

Palladium-Catalyzed Oxidative Borylation of Allylic C–H Bonds in Alkenes

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Supporting Information

ABSTRACT: This communication describes an efficient palladium pincer complex-catalyzed allylic C–H borylation of alkenes. The transformation exhibits high regio- and stereo-selectivity with a variety of linear alkenes. A synthetically useful feature of this allylic C–H borylation method is that all allyl-Bpin products can be isolated in usually high yields. Preliminary mechanistic studies indicate that this C–H borylation reaction proceeds via Pd(IV) pincer complex intermediates.

llyl boronates are important synthetic intermediates that react with aldehydes to afford stereodefined homoallylic alcohols.¹ Therefore, there is a great demand for efficient methodologies to synthesize allyl boronates from readily available substrates. Although borylations of allylic halides,^{2a-} carbonates,^{2b,d-h} ethers,²ⁱ and alcohols³ have been successfully developed, they all require extra steps to prepare the prefunctionalized starting materials. Szabó and co-workers developed an iridium-catalyzed allylic borylation of cycloalkenes, in which the selectivity was controlled by the addition of 1,8-diazabicyclo[5.4.0]undecane (DBU) or methylimidazole,^{4a,b} and a Pd(TFA)₂-catalyzed allylic borylation of exocyclic alkenes via allyl-Pd(II) intermediates^{4c} (Scheme 1). Recently, Gong and co-workers reported a Pd-catalyzed allylation of simple alkenes via oxidative C-H borylation, which mainly focused on allylbenzene and its derivatives.⁵ A general problem with these allylic C-H borylation methods is that the catalysts react with the allyl-Bpin products, and therefore, they must be trapped within the reaction system. Accordingly, several methods for one-pot C-H borylation-allylboration reactions have been reported. However, a more general allylic C-H borylation process that would allow the isolation of the allyl-Bpin products is still highly desirable.

Palladium-catalyzed C-H bond functionalization reactions have emerged as powerful strategies in organic synthesis,⁶ and oxidative C-H borylation reactions have been reported by several research groups,^{4c,5,7} in which Pd(II) species were proposed to be generated in situ and act as the active catalysts. Alternatively, C-H functionalization mediated by high-valent palladium species with unique reactivity and selectivity⁸ was also shown to be an efficient methodology to transform allylic C-H bonds into C-O⁹ and C-Si¹⁰ bonds. To the best of our knowledge, only the allylic C-H borylation of cycloheptene has been demonstrated by Szabó and co-workers, involving a







Pd(IV) species as the key intermediate, in which the selectivity is controlled by conformational factors.^{8a} Marder and coworkers reported catalytic borylations of both C–H and C–X bonds,¹¹ including the synthesis of allyl boronates.^{11j,k} Herein we present a Pd-catalyzed highly regio- and stereoselective allylic C–H borylation of alkenes, the isolation of the allyl-Bpin products, and also a one-pot route to homoallyl alcohols directly from alkenes.

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As palladium pincer complexes have proved to be highly selective catalysts for many C–H functionalization reactions, ^{6c} we applied these catalysts in the C–H borylation reaction. We found that in the presence of F-TEDA-BF₄ (Selectfluor) as an oxidant, NCN pincer complex **A** is an effective catalyst precursor for allylic C–H borylation, giving the desired product **2a** in 83% isolated yield with excellent regio- and stereo-chemistry (Table 1, entry 1). The reaction was scaled up to 1



^{*a*}Standard conditions: Pd–NCN complex **A** (10 mol %), **1a** (1 equiv), K_2CO_3 (2 equiv), B_2pin_2 (1.5 equiv), F-TEDA-BF₄ (1 equiv), MeNO₂ (1 mL), 60 °C. All of the reactions were carried out on a 0.2 mmol scale. ^{*b*}Yields were determined by GC–MS analyses vs a calibrated internal standard and are averages of two experiments. ^{*c*}E/Z isomer ratios were determined by ¹H NMR analyses of the crude products. ^{*d*}Isolated yield. ^{*e*}Yield of **3a** = 67%. ^{*f*}Yield of **3a** = 79%. ^{*g*}N.D. = not detected. ^{*h*}Yield of **3a** = 73%.

