Alkenes

Deutsche Ausgabe: DOI: 10.1002/ange.201506328
Internationale Ausgabe: DOI: 10.1002/anie.201506328

Rhodium-Catalyzed Dehydrogenative Borylation of Aliphatic Terminal Alkenes with Pinacolborane

Masao Morimoto, Tomoya Miura, and Masahiro Murakami**

Abstract: *Aliphatic terminal alkenes react with pinacolborane at ambient temperature to afford dehydrogenative borylation compounds as the major product when iPr-Foxap is used as the ligand with cationic rhodium(I) in the presence of norbornene, which acts as the sacrificial hydrogen acceptor. The reaction is applied to the one-pot syntheses of aldehydes and homoallylic alcohols from aliphatic terminal alkenes.*

The hydroboration of alkenes with borane reagents to give the corresponding alkylboranes is a fundamental textbook reaction. The use of transition-metal catalysts makes it possible to use dialkoxyborane reagents [$HB(OR)_2$] for the hydroboration under mild reaction conditions.[1] A variety of transition-metal complexes such as rhodium(I),[2] iridium(I),[3] ruthenium(II),[4] iron(0),[5] and cobalt(I)[6] catalyze the hydroboration of terminal alkenes with pinacolborane (HBpin), thus forming alkyl pinacolboronates in a regioselective way [Figure 1 a]. Interestingly, the dehydrogenative borylation competes with the hydroboration in some cases to afford alkenyl pinacolboronates as the major product.[7–9] For example, Masuda et al. reported that the reaction of styrene with HBpin in the presence of neutral $[RhCl(cod)]_2$ gave the dehydrogenative borylation product along with a small amount of the hydroboration products.[8a,c] Concurrently, ethylbenzene was generated along with styryl pinacolboronate in similar amounts, thus showing that a half of styrene was used as the hydrogen acceptor. Therefore, an excess amount of styrene was required. Moreover, the substrates for the successful dehydrogenative borylation are limited to arylethenes and alkoxyethenes. There is no facile method to obtain the dehydrogenative borylation compounds from aliphatic terminal alkenes and HBpin.[10,11] Herein, we report a rhodium(I)-catalyzed reaction of aliphatic terminal alkenes with HBpin, which preferentially produce dehydrogenative borylation compounds (Figure 1 b). The use of *i*Pr-Foxap as the ligand of cationic rhodium(I) and norbornene as the sacrificial hydrogen acceptor is the key for the dehydrogenative borylation. Hydroboration of terminal alkynes with HBpin is a straightforward and reliable method for the stereoselective preparation of *E*-alkenyl pinacolboronates.[12] Even *Z* isomers have become accessible by hydroboration of terminal alkynes.[13] Sometimes, over-reduction of the alkyne to give saturated diboronates compounds,[14] along with issues of regioselectivity, complicates this route. The attractiveness of the dehydrogenative borylation is the use of readily available terminal alkenes as starting materials instead of terminal alkynes.

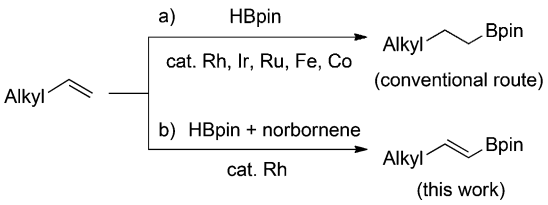

Figure 1. Two pathways of the borylation reaction of aliphatic terminal alkenes with pinacolborane (HBpin).

