4$Fe-catalyzed reaction of α-methylstyrene with HBpin. The selected examples of these experiments are summarized in Table 1. These reactions were conducted with HBpin as the limiting reagent and a variety of alkenes as the hydrogen acceptor in the presence of 5 mol % of (PMe$_3$)$_4$Fe at 50 °C. The reaction conducted in the absence of hydrogen acceptors afforded only a trace amount of desired product (entry 1), and this result indicated that α-methylstyrene is not an effective hydrogen acceptor for this reaction. Similar results were obtained for the reaction with norbornadiene as a hydrogen acceptor (entry 2). Improved results were obtained for the reactions with other monoalkenes as hydrogen acceptors (entries 3–6) and the reaction conducted in the presence of norbornene selectively provided the product derived from the dehydrogenative borylation in high yield (entry 3). The stereochemistry for the VBE product was confirmed to be *trans* by the 2D NMR (NOESY) analysis. We also tested the reaction with α-methylstyrene as the limiting reagent in the presence of norbornene (entry 7). This reaction gave the desired product in 78% GC yield together with a significant amount (20%) of alkyl boronate ester derived from hydroboration of norbornene.

Table 1. Evaluation of the Reaction Conditions^a



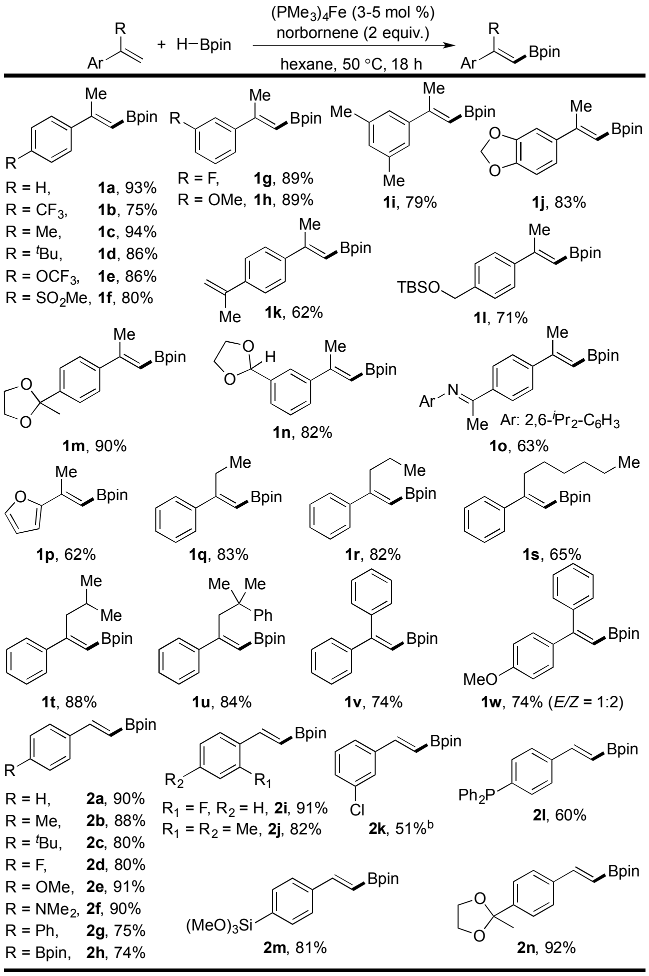
entry	additive	solvent	yield (*E*/*Z*)(**1a**)^b	yield (**1a'**)^b
1	----	hexane	<5% (99:1)	0
2		hexane	<5% (99:1)	0
3	 (nbe)	hexane	95% (98:2)	0
4		hexane	58% (99:1)	0
5	^{t}Bu 	hexane	40% (99:1)	0
6	^{n}Bu 	hexane	73% (98:2)	0
7^c	nbe	hexane	78% (98:2)	0
8	nbe	toluene	58% (99:1)	0
9	nbe	THF	33% (99:1)	0
10	nbe	1,4-dioxane	35% (99:1)	0

^{a}Conditions: α-methylstyrene (0.600 mmol), HBpin (0.500 mmol), iron precursor (25.0 μmol), solvent (1 mL), 50 °C, 18 h. ^{b}Determined by GC analysis with dodecane as the internal standard. ^{c}α-methylstyrene (0.500 mmol), HBpin (0.600 mmol).