mmol, and 2a was isolated in 79% yield. A much lower yield of 2a (42%) was obtained at ca. 49% conversion¹² when we replaced **A** with its bromide analogue **B** (Table 1, entry 2). The yield of 2a dropped to 24% and 15%, and isomerization product 3a was formed in yields of 67% and 79% using Se pincer complexes C and D, respectively (Table 1, entries 3 and 4), possibly because they are less stable.¹³ F-TEDA-PF₆ was similar to the BF4⁻ salt as an oxidant, and the desired product 2a was obtained in 82% yield (Table 1, entry 5).¹⁴ No desired product 2a was obtained in the absence of a Pd catalyst or F-TEDA-BF₄ (Table 1, entries 6 and 7). Product 2a was formed in only 14% yield without K_2CO_3 (Table 1, entry 8), but the use of Na_2CO_3 as an alternative was successful (Table 1, entry 9), whereas KF was significantly less effective (Table 1, entry 10). THF and CH₂Cl₂ proved less effective as solvents than MeNO₂ (Table 1, entries 11 and 12). Additional screening experiments are described in the Supporting Information.¹⁴

With the optimized conditions in hand, we next started to investigate the scope of the reaction (Scheme 2). Simple alkenes, such as 1-hexene (1b) and 1-pentene (1c), are suitable





^{*a*}Standard conditions: 1 (0.2 mmol, 1 equiv), Pd–NCN complex A (10 mol %), F-TEDA-BF₄ (0.2 mmol, 1 equiv), K_2CO_3 (0.4 mmol, 2 equiv), B_2pin_2 (0.3 mmol, 1.5 equiv), MeNO₂ (1 mL), 60 °C. ^{*b*}Isolated yields are shown. ^{*c*}E/Z isomer ratios were determined by ¹H NMR analyses of the crude products.

for the allylic C-H borylation, and the corresponding products 2b and 2c were obtained in good yields of 84% and 79%, respectively. A particular merit of this reaction is that the allyl boronate products 2b and 2c (as well as the rest of the allyl-Bpin products) could be isolated.¹⁵ As mentioned above, the previously reported palladium (and iridium)-catalyzed C-H borylation methods usually did not allow isolation of the allyl boronate products.^{4,5} Exocyclic allyl boronates 2d and 2e were obtained from the allylic C-H borylation in yields of 86% and 78%, respectively. With disubstituted alkenes 1f and 1g, the desired allyl boronates 2f and 2g were obtained in yields of 83% and 68%, respectively. The nonconjugated diene 1h was borylated smoothly, and 2h was produced in 72% yield. With allylbenzene 1i as the starting material, product 2i was formed in a moderate yield of 69%. Allyl boronate 2j was obtained in 61% yield when allyl phthalimide 1j was employed as the starting material. Cyclohexene 1k was also borylated smoothly and provided the allylic product 2k in 71% yield.

 α -Methyl allylbenzene 11 gave allyl boronate 21 in 71% yield with the *Z* geometry at the C==C bond (Scheme 3). With the phenyl ring bearing Me, OMe, or F substituents (1m-q), the



^aStandard conditions: 1 (0.2 mmol, 1 equiv), Pd–NCN complex A (10 mol %), F-TEDA-BF₄ (0.2 mmol, 1 equiv), K_2CO_3 (0.4 mmol, 2 equiv), B_2pin_2 (0.3 mmol, 1.5 equiv), MeNO₂ (1 mL), 60 °C. ^bIsolated yields are shown. ^cE/Z isomer ratios were determined by ¹H NMR analyses of the crude products, and the stereochemistry at the C=C bond was determined by ¹H,¹H NOESY.

corresponding allyl boronates (2m-q) were obtained in good yields of 70–79% with good stereoselectivity. When the phenyl group was replaced by a naphthalenyl group, the desired product 2r was isolated in 64% yield.

As allyl boronates have significant applications in the synthesis of homoallyl alcohols,¹ we investigated the use of our allylic C–H borylation of alkenes in a one-pot carbonyl allylation reaction (see Schemes 4 and S1). Homoallyl alcohols can thus be prepared directly from alkenes with high efficiency and in high overall yields.

Scheme 4. Application in One-Pot Carbonyl Allylation Reactions

R^1 R^2 1	Step 1: Pd-NCN complex A (10 mol %) F-TEDA-BF ₄ (1 equiv) B ₂ pin ₂ (1.5 equiv), K ₂ CO ₃ (2 equiv MeNO ₂ (1 mL), 60 °C, 9 h	/) _{ОН}
	Step 2: ArCHO (1.2 equiv) 40 °C, 12 h	Ar X R ² R ¹ 4 or 5 or 6 15 examples 75%-88% overall yields

