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Authors: Xiaolong Yu, Hongling Zheng, Haonan Zhao, Boon Chong Lee, and Ming Joo Koh

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# Iron-Catalyzed Regioselective Alkenylboration of Olefins

Xiaolong Yu,<sup>[a]</sup> Hongling Zheng,<sup>[a]</sup> Haonan Zhao,<sup>[a]</sup> Boon Chong Lee,<sup>[a]</sup> and Ming Joo Koh\*<sup>[a]</sup>

[a] Prof. Dr. M. J. Koh

Department of Chemistry, National University of Singapore,

12 Science Drive 2, Republic of Singapore, 117549

\* E-mail: chmkmj@nus.edu.sg

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**Abstract:** The first examples of an iron-catalyzed three-component synthesis of homoallylic boronates from regioselective union of bis(pinacolato)diboron, an alkenyl halide (bromide, chloride or fluoride) and an olefin are disclosed. Products that bear tertiary or quaternary carbon centers could be generated in up to 87% yield as single regioisomers with complete retention of the olefin stereochemistry. With cyclopropylidene-containing substrates, ring cleavage leading to trisubstituted *E*-alkenylboronates were selectively obtained. Mechanistic studies revealed reaction attributes that are distinct from previously reported alkene carboboration pathways.

Catalytic transformations that are capable of rapidly introducing molecular complexity pertain to alkene difunctionalizations.<sup>[1]</sup> In particular, the simultaneous installation of C–C and C–B bonds through multicomponent olefin carboboration reactions<sup>[2]</sup> represents a powerful strategy to access synthetically useful organoboronates from readily available carbon- and boron-based reagents. Given the broad utility of boron-containing compounds, notably as precursors to other organic molecules by established C–B→C–X (X = C, N, O, halogen etc.) bond conversions,<sup>[3]</sup> various transition metal-catalyzed<sup>[2]</sup> and metal-free<sup>[4]</sup> methods for alkene carboboration have been introduced in the last decade.

A. Olefin carboboration with aryl and alkenyl halides



Scheme 1. Catalytic regioselective carboboration of alkenes with sp<sup>2</sup>-hybridized organohalides.

Amongst metal-catalyzed regimes that were more widely explored, strategies that involved additions across  $\pi$ -bonds

followed by reaction with an organohalide (or pseudohalide) enable access to a diverse assortment of alkylboron products.<sup>[2c-o]</sup> Notably, extensive efforts have been devoted to implementing aryl-boryl additions to olefins, mediated by either two-catalyst (e.g. Pd/Cu, Ni/Cu)<sup>[2c-g.o]</sup> or one-catalyst (e.g. Ni, Cu)<sup>[2]-m]</sup> systems (Scheme 1A). On the other hand, alkenylboration reactions were shown as logical extensions of arylboration, although reported examples remain scarce.<sup>[2e-f,k,m]</sup> For most transformations promoted by a single catalyst, the boroalkylmetal intermediate I (generated upon olefin borometallation) typically undergoes an oxidative insertion-type process with the sp<sup>2</sup>-hybridized halide cross-partner to give II before the ensuing reductive elimination delivers the final adduct<sup>[2]-m]</sup> (grey inset).

Our interest in organoiron catalysis<sup>[5]</sup> led us to speculate if earth-abundant iron-based complexes<sup>[6]</sup> could serve as effective catalysts to promote alkene carboboration.<sup>[7]</sup> Specifically, we sought to design a single-catalyst manifold that efficiently merges olefins with terminal (without directing groups)<sup>[8]</sup> bis(pinacolato)diboron and an alkenyl halide (Scheme 1B), as a complementary method to previous Ni-catalyzed reports where diminished yields and/or regioselectivity were observed with certain olefin substrates.<sup>[2k,m]</sup> Our studies showed that these transformations proceed through a carbometallation-elimination mechanism<sup>[9]</sup> via III and IV (grey inset) rather than conventionally reported oxidative cleavage pathways (cf. Scheme 1A grey inset).



**Scheme 2.** Identified reaction conditions for Fe-catalyzed alkenylboration of activated and unactivated olefins. [a] The gram-scale reaction was conducted for 20 h and afforded **3a** in 1.15 g. Regioisomeric ratios (r.r.) and *E:Z* ratios were determined by <sup>1</sup>H NMR analysis. Yields are for isolated and purified products.