We tested various solvents for this dehydrogenative borylation and found that the solvent effect on this reaction was pronounced (entries 3 and 8–10). This observed solvent effect might result from the coordinating ability of these solvents (1,4-dioxane ~ THF > toluene > hexane). In addition, we also tested the combination of (PMe$_3$)$_4$Fe and chelating ligands for this reaction and found that these reactions either did not proceed or afforded the desired products in lower yields (see the SI for details).

The scope of vinylarenes that undergo this transformation is summarized in Table 2. In general, a wide range of di- and mono-substituted vinylarenes containing electronically varied aryl groups reacted smoothly at 50 °C, yielding the corresponding *E*-vinyl boronate esters (**1a**–**1v** and **2a**–**2m**) in modest to excellent isolated yields (51–94%). The GC-MS analysis on the crude mixtures of these reactions indicated the formation of trace amounts (< 2%) of *Z*-vinyl boronate esters. The low isolated yields for compounds **1o**, **1p**, and **1s** resulted from low conversions of the corresponding vinylarenes.

Table 2. The Scope of Vinylarenes^a



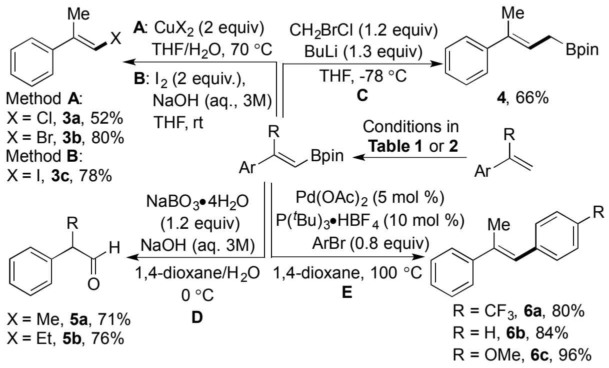
^{a}Conditions: α-substituted vinylarene (0.600 mmol), HBpin (0.500 mmol), (PMe$_3$)$_4$Fe (25.0 μmol for **1a**–**1v**; 15μmol for **2a**–**2m**), norbornene (1.00 mmol), hexane (1 mL), 50 °C, 18 h, and isolated yields after column chromatography. ^{b}10 mol % (PMe$_3$)$_4$Fe.

The dehydrogenative borylation of vinylarenes tolerates a range of functionalities, including ether (**1h**, **1j**, and **2e**), alkene (**1k**), trifluoromethylether (**1e**), sulfone (**1f**), siloxy (**1l** and **2m**), imine (**1o**), tertiary amine (**2f**), tertiary phosphine (**2l**), pinacolboryl (**2h**), and chloro (**2k**) moieties. Carbonyl, cyano, and free hydroxyl and amino groups are not compatible with the reaction conditions. However, vinylarenes containing a ketone (**1m** and **2n**) or aldehyde (**1n**) protected as acetal and an alcohol (**1l**) protected as silyl ether reacted to afford the corresponding VBE product in high yields. In addition, α-methyl vinylfuran (**1p**) reacted to give the desired product in modest yield (62%), but vinylpyridines did not undergo this transformation under the identified conditions. Furthermore, dienes and trisubstituted alkenes do not undergo this Fe-catalyzed dehydrogenative borylation under the identified conditions.

We also tested vinylarenes containing an aliphatic or aromatic substituent at the α-position for this Fe-catalyzed process. Increasing the steric bulkiness of these substituents from Et (**1q**), *n*-Pr (**1r**), *n*-Hex (**1s**), *i*-Bu (**1t**), to $CH_2C(Me_2)Ph$ (**1u**) has little influence on this reaction and the corresponding *E*-VBE products are isolated in similarly high yields. 1,1-Diarylethenes (**1v** and **1w**) also underwent this reaction to afford the desired VBEs in good yields. However, the reaction of 1,1-diarylethene (**1w**) containing two different aryl groups gave a mixture of *E*- and *Z*-product, with the preference for *Z*-isomer.