Initially, 4-phenylbut-1-ene (**1a**, 1.0 equiv) was subjected to the reaction with HBpin (**2**, 1.7 equiv) in the presence of $[Rh(cod)_2]BF_4$[2c] and norbornene (nbe; 2.3 equiv) as the sacrificial hydrogen acceptor (Table 1, entry 1). After the reaction mixture was stirred at 28 °C for 9 hours, a mixture of the dehydrogenative borylation products **3a** and **4a**, and the hydroboration product **5a** was formed in a ratio of **3a**/**4a**/**5a** = 15:5:80, albeit in 20% total yield. The hydrogenation of **1a** also occurred as a side reaction. Next, various ligands were examined using $[Rh(cod)_2]BF_4$ as the catalyst precursor. Whereas the use of simple phosphine ligands such as PPh_3 and dppe preferentially yielded the hydroboration product **5a** (entries 2 and 3), a P,N bidentate ligand (**L1**) gave a better product selectivity for **3a** (**3a**/**4a**/**5a** = 40:2:58; entry 4). A commercially available P,N bidentate ligand, *i*Pr-Foxap,[15] exhibited a dramatic effect to favor the formation of **3a**.[16] After chromatographic purification, the product **3a** was obtained along with **4a** and **5a** (**3a**/**4a**/**5a** = 91:3:6) in 86% total yield (entry 5).[17] The *E*/*Z* ratio of **3a** was 85:15. The counterions of rhodium(I) complexes also affected the product selectivity. The tetraphenylborate complex $[Rh(cod)_2]BPh_4$ showed a comparable product selectivity (**3a**/**4a**/**5a** = 93:3:4), but the hexafluorophosphate complex $[Rh(cod)_2]PF_6$ resulted in a lower product selectivity (**3a**/**4a**/**5a** = 28:3:69; entries 6 and 7). While the neutral complex $[RhCl(cod)]_2$ is known as the effective precursor for the dehydrogenative borylation of styrene,[8a,c] it gave a result inferior to that of $[Rh(cod)_2]BF_4$ in terms of both yield and product selectivity (entry 8). Furthermore, the choice of hydrogen acceptor was important. When norbornadiene or styrene was used as the hydrogen acceptor, the yield of **3a** markedly decreased (entries 9 and 10).[18]

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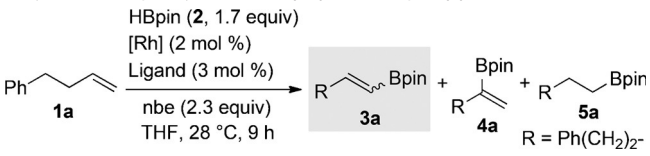
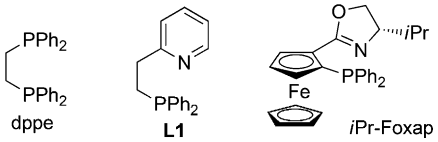
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201506328.

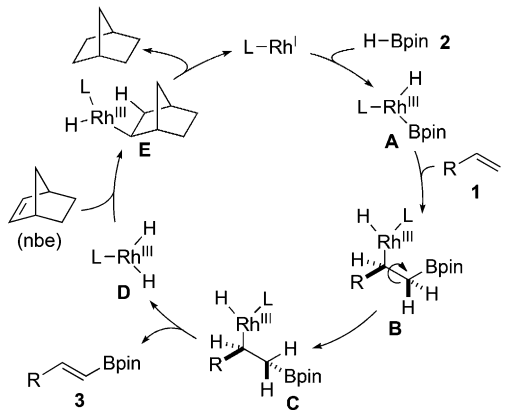
Table 1: Optimization of reaction conditions for the dehydrogenative borylation of 4-phenylbut-1-ene (**1a**) with HBpin (**2**).[a]



Entry	[Rh]	Ligand	Conv. [%]	Yield [%][b]	**3a**(*E*/*Z*)/**4a**/**5a**[c]
1	$[Rh(cod)_2]BF_4$	none	>95	20	15(>95/5):5:80
2	$[Rh(cod)_2]BF_4$	PPh_3[d]	88	37	27(89/11):3:70
3	$[Rh(cod)_2]BF_4$	dppe	50	49	0:0:100
4	$[Rh(cod)_2]BF_4$	L1	63	50	40(87/13):2:58
5	**$[Rh(cod)_2]BF_4$**	***i*Pr-Foxap**	**>95**	**92 (86)**	**91(85/15):3:6**
6	$[Rh(cod)_2]BPh_4$	*i*Pr-Foxap	95	90 (78)	93(83/17):3:4
7	$[Rh(cod)_2]PF_6$	*i*Pr-Foxap	79	58	28(81/19):3:69
8[e]	$[RhCl(cod)]_2$	*i*Pr-Foxap	93	82 (76)	77(83/17):3:20
9[f]	$[Rh(cod)_2]BF_4$	*i*Pr-Foxap	22	19	21(71/29):5:74
10[g]	$[Rh(cod)_2]BF_4$	*i*Pr-Foxap	72	26	73(82/18):4:23

[a] On a 0.50 mmol scale. [b] Total yield of **3**, **4**, and **5** as detemined by GC. The value within parentheses reflects the total yield of the product after chromatographic purification. [c] Product ratio determined by GC. [d] Using PPh_3 (6 mol%). [e] Using $[RhCl(cod)]_2$ (1 mol%). [f] Using norbornadiene (2.3 equiv) instead of nbe. [g] Using styrene (2.3 equiv) instead of nbe.