Evaluation of reaction parameters for the union of styrenyl alkene **1a**,  $B_2(pin)_2$  and *E*-alkenyl bromide **2a** in the presence of various catalysts, bases and solvents at 60 °C revealed that the desired alkenylboration product **3a** bearing a fully-substituted

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quaternary carbon center could be isolated in 85% yield exclusively as a single regio- and *E* isomer within 12 hours, using 10 mol % of FeBr<sub>2</sub> and LiO*t*-Bu as base in DMA (Scheme 2A). Excess **1a** was utilized to overcome competitive boryl additions to **2a**. Notably, **3a** was not detected when a Ni(II) complex, previously shown to promote arylboration,<sup>[2k-m]</sup> was employed under analogous conditions (see Supporting Information (SI) for details). Lower yields were obtained when other Fe(II) or Fe(III) salts were examined, and changing the alkoxide base, solvent or temperature similarly led to inferior results (see SI for details). The catalytic transformation is amenable to gram-scale synthesis, furnishing **3a** in 76% yield (1.15 g) without detectable diminution in selectivity levels.



Scheme 3. The scope of Fe-catalyzed olefin alkenylboration. Regioisomeric ratios (r.r.) and *E:Z* ratios were determined by <sup>1</sup>H NMR analysis. Yields are for isolated and purified products. [a] The reaction was conducted with *E*-alkenyl chloride at 80 °C. [b] The reactions were conducted with *Z*-alkenyl fluoride. [c] The reaction was conducted with 1,1-difluoroalkene and 3t was generated in 93:7 *E:Z* ratio. See SI for details.

Additions to unactivated alkenes such as **4a** using the FeBr<sub>2</sub> system was inefficient, which led us to reexamine conditions for alkenylboration (see SI for details). After an extensive survey, best results were obtained using (dppe)FeBr<sub>2</sub> (10 mol %), LiO*t*-Bu and **4a** (3 equiv.) in DMF, delivering *E*-**5a** in 54% isolated yield and >95% regioselectivity (Scheme 2B). We next assessed the generality of the developed conditions with various monosubstituted and 1,1-disubstituted olefins as well as alkenyl bromides (Scheme 3). In the presence of activated alkenes (Scheme 3A), the desired homoallylic boronates were secured in up to 87% yield with >95:5 regio- and stereoselectivities. These include molecules containing both quaternary centers (**3a**–**f**, **3s**–**t**)

and tertiary centers (3g-r). Reactions are compatible with a Lewis basic pyridine (3d) as well as electronically diverse arenes. Exocyclic (3f) and Si-substituted (3k) C=C bonds also underwent reaction to deliver the expected products, but 1,2-disubstituted olefins were less efficient (cf. Scheme 4).

Functionalized aryl-substituted alkenyl halides typically participated in alkenylboration, including one case with a trisubstituted substrate (**3q**). The corresponding alkenyl chlorides require a higher temperture (80 °C) in order to react (**3a**). It merits mention that less reactive alkyl-substituted haloalkenes failed to undergo reaction. On the other hand, *Z*-aryl-substituted alkenyl bromides were found to decompose in the presence of base

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(presumably by base-promoted 1,2-elimination) to the corresponding terminal alkynes that could further react through Fe-catalyzed cyclotrimerization to give arenes<sup>[10]</sup> (see SI for details). Remarkably, subjecting an 85:15 E:Z mixture of an alkenyl bromide to the established conditions followed by oxidation furnished the corresponding homoallylic alcohol in 53% overall yield as a single E isomer (derived from reaction of the Ealkenyl bromide), meaning that the starting bromoalkene does not need to be isomerically pure (see SI for details).

To access Z-homoallylic boronates, we opted to use the less base-labile Z-alkenyl fluorides,[11] which successfully afforded the desired products 3r-s in 66-87% yield and complete stereoretention. Reaction with a 1,1-difluoroalkene led to 3t bearing a trisubstituted fluoroolefin in 93% E selectivity. Unlike haloalkenes, aryl halides did not react in our catalytic regime, indirectly suggesting that an oxidative addition-reductive elimination sequence is less likely to be involved (cf. Scheme 4 for further discussion). Transformations using aliphatic olefins also proceeded smoothly, furnishing the expected Ehomoallylboron products 5b-m in 35-72% yield and >95% site selectivity even with alkene substrates that lack  $\alpha$ -branched groups<sup>[2k,m]</sup> (Scheme 3B). However, 1,1- and 1,2-disubstituted internal olefins did not undergo alkenylboration owing to poor reactivity.

