



1,2-Arylboration of aliphatic alkenes by cooperative palladium/copper catalysis

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ABSTRACT

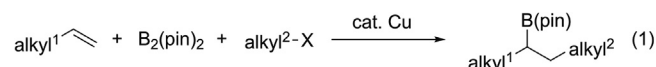
A method for the 1,2-arylboration of aliphatic alkenes to afford alkylboronic esters by cooperative palladium/copper catalysis was developed. The reaction proceeds in a highly regioselective manner, and various functional groups such as silyl ether, alkoxycarbonyl, and cyano groups are tolerated under the applied reaction conditions.

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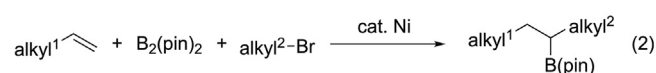
Alkylboronic acids and their derivatives are useful intermediates in organic synthesis, considering that they are sufficiently stable to be isolated and stored, and that their C–B bonds can subsequently be easily transformed into C–C, C–N, or C–O bonds [1]. Representative methods for their preparation are the hydroboration of alkenes [2], the borylation of alkyl halides [3], and the C–H borylation of alkanes [4]. The transition-metal-catalyzed carboboration [5] of alkenes provides alternative access to complex alkylboronic acids and their derivatives, as C–C and C–B bonds are formed simultaneously across the double bond of readily available alkenes. Although carboboration reactions of conjugated alkenes such as 1-arylalkenes [6], 1,3-enynes [7], 1,3-dienes [8], Michael acceptors [9], 1,2-dienes [10], and strained alkenes [11] have been developed, examples of the carboboration of aliphatic alkenes remain rare [12]. While the carboboration of aliphatic alkenes that bear a heteroatom at the allylic or homoallylic position, and an 8-aminoquinoline directing group has been reported,^{12a–e} the carboboration of electronically non-biased aliphatic alkenes is still limited. As for terminal aliphatic alkenes, Cu-catalyzed 1,2-alkylboration [6d,12b], Ni-catalyzed 1,1-alkylboration [12h], Ni-catalyzed 2,1-arylboration,^{12f,g} and Pd-catalyzed 1,2-arylboration^{12k} have been reported (eq. 1–4). Herein, we report the 1,2-arylboration of aliphatic alkenes with aryl bromides and bis(pinacolato)diboron [B₂(pin)₂] by cooperative Pd/Cu catalysis (eq 5). It is worth mentioning that aryl bromides, which are not

viable under Yin's conditions,^{12k} are viable under the present conditions.

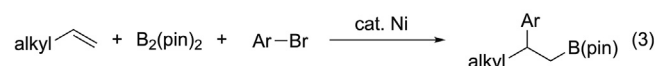
1,2-alkylboration by Yoshida (ref. 6d) and Fu (ref. 12b)



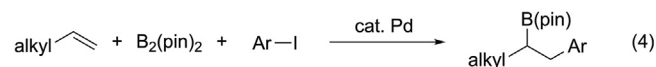
1,1-alkylboration by Yin (ref. 12h)



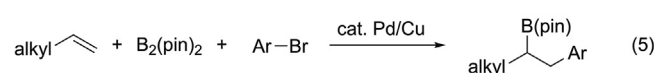
2,1-arylboration by Brown (refs. 12f and 12g)



1,2-arylboration by Yin (ref. 12k)



1,2-arylboration (**this work**)



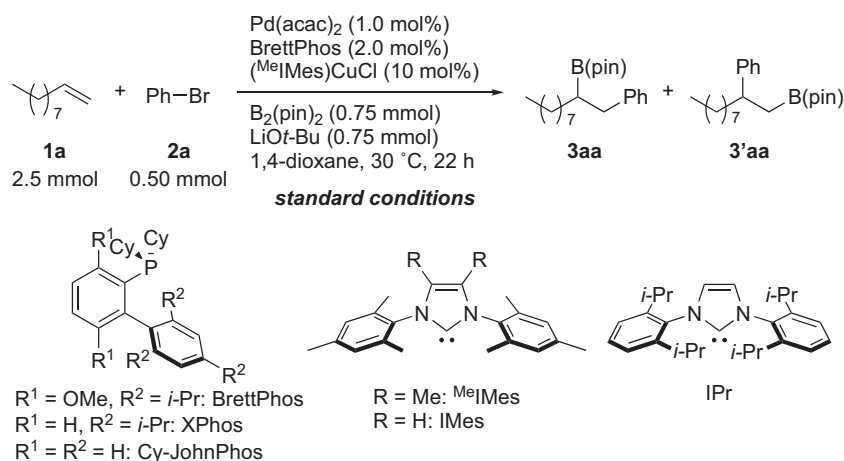
^{*} Corresponding authors.