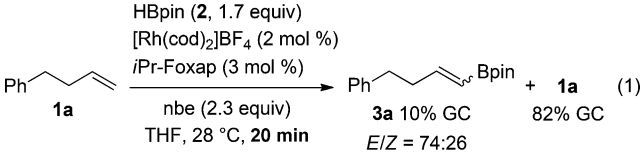




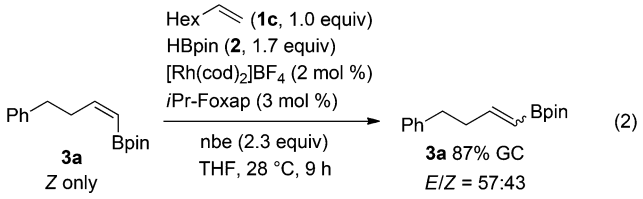
Scheme 1. Plausible catalytic cycle for the dehydrogenative borylation.

Although it is difficult to explain the reaction pathway leading to the alkenyl boronate **3** from the aliphatic terminal alkene **1** and HBpin (**2**), a possible mechanism is depicted in Scheme 1. It is similar to the one proposed by Hartwig et al. for the iridium(I)-catalyzed dehydrogenative silylation using norbornene as the hydrogen acceptor.[19] Oxidative addition of the B–H bond of **2** onto rhodium(I) affords the boryl(hydride)rhodium species **A**. Subsequent insertion of the alkene **1** into the Rh–B bond of **A** takes place to give the alkyl-rhodium intermediate **B**. The initial conformer undergoes rotation along the C–C bond axis to form the other conformer **C**. Then, syn β-hydride elimination furnishes the *E* isomer of the alkenyl boronate **3**. The (dihydride)rhodium species **D** reacts with norbornene to generate an active rhodium(I) species together with norbornane.[17,20] The strained structure of norbornene enhances the reactivity toward **D**.[18] Therefore, hydroboration of norbornene is preferred over the alkenyl pinacolboronate **3a**.

The following experiments were carried out to obtain mechanistic insights into the stereoselectivity. First, the rhodium(I)-catalyzed reaction of **1a** with **2** was monitored by GC after 20 minutes [Eq. (1)]. The *E*/*Z* ratio of **3a** was 74:26 at 18% conversion of **1a**. Thus, the *E*/*Z* ratio of **3a** changed during the reaction (vs. 9 h; Table 1, entry 5).

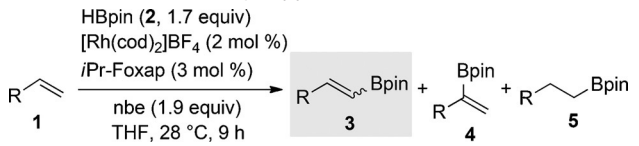


Secondly, the purified *Z* isomer of **3a** was subjected to the standard reaction conditions using oct-1-ene (**1c**) as a substrate [Eq. (2)]. The *E*/*Z* isomerization of **3a** took place to give an *E*/*Z* = 57:43 mixture. Based on these results, the stereochemistry seems to be subject to thermodynamics rather than kinetics.



A variety of terminal alkenes **1** were subjected to the dehydrogenative borylation with **2** by using a combination of $[Rh(cod)_2]BF_4$/*i*Pr-Foxap and norbornene (Table 2). Monosubstituted alkenes **1b–f** readily reacted with **2** to afford the corresponding alkenyl pinacolboronates **3b–f** with good yields, product selectivities, and *E*/*Z* ratios (entries 1–5), whereas the reactions of 3-*tert*-butylprop-1-ene (**1g**) and cyclohexylethene (**1h**) were rather sluggish, probably owing to the steric hindrance (entries 6 and 7). Functional groups such as siloxy, chloro, methoxycarbonyl, and epoxy groups were tolerated in the alkyl chain under the reaction conditions (entries 8–13). The reaction of 1,1- and 1,2-disubstituted alkenes such as 1,1-diethylethene and cyclohexene failed to give the desired alkenyl pinacolboronates.[21] Therefore, in the case of 2-methylhexa-1,5-diene (**1o**), including 1,1-disubstituted alkene moiety, only the terminal monosubstituted alkene moiety underwent the dehydrogenative borylation to afford the monoborylated product **3o** (entries 14). Similarly, 4,8-dimethylnona-1,7-diene (**1p**) selectively produces the monoborylated product **3p** (entry 15). 1,1-Dimethylbuta-