Control experiments were performed to gain more insights into the mechanistic underpinings of the Fe-catalyzed alkenylboration (Scheme 4). As depicted in Scheme 4A, deuteroboration of E-Bmethylstyrene (E-6) under analogous conditions using MeOD in the absence of the alkenyl halide furnished the expected synaddition product 7 in 79% yield and >98% diastereospecificity (residual protoboration adduct arising from adventitious t-BuOH formed by deprotonation of DMA with base<sup>[5]</sup> also detected). Consistent with our previous study,<sup>[5]</sup> this implies that an in situgenerated iron-boryl species selectively adds across the  $\pi$ -bond in a syn fashion to form the putative intermediate III (cf. Scheme 1B) prior to deutero(protonolysis) in irreversible manner. At this stage, it remains to be determined how III reacts when a haloalkene is involved instead of protons.

Conducting the FeBr2-catalyzed reaction with E-6 using a haloalkene partner, however, led to a 1:1 diastereomeric mixture of 8 in 33% overall yield following oxidation (>95:5 regioisomeric ratio; Scheme 4A). The analogous alkenylboration-oxidation sequence using Z-6 was also poorly diastereospecific (8 obtained in 11% overall yield and 2.5:1 diastereomeric ratio). No isomerization of E-6 or Z-6 was detected in these cases. These results intimated that the C-Fe bond formed upon olefin borometallation likely ruptures leading to epimerization of the Fesubstituted carbon center before it engages with the haloalkene. The question is whether the epimerization is homolytic<sup>[12]</sup> (i.e. giving rise to radicals) or heterolytic<sup>[2h,13]</sup> in nature (cf. Scheme 4 for further discussion). In contrast to the observations with aryl olefins, alkenylboration of stereodefined deuterium-labeled aliphatic alkenes *E*-*d*-**9** and *Z*-*d*-**9** under the optimized conditions with (dppe)FeBr<sub>2</sub> were completely diastereospecific. Further information on the alkenylation step could be obtained from radical clock experiments (Scheme 4B). Treatment of 1,6heptadiene, previously shown to cyclize under carboboration conditions,<sup>[4,14]</sup> to both sets of Fe-catalyzed alkenylboration conditions delivered the expected products 11 or 12 with no trace

of ring-closing adducts, meaning that long-lived radical species are unlikely to be involved.



Scheme 4. Mechanistic investigations.

Pathway 1 is more likely to be involved

Ar = 4-OMeC<sub>6</sub>H

Z-2c (1 equiv.)

>95:5 r.r., >95:5 Z:E

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More evidence for a non-radical pathway could be derived from control experiments with stereodefined haloalkenes (Scheme 4C). The observations that alkenyl fluorides served as competent substrates for alkenylboration (cf. Scheme 2) point in favor of an addition-elimination pathway,<sup>[9,15]</sup> since C(sp<sup>2</sup>)-F bonds are typically resistant to oxidative cleavage by an organoiron species. Hypothetically, a syn-diastereoselective carbometallation across the alkenyl halide  $\pi$ -bond followed by established base-promoted anti-selective β-halide-elimination,<sup>[16]</sup> would lead to stereoretention of the starting haloalkene geometry in each case (pathway 1, III→IV). Conversely, if a long-lived radical species V is indeed generated (by adventitious homolytic fission of C-Fe bond in III),<sup>[12]</sup> radical addition likely proceeds anti to an iron-coordinated E-haloalkene<sup>[15]</sup> (i.e. to minimize steric repulsions), which would give **VI** that subsequently undergoes  $\beta$ halide-elimination to furnish an adduct that bears a Z olefin motif (stereoinversion) as the major isomer (pathway 2.  $III \rightarrow V \rightarrow VI$ ). Thus, use of a Z-haloalkene should predominantly give the corresponding homoallylic boronate containing an *E* alkene unit.

As highlighted in Scheme 4C, the respective olefin stereochemistry was preserved in the final products during the course of alkenylboration with E-haloalkenes (2a,b) or Zfluoroalkene (2c). These stereochemical outcomes arguably support a heterolytic C-Fe bond dissociation/reformation pathway (partly owing to electronic stabilization by the phenyl group at the benzylic site)<sup>[2h]</sup> as the reason for epimerization detected in Scheme 4A, although homolytic fission/reformation cannot be completely ruled out. It is worth noting that adventitious Fe-H elimination within the alkyliron intermediate III (which yields an alkenyl-B(pin)) followed by re-addition would afford а homobenzylic Fe-C bond instead, implying that epimerization does not originate from Fe-H elimination.<sup>[2h,17]</sup>



Scheme 5. Proposed mechanism for catalytic olefin alkenylboration.