During our studies on the carboboration of compounds with unsaturated carbon–carbon bonds by cooperative metal catalysis, we have reported the arylboration of vinylarenes by cooperative Pd/Cu or Ni/Cu catalysis.^{6e,f} Our first attempt to achieve the arylboration of aliphatic alkenes was thus carried out under the optimized conditions developed for the arylboration of vinylarenes (Entries 1 and 2, Table 1). The corresponding arylboration products were not detected in either case, and the borylated arene was obtained as the major product. Subsequently, we extensively screened a variety of reaction parameters, including a series of Pd and Cu precursors, ligands, bases, and solvents (Table 1). Finally, we discovered that the arylboration of 1-decene (**1a**) (2.5 mmol) with bromobenzene (**2a**) (0.50 mmol) and B₂(pin)₂ (0.75 mmol) in the presence of Pd(acac)₂ (1.0 mol%), BrettPhos (2.0 mol%), (^{Me}IMes)CuCl (10 mol%), and LiOt-Bu (0.75 mmol) in 1,4-dioxane at 30 °C afforded the corresponding regioisomeric products (**3aa** and **3'aa**) with high regioselectivity, i.e., the 1,2-arylboration product **3aa** was the major regioisomer (61% combined yield; entry 3). The effect of different phosphines is shown in entries 3–8. Dicyclohexyl(*o*-biaryl)phosphines, in particular BrettPhos, were effective (Entries 3–5), whereas other phosphines such as triphenylphosphine (PPh₃), tricyclohexylphosphine (PCy₃), and 1,2-bis(diphenylphosphino)ethane (dppe) were ineffective (Entries 6–8). The *N*-heterocyclic carbene (NHC) in the (NHC)CuCl complex also influences the yield and regioselectivity of the products. For exam-

ple, (IMes)CuCl affords the products with high regioselectivity in 53% combined yield (Entry 9), whereas the sterically demanding (IPr)CuCl regioselectively afforded **3aa** in 8% yield together with a large amount of Ph–B(pin) (Entry 10). Moreover, the choice of base is crucial for the success of the arylboration reaction. For example, NaOt-Bu afforded the arylboration products in 46% total yield (Entry 12), whereas **3aa** and **3'aa** were not obtained with LiOMe and CsF (Entries 11 and 13). When toluene was used as the solvent instead of 1,4-dioxane, the total yield of **3aa** and **3'aa** decreased to 22% (Entry 14). Furthermore, the cooperative catalysis by Pd and Cu was confirmed to be indispensable to promote the desired reaction (Entries 15 and 16).

Next, the scope of substrates was examined under the optimized reaction conditions (Table 2). The arylboration of primary alkyl-substituted terminal alkenes **1a–d** and **1h** proceeded with high regioselectivity to afford the corresponding *sec*-alkylboronates in moderate to good yield (Entries 1–4 and 10). Vinylcyclohexane (**1e**) also furnished the arylboration product in moderate yield (Entry 5). In the case of 1,5-diene **1f**, the arylboration product derived from the mono-substituted double bond was selectively obtained in 35% isolated yield without formation of any arylboration products derived from the di-substituted double bond (Entry 6). Under these optimized conditions, cyclohexene (**1g**) was not a viable substrate (Entry 7). The scope of aryl bromides is shown in entries 8–13. Electron-donating or -withdrawing sub-

Table 1
Optimization of the reaction conditions.



Entry	Deviation from the standard conditions	Total yield of 3aa + 3'aa (%) ^a (3aa / 3'aa) ^b	Yield of Ph–B(pin) (%) ^a
1 ^c	optimized conditions in ref. 6e	0	19
2 ^d	optimized conditions in ref. 6f	0	16
3	none	61 (91:9)	20
4	XPhos instead of BrettPhos	38 (92:8)	34
5	Cy-JohnPhos instead of BrettPhos	8 (87:13)	13
6	PPh ₃ instead of BrettPhos	0	0
7	PCy ₃ instead of BrettPhos	0	11
8	dppe instead of BrettPhos	0	0
9	(IMes)CuCl instead of (^{Me} IMes)CuCl	53 (87:13)	19
10	(IPr)CuCl instead of (^{Me} IMes)CuCl	8 (>95:5)	39
11	LiOMe instead of LiOt-Bu	0	76
12	NaOt-Bu instead of LiOt-Bu	46 (85:15)	31
13	CsF instead of LiOt-Bu	0	0
14	toluene instead of 1,4-dioxane	22 (89:11)	38
15	w/o Pd(acac) ₂	0	0
16	w/o (^{Me} IMes)CuCl	0	0

^a Determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard.