We briefly studied the mechanistic features of the above Pdcatalyzed allylic C-H borylation reactions. F-TEDA-BF₄ is reported to be capable of oxidizing Pd(II) to form a Pd(IV)-Fspecies.¹⁶ The observation of an ¹⁹F signal at -324 ppm is consistent with the presence of a fluoride ligand coordinated to Pd(IV). For example, Sanford and co-workers reported an ¹⁹F shift at -324 ppm for a Pd(IV)-F species.¹⁷ In addition, NCN pincer complexes are known to form Pd(IV) complexes. For example, the groups of Canty¹⁸ and Szabó^{8a} reported oxidation of Pd(II)-NCN complexes to their Pd(IV) analogues using strong oxidants, such as hypervalent iodine reagents. Indeed, when we monitored the change of the ¹H NMR spectrum of NCN pincer complex A upon addition of F-TEDA-BF4, we observed systematic changes in the ¹H NMR signals characteristic of the increase in coordination number from square-planar Pd(II) to a Pd(IV) species with a square-pyramidal or octahedral geometry (p S22 in the Supporting Information). Therefore, we suggest that in the initial step, NCN pincer complex A is oxidized by F-TEDA-BF₄ to generate Pd(IV)-F species I containing a vacant coordination site (Scheme 5). Then alkene 1 undergoes C–H activation to form η^1 -allyl complex II. The C-H activation step probably proceeds by a concerted metalation-deprotonation-type mechanism¹⁹ in which the coordinated acetate assists in the deprotonation of 1. Subsequently, $B_2 pin_2$ undergoes transmetalation with Pd(IV)–F to give III, facilitated by the formation of F-Bpin. Finally, C-B reductive elimination gives product 2 and regenerates the catalyst. A possible explanation of the surprising Z selectivity of the product formation is that the reaction involves η^1 -allyl palladium complexes (II and III), which are unable to undergo isomerization to give the thermodynamically more stable *E* product.²⁰

In conclusion, we have developed an efficient method to synthesize and isolate allyl boronates that exhibits high regioand stereoselectivity with a variety of alkenes and has been extended to a one-pot carbonyl allylation reaction that proceeds in high overall yields. An interesting mechanistic feature is that the reaction proceeds via a Pd(II)/Pd(IV) catalytic cycle. Formation of the Pd(IV) intermediate occurs by a unique combination of NCN incer complex **A** and application of F-TEDA-BF₄ as the oxidant. An important novelty of the present Scheme 5. Plausible Mechanism of the Allylic C–H Borylation



C–H borylation reaction is that the allyl-Bpin products can be isolated in high yields. This is probably a consequence of the application of pincer complex **A** as the catalyst, which selectively catalyzes C–B bond formation while avoiding subsequent C–B bond cleavage-based side reactions. In previous Pd-catalyzed C–H borylation reactions with non-pincer complex catalyst sources (e.g., $Pd(OAc)_2$), the reactions stopped because of product inhibition, i.e., reaction of the allyl-Bpin product with the Pd catalyst.^{4c} Another interesting and fortunate feature of our catalyst system is that F-TEDA-BF₄ is able to oxidize Pd(II) to Pd(IV) in the pincer complex but does not oxidize boron in either the diboron reagent or the allyl boronate product.

ASSOCIATED CONTENT

Supporting Information

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Experimental procedures and compound characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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(12) Conversions were determined via ${}^1\mathrm{H}$ NMR analyses of the crude reaction mixtures.

(13) A black precipitate formed right after F-TEDA-BF₄ was added to the solution of the Pd-pincer complex. The yields of isomerization product **3a** were determined by ¹H NMR analyses of the crude reaction mixtures.

(14) F-TEDA-BF₄ is more soluble in CH_3NO_2 than in THF or CH_2Cl_2 . The solubility of F-TEDA-PF₆ in THF or CH_2Cl_2 is better than that of F-TEDA-BF₄, but it is not commercially available. Therefore, we chose F-TEDA-BF₄ as the oxidant. Additionally, F-TEDA-BF₄ is not only used for electrophilic fluorination but can act as an oxidant in the metal-catalyzed functionalization of C–H bonds. For reviews, see: (a) Engle, K. M.; Mei, T.-S.; Wang, X.; Yu, J.-Q. Angew. Chem., Int. Ed. 2011, 50, 1478. (b) Liang, T.; Neumann, C. N.; Ritter, T. Angew. Chem., Int. Ed. 2013, 52, 8214. PhI(OAc)₂ was also employed as the oxidant in the borylation of 1a, and a 23% yield of oct-2-en-1-yl acetate and a 75% yield of 1a were observed by ¹H NMR spectroscopy.

(15) The isolated yield is limited by some decomposition of the allyl boronate on silica gel.

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(20) We hypothesize that η^1 -allyl palladium complexes II and III are formed during the reaction and that isomerization to the γ -position is not favorable, probably because of the steric effects of R¹ and R². Therefore, no branched products were observed.