Based on the aforementioned investigations, a tentative mechanistic proposal is illustrated in Scheme 5. A catalytically active iron-boryl species ii generated from iron-alkoxide i through ligand substitution with B<sub>2</sub>(pin)<sub>2</sub> adds to alkene substrate in a syn fashion to afford an iron-alkyl complex iii. At this juncture, if the C-Fe bond is adjacent to an aryl unit, heterolytic bond dissociation and reformation (possibly via a putative resonancestabilized intermediate v)[2h,18] may potentially occur prior to alkenylation. Association of the haloalkene  $\pi$ -bond with the iron

center then triggers a syn-selective carbometallation process to form a second iron-alkyl species iv, which is susceptible to LiOt-Bu-promoted anti-selective 1,2-elimination to deliver the alkenylboration product and regenerate iron-alkoxide i (concomitant extrusion of LiX; X = halide). Electron paramagnetic resonance (EPR) experiments showed that the Fe-catalyzed reaction mixture remained EPR-silent with no signals that are expected to arise from long-lived radical species (see SI for details). Detailed studies to elucidate the nature of the in situformed organoiron species are ongoing and will be disclosed in due course.

The synthetic versatility of the boronate and olefin moieties within the homoallylboron compounds may be leveraged to access functionalized heterocycles (Scheme 6A). Treatment of the homoallyl alcohol generated from facile oxidation of 3n with 4methoxybenzyl alcohol in the presence of Ti(Oi-Pr)4 and HFIP solvent<sup>[19]</sup> efficiently furnished furan **13/13'** bearing three contiguous stereogenic centers in 50% yield and 7:1 d.r. In another instance, iodoetherification using iodine under alkaline conditions afforded 14 in 63% yield as a single diastereomer. Application towards the concise synthesis of (±)-imperanene, a natural product found in Chinese medicine with platelet aggregation inhibitory properties,<sup>[20]</sup> is highlighted in Scheme 6B. The core scaffold can be readily assembled through Fe-catalyzed alkenvlboration of alkene 4b (derived from abundant and inexpensive eugenol) with *E*-bromoalkene 2d and  $B_2(pin)_2$ followed by oxidation, generating the corresponding homoallyl alcohol in 36% overall yield and 87% site selectivity. Global silyl ether deprotection then delivers (±)-imperanene in 77% yield.



Scheme 6. Synthetic applications of homoallylic boronates.

With cyclopropylidene-functionalized substrates 15, rather than the typical homoallylboron compounds, synthetically useful 1,5-dienes 16a-e comprising of a trisubstituted E-alkenylboronate and a disubstituted E-olefin appendage were selectively generated in 36-57% yield under the standard Fe-catalyzed conditions (Scheme 7). These transformations are postulated to proceed by initial iron-boryl addition followed by an intramolecular stereocontrolled  $\beta$ -carbon elimination,<sup>[13]</sup> resulting in heterolytic cyclopropane rupture to give an alkyliron intermediate before the ensuing alkenylation with the haloalkene partner. These results are distinct from a previous Cu-catalyzed carboboration report<sup>[2h]</sup>

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in which cyclopropane ring-opening was not detected when similar substrates were used.



Scheme 7. Alkenylboration of 15 leading to stereoisomerically pure 1,5-dienes.

To conclude, we have disclosed the first cases of ironcatalyzed alkene carboboration that regioselectively installs an olefin and boryl unit across both activated and unactivated C=C bonds. Synthesis of a diverse variety of stereodefined homoallylic boronates as well as 1,5-dienes were achieved through alkenylboration, and our studies revealed reaction features that differ mechanistically from currently known carboboration pathways.

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Highly regioselective and stereoretentive union of olefins with haloalkenes and bis(pinacolato)diboron to deliver homoallylic boronates has been achieved through iron catalysis. Contrary to previous pathways, these reactions proceed through stereospecific carbometallation-β-halide elimination. With cyclopropylidene-containing substrates, stereodefined 1,5-dienes are obtained. The method is amenable to complex molecule and gram-scale synthesis.