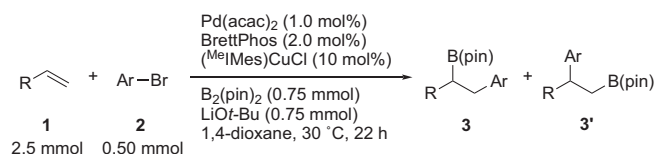
^b Regioselectivity of the crude mixture determined by ¹H NMR spectroscopy.

^c Pd(OAc)₂ (1.0 mol%), XPhos (2.0 mol%), (IPr)CuCl (10 mol%), NaOMe (0.75 mmol), toluene, 80 °C, 12 h.

^d Ni(acac)₂ (2.0 mol%), CuCl (1.0 mol%), P(*n*-C₄H₉)₃ (6.0 mol%), LiOt-Bu (0.75 mmol), toluene, 80 °C, 12 h.

Table 2

Arylboration of aliphatic alkenes by cooperative Pd/Cu catalysis.



Entry	1	2	Total yield of 3+3' (%) ^a	3/3' ^b
1			64 (54)	92:8
2		2b	74 (60)	92:8
3		2b	68 (59)	91:9
4 ^c		2b	70 (61)	88:12
5 ^c		2b	55 (47)	86:14
6		2b	40 (35)	89:11
7		2b	<5	–
8	1b		66 (47)	91:9
9	1b		69 (45)	92:8
10			57 (49)	90:10 ^d
11	1b		80 (70)	93:7
12	1b		59 (43)	82:18 ^d
13	1b		55	80:20 ^d

^a Yield estimated by ¹H NMR spectroscopy. The yield of the isolated products is given in parentheses.^b Regioselectivity of the crude mixtures determined by GC analysis.^c Pd(acac)₂ (0.50 mol%), BrettPhos (1.5 mol%), **1** (0.50 mmol), **2b** (0.75 mmol).^d Regioselectivity of the crude mixtures determined by ¹H NMR spectroscopy.

stituents at the *para*-position of bromobenzene were well tolerated and their presence did not affect yield or regioselectivity (Entries 8–10). The arylboration products were also obtained in high yield in the case of *ortho*-tolyl bromide (**2f**) (Entry 11). Heteroaromatic bromides such as 3-bromothiophene (**2g**) and 2-bromopyridine (**2h**) also participated in the reaction (Entries 12 and 13), although the isolation of **3bh** was difficult due to its instability. Functional groups such as silyl or benzyl ether, as well as alkoxycarbonyl or cyano moieties remained intact under the applied reaction conditions. According to the literature [13], a robustness screen was undertaken to evaluate the functional group tolerance of the present reaction (Table S1) [14]. Alkyl or aryl chlorides, alkyl bromide, aliphatic nitrile, and tertiary amide groups are well tolerated,

whereas primary alkyl alcohol, secondary amide, and aliphatic ketone groups retarded the arylboration. In the case of primary alkyl alcohol and secondary amide groups, the yield of the hydroboration products increased.

To gain insight into the mechanism of this reaction, the hydroboration of 1-decene (**1a**) with B₂(pin)₂ and MeOH was carried out in the presence of (MeImes)CuCl (10 mol%) (Entry 1, Table 3). To our surprise, the regioselectivity of **4a/4'a** (52:48) differed significantly from that of the arylboration of **1a** (91:9; entry 1, Table 1). This result suggests that the regioselectivity of the arylboration is not governed by the borylcupration [15] of **1a**, as in the case of the arylboration of vinylarenes. To clarify the origin of the observed regioselectivity, the hydroboration of **1a** was carried

Table 3Hydroboration of **1a** under various conditions.