Subsequently, we developed one-pot procedures for the functionalization of vinylic C-H bonds in vinylarenes and these results are listed in Scheme 2. This Fe-catalyzed dehydrogenative borylation followed by halogenation with CuX_2 (X = Cl and Br, **A** in Scheme 2) or iodide (**B** in Scheme 2) provides a one-pot method to synthesize *E*-vinyl halides (**3a**–**3c**) from vinylarenes. Homologation of VBE generated in situ from the vinylic C-H borylation of α-methylstyrene with $LiCH_2Cl$ afforded allylic boronate ester (**4**) in 66% yield (**C** in Scheme 2). Oxidative hydrolysis of VBEs with $NaBO_3$ (**D** in Scheme 2) provided a sequential one-pot procedure to prepare α-aryl aldehydes (**5a**–**5b**), which are not accessible by the Pd-catalyzed direct α-arylation of aliphatic aldehydes.[19] In addition, the VBEs generated in situ underwent the Pd-catalyzed Suzuki coupling with aryl bromides to afford stilbenes (**6a**–**6c**) in high yields (**E** in Scheme 2).

Scheme 2. One-pot Procedures for the Functionalization of Vinylic C-H bond

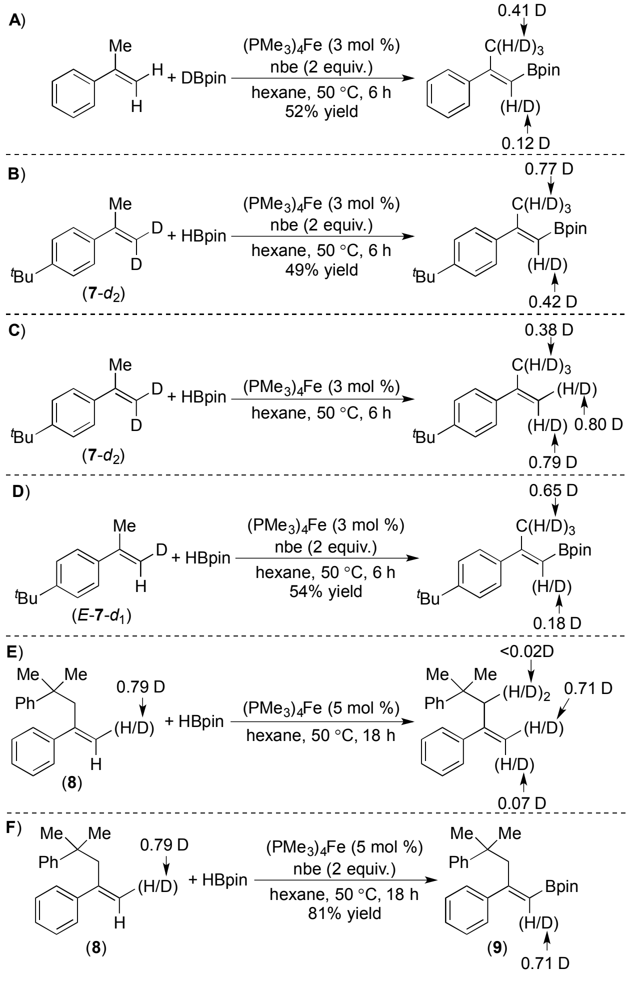


To study the activation of HBpin with a low-valent Fe(0) complex, we conducted a stoichiometric reaction of $(PMe_3)_4Fe$ and HBpin. Well-resolved NMR spectra were not obtained for this reaction. However, HR-MS (ESI) analysis of the reaction mixture indicated the formation of $(PMe_3)_4Fe(H)(Bpin)$, as both cationic fragments $[(PMe_3)_4Fe(H)]^+$ (*m/z* calc'd: 361.1195; found: 361.1192) and $[(PMe_3)_4Fe(Bpin)]^+$ (*m/z* calc'd: 487.2047; found: 487.2050) were observed. Such oxidative addition between H-B and Fe(0) species was previously reported for the reaction of HBpin with "$(dmpe)_2Fe(0)$".[10]

To understand the mechanism of this Fe-catalyzed dehydrogenative borylation reaction, we conducted a series of deuterium labelling experiments (Scheme 3). The reaction of α-methylstyrene with DBpin (**A** in Scheme 3) and the reaction of vinylarene **7**-d_2 with HBpin (**B** in Scheme 3) afforded the corresponding products with deuterium atoms located on both the α-methyl and the terminal vinylic carbons. The incorporation of deuterium into norbornane was detected by the GC-MS analysis (see the SI for the isotope analysis of norbornane). These results support the formation of a Fe-H intermediate as the H/D exchange occurs through the reversible olefin insertion into the Fe-H/D bond. The reaction of **7**-d_2 with HBpin in the absence of norbornene (**C** in Scheme 3) resulted in low conversion (<10%) of vinylarene **7**-d_2. Analysis of the unconverted vinylarene by ^2H NMR indicated the deuterium scrambling between the vinylic C-D and the α-methyl C-H.

