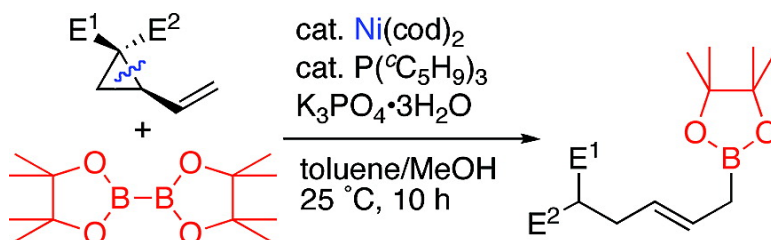


Nickel-Catalyzed Borylative Ring-Opening Reaction of Vinylcyclopropanes with Bis(pinacolato)diboron Yielding Allylic Boronates

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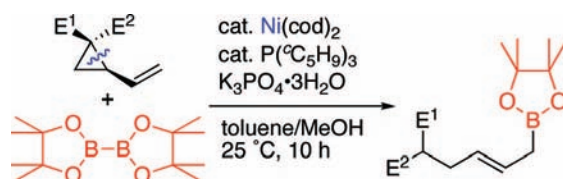
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ABSTRACT



Vinylcyclopropanes bearing one or two electron-withdrawing groups on the cyclopropane ring undergo nickel-catalyzed borylative ring opening with bis(pinacolato)diboron to yield allylic boronates. The reaction proceeded with high *E* selectivity.

Allylic boron reagents are among the most important reagents in organic synthesis.¹ Modern organic synthesis requires more complex and functionalized allylic boron reagents than ever for synthesis of a wider variety of biologically intriguing compounds. However, functionalized allylic boron reagents are not always easy to synthesize, and development of new methods for the synthesis of allylic boron reagents is expected.^{2,3} Here we report nickel-catalyzed borylative ring-opening reactions of vinylcyclopropanes with bis(pinacolato)diboron which provide allylic boron reagents.^{4–6}

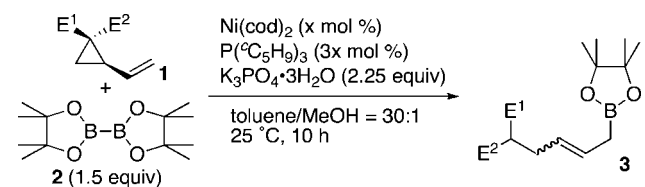
Treatment of bis(ethoxycarbonyl)-substituted vinylcyclopropane **1a** with bis(pinacolato)diboron (**2**) in the presence of potassium phosphate trihydrate and catalytic amounts of Ni(cod)₂ and tricyclopentylphosphine in toluene/methanol afforded allylic boronate **3a** (Table 1, entry 1).⁷ The reaction was high yielding and proceeded with high *E* selectivity. Analogous to the previous reports on nickel-catalyzed

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(2) Reviews: (a) Hall, D. G. *Pure Appl. Chem.* **2008**, *80*, 913–927. (b) Ito, H.; Ito, S.; Sasaki, Y.; Matsuura, K.; Sawamura, M. *Pure Appl. Chem.* **2008**, *80*, 1039–1045. (c) Ishiyama, T.; Miyaura, N. *Chem. Rec.* **2004**, *3*, 271–280. (d) Darses, S.; Genet, J. P. *Chem. Rev.* **2008**, *108*, 288–325. (e) Pietruszka, J.; Schone, N.; Frey, W. G.; Grundl, L. *Chem.—Eur. J.* **2008**, *14*, 5178–5197. (f) Knochel, P.; Ila, H.; Korn, T. J.; Baron, O. In *Handbook of Functionalized Organometallics*; Knochel, P., Ed.; Wiley-VCH: Weinheim, Germany, 2005; Chapter 3.5.

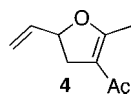
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Table 1. Scope of Vinylcyclopropanes

entry	E ¹	E ²	1	<i>x</i>	3	yield /% ^a	<i>E/Z</i>
1	CO ₂ Et	CO ₂ Et	1a	5	3a	84 (98)	94:6
2	CO ₂ Me	CO ₂ Me	1b	2	3b	73 (80)	91:9
3	CO ₂ ^{<i>t</i>} Bu	CO ₂ ^{<i>t</i>} Bu	1c	7.5	3c	66 (84)	95:5
4	CO ₂ Et	Ac	1d	2	3d	57 (75)	80:20
5	Ac	Ac	1e	2	3e	(20) ^b	<i>c</i>
6	CO ₂ ^{<i>t</i>} Bu	H	1f ^{<i>t</i>}	5	3f	85	91:9
7	H	CO ₂ ^{<i>t</i>} Bu	1g	10	3f	44	85:15

^a Isolated yields. NMR yields are in parentheses. The lower isolated yields would be attributed to partial decomposition of **3** during silica gel column purification. ^b Furan derivative **4** was obtained in 6% yield.