Table 2: Rhodium(I)-catalyzed dehydrogenative borylation of various terminal alkenes **1** with HBpin (**2**).[a]

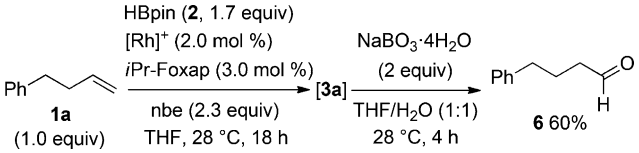


Entry	1	3	Yield [%][b]	3a(*E*/*Z*)/4a/5a[c]
1	1b	*n* = 2 **3b**	79[d]	90(91/9):4:6
2	1c	*n* = 5 **3c**	75	91(91/9):3:6
3	1d	*n* = 9 **3d**	82	91(90/10):3:6
4	1e	**3e**	78[e,f]	89(88/12):0:11
5	1f	**3f**	71	92(91/9):2:6
6	1g	**3g**	56	93(89/11):1:6
7	1h	**3h**	52[g]	88(>95/5):1:11
8	1i	*n* = 2 **3i**	83	89(90/10):3:8
9	1j	*n* = 4 **3j**	80	89(91/9):3:8
10	1k	**3k**	78[g]	92(83/17):2:6
11	1l	**3l**	74[h]	90(86/14):3:7
12	1m	**3m**	83	91(90/10):3:6
13	1n	**3n**	77	88(89/11):3:9
14	1o	**3o**	71[e]	92(91/9):3:5
15	1p	**3p**	79[g]	92(88/12):3:5
16	1q	**3q**	80[d]	91(95/5):0:9
17	1r	**3r**	82[g]	93(85/15):0:7
18	1s	**3s**	78[i]	96(>95/5):0:4

[a] On a 0.50 mmol scale. [b] Total yield of **3**, **4**, and **5** after chromatographic purification. [c] Product ratio determined by ^{1}H NMR analysis. [d] Yield determined by NMR spectroscopy. [e] Using nbe (2.3 equiv). [f] Containing 2-cinnamyl-Bpin (4%). [g] Using nbe (1.7 equiv). [h] Using nbe (2.5 equiv). [i] Containing 1-(4-methoxyphenyl)ethyl-Bpin (2%).

1,3-diene (**1q**) was also a suitable substrate to give the corresponding dienylboronate **3q** with high product selectivity and *E*/*Z* ratio (entry 16). Allyltriphenylsilane (**1r**) and 4-methoxystyrene (**1s**) successfully participated in this reaction (entries 17 and 18). The *E* isomer was exclusively formed with **3s**.

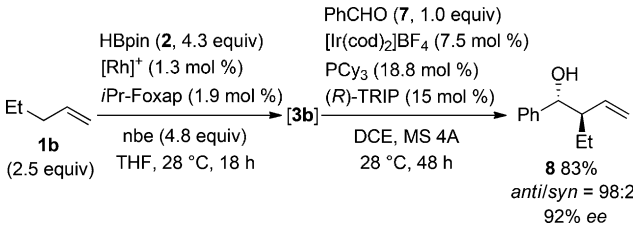
The resulting alkenyl pinacolboronates were useful intermediates in organic synthesis.[1b] Thus, we examined one-pot, two-step transformations via the formation of alkenyl boronates, thus saving time and solvents required for a workup/purification procedure. After volatile materials in the reaction mixture of **1a** with **2** were removed under reduced pressure, an aqueous THF solution of sodium perborate was directly added to the residue including the alkenyl pinacolboronate **3a**. Oxidation of **3a** occurred to form the corresponding aldehyde **6** in 60% yield upon isolation (based on **1a**; Scheme 2). Formally, this one-pot reaction achieved *anti*-



Scheme 2. One-pot synthesis of aldehydes from terminal alkenes.

Markovnikov oxidation of terminal alkenes at ambient temperature,[22] thus complementing the Wacker–Tsuji oxidation by palladium catalyst. Furthermore, it avoids the need for two oxidation steps to convert a hydroboration product (alkyl boronate) of an alkene into an aldehyde.