To reveal the origin of the *E*-selectivity for this Fe-catalyzed transformation, we tested the reaction of *E*-**7**-d_1 with HBpin to check whether the vinylic C-H or C-D is substituted by the Bpin group (**D** in Scheme 3). This reaction afforded the product with deuterium on the α-methyl group (major) and the terminal vinylic carbon (minor). Based on the results from reactions **C** and **D**, we can not conclude whether the vinyl C-<u>H</u> or C-<u>D</u> is substituted by the Bpin group.

Scheme 3. Deuterium-Labeling Experiments

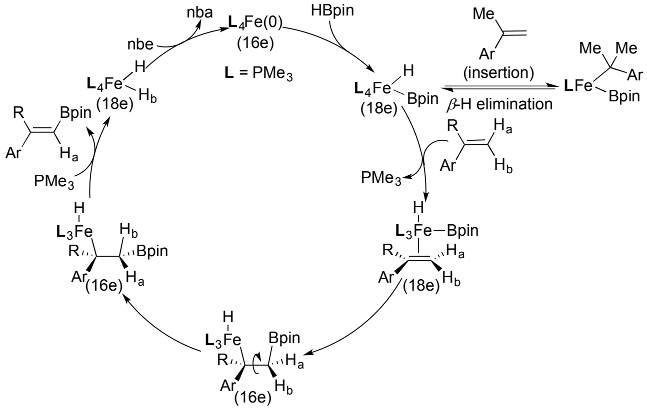


We anticipated that a bulky alkyl group on the *α*-position could minimize the above-mentioned deuterium scrambling observed for reaction **C**. To test this, *trans*-2,4-diphenyl-4-methyl-1-[1D]-pentene (**8**) was subjected to this deuterium scrambling reaction (**E** in Scheme 3) for this reaction. As expected, only trace amounts of deuterium are detected on the allylic methylene group and the terminal *Z*-vinylic C-H position. Subsequently, we tested this vinylarene for the Fe-catalyzed dehydrogenative borylation reaction (**F** in Scheme 3). This reaction gave the *trans*-VBE (**9**) containing deuterium at the vinylic position as the major product. These results indicated that the vinylic C-H̲ in vinylarene **8** was substituted by the Bpin group.

Lastly, the *Z*-isomer of **1a** was subjected to the standard reaction conditions for the dehydrogenative borylation of *p*,α-dimethylstyrene, and <10% of *Z*-**1a** was isomerized to *E*-**1a** in 18 h (see the SI for details). This *Z*/*E*-isomerization further supports the formation of the Fe-H intermediate. The low conversion of *Z*-**1a** to *E*-**1a** was due to the slow migratory insertion of tri-substituted alkene **1a** into the Fe-H bond. Based on this result, it is unlikely that the *E*-selectivity for this Fe-catalyzed dehydrogenative borylation is originated from the isomerization of *Z*-isomer.

Based on the results of the stoichiometric reaction and the series of deuterium labelling experiments, we propose a catalytic cycle depicted in Scheme **4** for this Fe-catalyzed borylation reaction. The key step for this reaction is the *syn*-insertion of vinylarene into the Fe-B bond followed by β-hydrogen elimination from a *syn* coplanar conformation of the iron borylalkyl intermediate. The preference for β-hydrogen elimination from the borylmethylene group can be explained by the formation of a more stable boryl-stabilized internal alkene, due to the interaction of the empty *p*-orbital on boron with the adjacent π-electrons of alkene. Minimizing the steric repulsion between the aryl and Bpin groups by rotation of the Bpin group away from the bulkier aryl group to place H_b *syn* to Fe accounts for the observed *E*-selectivity.[20]

Scheme 4. The Proposed Catalytic Cycle for This Iron-Catalyzed Dehydeogenative Borylation



In summary, we have developed a convenient and efficient protocol for the synthesis of β-aryl VBEs through dehydrogenative borylation of vinylarenes with HBpin catalyzed by $(PMe_3)_4Fe$. A broad range of mono- and disubstituted vinylarenes underwent this reaction to afford *E*-VBEs in high isolated yields. This Fe-catalyzed dehydrogenative process provides a versatile foundation to develop various one-pot procedures for functionalization of vinylic C-H bonds of vinylarenes. Studies on dehydrogenative borylation of aliphatic alkenes and other dehydrogenative functionalization reactions of alkenes catalyzed by base metals are ongoing.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experiment procedures and characterization data for reaction products (PDF)

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Note

The authors declare no competing financial interest.