^c Not determined. ^d A mixture of *cis* and *trans* isomers (**1f**/**1g** = 84:16) was used.

reactions with boron reagents,^{6c,8} the reaction required base, which would activate boron species. The addition of methanol was essential for smooth protonation of the boron enolate^{6c,8c} (vide infra).

As the size of electron-withdrawing groups on the cyclopropane ring become larger, the reactions required higher catalyst loadings to attain high yields and the *E/Z* ratios were slightly improved (entries 1–3). Acetyl-substituted **1d** reacted with **2** to provide **3d** with moderate stereoselectivity (entry 4). Diacetyl-substituted vinylcyclopropane **1e** was converted to desired product **3e** in only 20% yield, along with furan derivative **4** as a byproduct (entry 5).^{5f}

(5) Nickel-catalyzed reactions of vinylcyclopropanes: (a) Murakami, M.; Nishida, S. *Chem. Lett.* **1979**, *8*, 927–930. (b) Hiroi, K.; Arinaga, Y.; Ogino, T. *Chem. Lett.* **1992**, *21*, 2329–2332. (c) Ryu, I.; Ikura, K.; Tamura, Y.; Maenaka, J.; Ogawa, A.; Sonoda, N. *Synlett* **1994**, 941–942. (d) Suginome, M.; Matsuda, T.; Yoshimoto, T.; Ito, Y. *Organometallics* **2002**, *21*, 1537–1539. (e) Zuo, G.; Louie, J. *J. Am. Chem. Soc.* **2005**, *127*, 5798–5799. (f) Bowman, R. K.; Johnson, J. S. *Org. Lett.* **2006**, *8*, 573–576. (g) Ikeda, S.; Obara, H.; Tsuchida, E.; Shirai, N.; Odashima, K. *Organometallics* **2008**, *27*, 1645–1648.

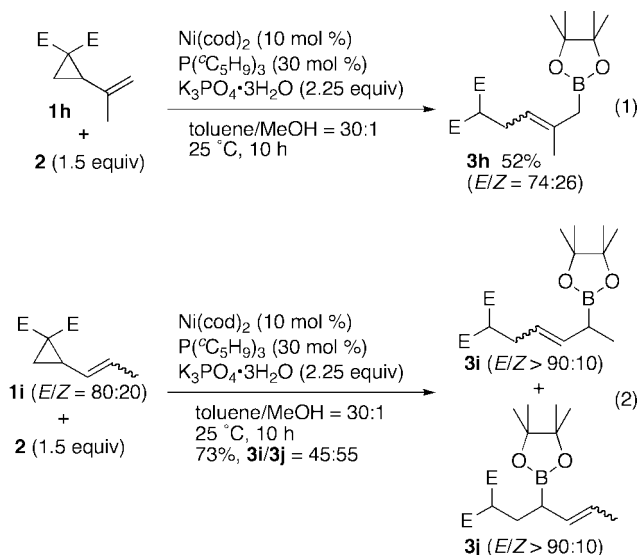
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(7) General procedure: Ni(cod)₂ (2.8 mg, 0.010 mmol) and K₃PO₄·3H₂O (120 mg, 0.45 mmol) were placed in a 20 mL reaction flask under argon. Toluene (1.0 mL) and tricyclopentylphosphine (0.50 M toluene solution, 0.06 mL, 0.03 mmol) were added. The resulting suspension was stirred for 10 min at 0 °C. Vinylcyclopropane **1a** (42 mg, 0.20 mmol) and bis(pinacolato)diboron (**2**, 76 mg, 0.30 mmol) in toluene (2.0 mL) were then added. Methanol (0.10 mL) was added, and the mixture was allowed to warm to 25 °C and stirred for 10 h. The reaction was quenched with water (3 mL). Extraction followed by concentration in vacuo afforded an oil. The crude oil was purified on silica gel (Kanto Chemical, silica gel 60N, hexane/ethyl acetate = 10:1) by using a dry ice/acetone-jacketed chromatographic column to yield **3a** (57 mg, 0.17 mmol, *E/Z* = 94:6) in 84% yield.

(8) (a) Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2005**, *7*, 4689–4691. (b) Hirano, K.; Yorimitsu, H.; Oshima, K. *Adv. Synth. Catal.* **2006**, *348*, 1543–1546. (c) Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2007**, *9*, 1541–1544.

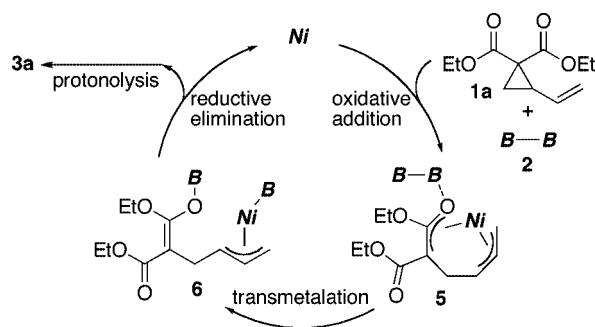
Vinylcyclopropane **1f** having only one *tert*-butoxycarbonyl group at the *cis* position underwent efficient borylative ring opening (entry 6). In contrast, the nickel-catalyzed reaction of **1g**, the *trans* isomer of **1f**, led to the formation of **3f** in only 44% yield, in addition to a mixture of unidentified byproducts (entry 7). These results are informative in considering the reaction mechanism (vide infra).