We recently reported an enantioselective synthesis of *anti*-homoallylic alcohols from terminal alkynes, HBpin, and aldehydes via the formation of alkenyl pinacolboronates, which act as γ-substituted allylboron species.[23] Thus, the reaction mixture containing the alkenyl pinacolboronate **3b** was treated with benzaldehyde (**7**) in the presence of [Ir(cod)$_2$]BF$_4$/PCy$_3$ and (*R*)-TRIP in 1,2-dichloroethane (DCE). The *anti*-homoallylic alcohol **8** was obtained with high diastereo- and enantioselectivities (Scheme 3). The above-mentioned reactions provide efficient methods to directly functionalize aliphatic terminal alkenes in one pot.



Scheme 3. One-pot synthesis of homoallylic alcohols from terminal alkenes. (*R*)-TRIP = (*R*)-3,3′-Bis(2,4,6-triisopropylphenyl)-1,1′-binaphthyl-2,2′-diyl hydrogenphosphate.

In summary, we have disclosed that the combined use of a cationic rhodium(I) complex, *i*Pr-Foxap, and norbornene enables the facile preparation of alkenyl pinacolboronates from aliphatic terminal alkenes and HBpin at ambient temperature. Since terminal alkenes are more easily accessible and often more desirable starting materials than terminal alkynes, the reaction represents an interesting alternative to alkyne hydroboration. Based upon the dehydrogenative borylation reaction, the one-pot syntheses of aldehydes and homoallylic alcohols starting from terminal alkenes have also been realized. Further studies to elucidate

the mechanism of this reaction and to expand its utility are in progress.

Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research (S) from MEXT and the ACT-C program of the JST. We thank Prof. Keiji Morokuma, Dr. Travis V. Harris, and Dr. W. M. C. Sameera for enriching discussion. M. Morimoto thanks the JSPS for Young Scientists for a Research Fellowship.

Keywords: alkenes · boron · reaction mechanisms · rhodium · synthetic methods

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 12659–12663
Angew. Chem. **2015**, *127*, 12850–12854

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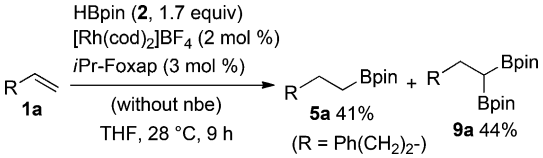
[16] When the reaction of **1a** with **2** was conducted using (*rac*)-[2-(oxazolin-2′-yl)ferrocenyl]diphenylphosphine (the *i*Pr group of *i*Pr-Foxap is lacking) in place of *i*Pr-Foxap, the yield of **3a** was significantly decreased. The result suggests that the bulkiness of the *i*Pr group would be one of the important factors.

[17] Norbornane (ca. 83%), 2-norbornyl pinacolboronate (ca. 46%), and butylbenzene (ca. 3%) were also formed (GC yield).

[18] When the reaction was conducted in the absence of norbornene, no alkenyl pinacolboronate **3a** was formed. The hydroboration product **5a** and the diboration product **9a** were formed in 41 and 44% yield, respectively. These results indicate that norbornene plays a crucial role of inhibiting over-reduction of **3a**. When cyclohexene was used in place of norbornene, it was too unreactive to act as the hydrogen acceptor, thus giving **5a** and **9a** as the major products.



[19] C. Cheng, E. M. Simmons, J. F. Hartwig, *Angew. Chem. Int. Ed.* **2013**, *52*, 8984; *Angew. Chem.* **2013**, *125*, 9154.

[20] For another possible mechanism involving insertion of norbornene into the Rh–H bond of **A** followed by the sequential insertion of the alkene **1** into the Rh–B bond, see: Ref. [8c].

[21] When the reaction of α-methylstyrene was carried out under modified reaction conditions [HBpin (**2**, 2.0 equiv), nbe (1.0 equiv), $[Rh(cod)_2]BF_4$ (2 mol%), *i*Pr-Foxap (3 mol%), THF (2 M), 35 °C, 6 h], the dehydrogenative borylation product and the hydroboration product were formed in 62 and 29% yield (NMR), respectively.

[22] For recent examples on the synthesis of aldehydes from terminal alkenes, see: a) G.-Q. Chen, Z.-J. Xu, C.-Y. Zhou, C.-M. Che,

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Received: July 9, 2015
Revised: August 5, 2015
Published online: September 2, 2015