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REFERENCES

(1) For examples: (a) Yoo, K. S.; Yoon, C. H.; Jung, K. W. *J. Am. Chem. Soc.* **2006**, *128*, 16384-16393. (b) Delcamp, J. H.; Brucks, A. P.; White, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 11270-11271. (c) Shang, R.; Ilies, L.; Asako, S.; Nakamura, E. *J. Am. Chem. Soc.* **2014**, *136*, 14349.

(2) (a) Kathryn, A. R.; Connie, M. R.; Jaime, A. Y.; Neal, M. D. *Curr. Clin. Pharmacol.* **2006**, *1*, 81-101. (b) Cottart, C.-H.; Nivet-Antoine, V.; Beaudeux, J.-L. *Mol. Nutr. Food Res.* **2014**, *58*, 7-21.

(3) (a) Meier, H. *Angew. Chem., Int. Ed.* **1992**, *31*, 1399-1420. (b) Lo, S.-C. P.; Burn, L. *Chem. Rev.* **2007**, *107*, 1097-1116. (c) Likhtenshtein, G. I.; *Stilbenes: Applications in Chemistry, Life Sciences, and Materials science*, Wiley, New York, **2010**.

(4) For examples: (a) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1975**, *97*, 5249-5255. (b) Haberberger, M.; Enthaler, S. *Chem. - Asian J.* **2013**, *8*, 50-54. (c) Obligacion, J. V.; Neely, J. M.; Yazdani, A. N.; Pappas, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2015**, *137*, 5855-5858. (d) Yang, Z.; Zhong, M.; Ma, X.; Nijesh, K.; De, S.; Parameswaran, P.; Roesky, H. W. *J. Am. Chem. Soc.* **2016**, *138*, 2548-2551.

(5) Brown, H. C.; Bhat, N. G. *Tetrahedron Lett.* **1988**, *29*, 21-24.

(6) Takagi, J.; Takahashi, K.; Ishiyama, T.; Miyaura, N. *J. Am. Chem. Soc.* **2002**, *124*, 8001-8006.

(7) For examples: (a) Blackwell, H. E.; O'Leary, D. J.; Chatterjee, A. K.; Washenfelder, R. A.; Bussmann, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 58-71. (b) Funk, T. W.; Efskind, J.; Grubbs, R. H. *Org. Lett.* **2005**, *7*, 187-190. (c) Gao, F.; Carr, J. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2014**, *136*, 2149-2161.

(8) Reid, W. B.; Spillane, J. J.; Krause, S. B.; Watson, D. A. *J. Am. Chem. Soc.* **2016**, *138*, 5539-5542.

(9) Geier, S. J., Westcott, S. A. *Rev. Inorg. Chem.* **2015**, *35*, 69-74.

(10) For examples: (a) Burgess, K.; Van der Donk,W. A.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 9350-9359. (b) Vogels, C. M.; Hayes, P. G.; Shaver, M. P.; Westcott, S. A. *Chem. Commun.* **2000**, 51-52. (c) Coapes, R. B.; Souza, F. E. S. R.; Thomas, L.; Hall, J. J.; Marder, T. B. *Chem. Commun.* **2003**, 614-615. (d) Mkhalid, I. A. I.; Coapes, R. B.; Edes, S. N.; Coventry, D. N.; Souza, F. E. S.; Thomas, R. L.; Hall, J. J.; Bi, S.-W.; Lin, Z.; Marder, T. B. *Dalton Trans.* **2008**, 1055-1064. (e) Brown, A. N.; Zakharov, L. N.; Mikulas, T.; Dixon, D. A.; Liu, S.-Y. *Org. Lett.* **2014**, *16*, 3340-3343. (f) Morimoto, M.; Miura, T.; Murakami, M.; *Angew. Chem., Int. Ed.* **2015**, *54*, 12659-12663.