Cyclopropanes having a substituted vinyl group also participated in the borylation reaction (Scheme 1). Isopro-

Scheme 1. Nickel-Catalyzed Reactions of Isopropenyl- and (1-Propenyl)cyclopropanes with **2** (E = COOEt)

penylcyclopropane **1h** underwent the reaction with low stereoselectivity (eq 1). When (1-propenyl)cyclopropane **1i** was employed, a mixture of regioisomers **3i** and **3j** was obtained with high *E* selectivity (eq 2).

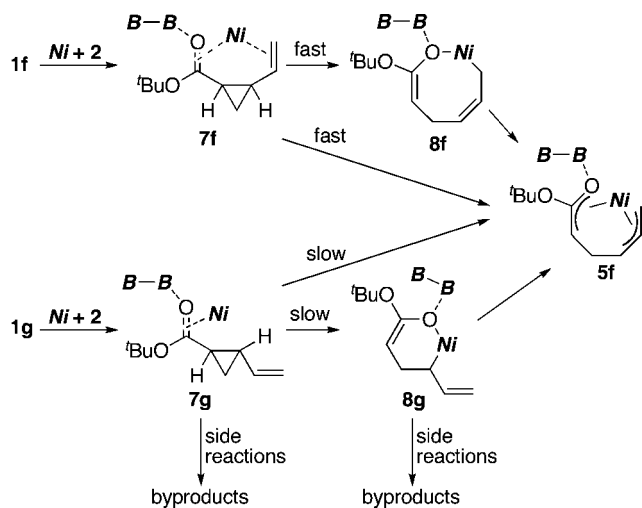
On the basis of these results as well as our previous reports,^{6c,8} we assume the reaction mechanism as follows (Scheme 2). Cyclopropane **1a** is activated by Lewis acidic **2**, and the activated **1a** undergoes oxidative addition to a

Scheme 2. Plausible Reaction Mechanism

Ni(0) complex^{6c,8-10} to afford π -allyl(oxa- π -allyl)nickel¹¹ **5**. Transmetalation then occurs to yield π -allylnickel **6** bearing a boron enolate moiety. Reductive elimination provides the boron enolate of **3a**, which is protonated in situ to afford **3a**, with concomitant formation of the initial Ni(0) complex.

The difference of the reactivities of **1f** and **1g** suggests that oxidative addition of **1f** would be more favorable than that of **1g** (Scheme 3). The *cis* configuration of **1f** would

Scheme 3. Plausible Detailed Mechanism of Oxidative Addition



allow for bidentate coordination to nickel to form **7f**, which would undergo smooth oxidative addition, yielding **5f** directly or via oxanickelacyclooctadiene **8f**. Similarly, **1g** would be transformed to **7g**. In contrast to the case of **7f**, the subsequent oxidative addition that yields **5f** directly or oxanickelacyclohexene **8g**^{11,12} would be slow, thereby competing with side reactions.

(9) Johnson, J. R.; Tully, P. S.; Mackenzie, P. B.; Sabat, M. *J. Am. Chem. Soc.* **1991**, *113*, 6172–6177.

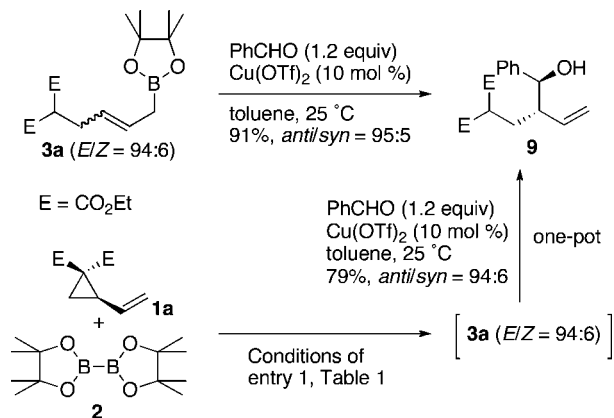
(10) In the absence of **2**, treatment of **1a** under the nickel catalysis resulted in no reactions.

(11) Ogoshi, S.; Nagata, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2006**, *128*, 5350–5351.

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Finally, the reaction of allylic boronate **3a** with benzaldehyde was examined (Scheme 4). Isolated **3a** reacted with

Scheme 4. Copper-Catalyzed Reaction of **3a** with Benzaldehyde



benzaldehyde smoothly in the presence of 10 mol % of $\text{Cu}(\text{OTf})_2$ ^{1e,13} in toluene to afford the corresponding homoallyl alcohol **9** in 91% yield with high *anti* selectivity. Notably, one-pot sequential borylative ring-opening/allylation reactions also provided **9** in high yield with similar diastereoselectivity.

In summary, we have found a new catalytic activity of nickel, which allows for synthesis of functionalized allylic boronates of synthetic use.

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Supporting Information Available: Characterization data of the products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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