(11) (a) Takaya, J.; Kirai, N.; Iwasawa, N. *J. Am. Chem. Soc.* **2011**, *133*, 12980-12983; (b) Kirai, N.; Iguchi, S.; Ito, T.; Takaya, J.; Iwasawa, N. *Bull. Chem. Soc. Jpn.* **2013**, *86*, 784-799.

(12) (a) Olsson, V. J.; Szabó, K. J. *J. Org. Chem.* **2009**, *74*, 7715-7723. (b) Sasaki, I.; Doi, H.; Hashimoto, T.; Kikuchi, T.; Ito, H.; Ishiyama, T. *Chem. Commun.* **2013**, *49*, 7546-7548.

(13) Ohmura, T.; Takasaki, Y.; Furukawa, H.; Suginome, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 2372-2375.

(14) For examples of Cu-catalyzed carboboration of alkynes to synthesize *β,β*-di-substituted vinyl boronate esters: (a) Alfaro, R.; Parra, A.; Alemán, J.; García Ruano, J. L.; Tortosa, M. *J. Am. Chem. Soc.* **2012**, *134*, 15165-15168. (b) Tai, C.-C.; Yu, M.-S.; Chen, Y.-L.; Chuang, W.-H.; Lin, T.-H.; Yap, G. P. A.; Ong, T.-G. *Chem. Commun.* **2014**, 43444346.

(15) (a) Dombray, T.; Werncke, C. G.; Jiang, S.; Grellier, M.; Vendier, L.; Bontemps, S.; Sortais, J.-B.; Sabo-Etienne, S.; Darcel, C. *J. Am. Chem. Soc.* **2015**, *137*, 4062-4065. (b) Jiang, S.; Quintero-Duque, S.; Roisnel, T.; Dorcet, V.; Grellier, M.; Sabo-Etienne, S.; Darcel, C.; Sortais, J.-B. *Dalton Trans.* **2016**, *45*, 11101-11108. (c) Romero, E. A.; Jazzar, R.; Bertrand, G. *Chem. Sci.* **2016**, doi: 10.1039/c6sc02668k.

(16) For examples: (a) Wu, J. Y.; Moreau, B.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 12915-12917. (b) Greenhalgh, M. D.; Thomas, S. P. *Chem. Commun.* **2013**, *49*, 11230-11232. (c) Obligacion, J. V.; Chirik, P. J. *Org. Lett.* **2013**, *15*, 2680-2683. (d) Zhang, L.; Peng, D.; Leng, X.; Huang, Z. *Angew. Chem., Int. Ed.* **2013**, *52*, 3676-3680. (e) Chen, J.; Xi, T.; Lu, Z. *Org. Lett.* **2014**, *16*, 6452-6455. (f) Zheng, J.; Sortais, J.-B.; Darcel, C. *ChemCatChem* **2014**, *6*, 763-766. (g) Tseng, K.-N. T.; Kampf, J. W.; Szymczak, N. K. *ACS Catal.* **2015**, *5*, 411-415;

(17) (a) Hartwig, J. F.; Richards, S.; Barañano, D.; Paul, F. *J. Am. Chem. Soc.* **1996**, *118*, 3626-3633. (b) Tanaka, D.; Romeril, S. P.; Myers, A. G. *J. Am. Chem. Soc.* **2005**, *127*, 10323-10333.

(18) (a) Karsch, H. H.; Klein, H. F.; Schmidbaur, H. *Angew. Chem., Int. Ed.* **1975**, *14*, 637-638. (b) Karsch, H. H.; Klein, H.-F.; Schmidbaur, H. *Chem. Ber.* **1977**, *110*, 2200-2212. (c) Bhattacharya, P.; Krause, J. A.; Guan, H. *Organometallics* **2011**, *30*, 4720-4729.

(19) (a) Terao, Y.; Fukuoka, Y.; Satoh, T.; Miura, M.; Nomura, M. *Tetrahedron Lett.* **2002**, *43*, 101-104. (b) Vo, G. D.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 2127-2130.

(20) The iron-catalyzed dehydrogenative borylation reaction of α-isopropylstyrene with HBpin proceeded very sluggishly to low converion (~10%), but produced a *E*/*Z*-mixture of vinyl boronate esters.