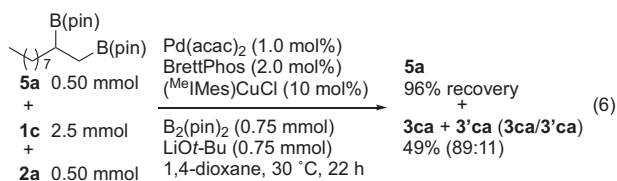
cat.
 MeOH (0.50 mmol)
 B₂(pin)₂ (0.75 mmol)
 LiOt-Bu (0.75 mmol)
 1,4-dioxane, 30 °C, 22 h

4a **4'a**

Entry	Cat.	Yield (%) ^a (4a / 4'a) ^b
1	(^{Me} IMes)CuCl (10 mol%)	18 (52:48)
2	(^{Me} IMes)CuCl (10 mol%)/BrettPhos (2.0 mol%)	23 (54:46)
3	(^{Me} IMes)CuCl (10 mol%)/Pd(acac) ₂ (1.0 mol%)/BrettPhos (2.0 mol%)	32 (49:51)
4	Pd(acac) ₂ (1.0 mol%)/BrettPhos (2.0 mol%)	0
5	(^{Me} IMes)CuCl (10 mol%)/Pd(acac) ₂ (1.0 mol%)/BrettPhos (2.0 mol%)/ 2a (0.50 mmol)	20 (80:20) 26 ^c (82:18) ^d

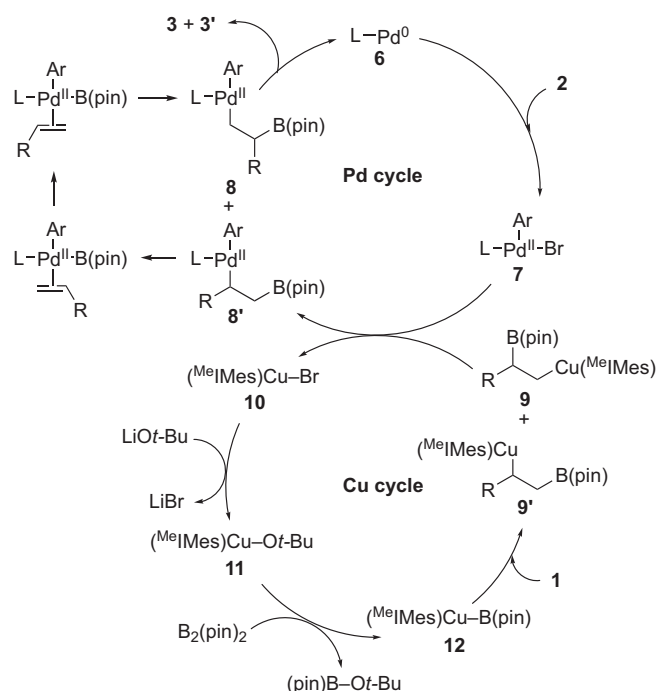
^a Yield estimated by GC analysis.^b Regioselectivity of the crude mixtures determined by GC analysis.^c Yield of **3aa**+**3'aa** determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard.^d Regioselectivity of **3aa**:**3'aa** determined by ¹H NMR analysis.

out under varying conditions (Table 3). For example, the regioselectivity was not affected by the addition of BrettPhos or BrettPhos/Pd(acac)₂ (Entries 2 and 3), while the reaction did not proceed in the absence of the copper catalyst (Entry 4). These results should indicate that under the conditions in entries 1–4, hydroboration of **1a** proceeds *via* borylcupration of **1a** followed by protonation of the resulting alkylcopper with MeOH. The regioselectivity reached a similar value to that of the aryloboration of **1a** when **2a** was used in the presence of Pd(acac)₂, BrettPhos, and (^{Me}I)Mes)CuCl (Entry 5). This hydroboration would proceed *via* protonation of a β -borylalkyl(aryl)palladium(II) species (*vide infra*), generated from the transmetalation between (BrettPhos)PdAr(Br) and a β -borylalkylcopper species, with MeOH. All of the results in Table 3 thus support the notion that a β -boryl elimination [16] from the β -borylalkyl(aryl)palladium(II) species determines the regioselectivity of the aryloboration. One could also argue that the reaction proceeds *via* the diboration of the alkene, [17] followed by the Suzuki–Miyaura coupling at the terminal boryl group in the 1,2-diborylated alkanes as seen in the cascade aryloboration reported by Morken. [18] However, the aryloboration of **1c** in the presence of 1,2-diborylalkane **5a** afforded **3ca** and **3'ca** in good yield, whereas the Suzuki–Miyaura coupling of **5a** was not successful (eq 6).



Based on the results of the mechanistic studies in Table 3 and eq 6, a plausible mechanism is proposed in Scheme 1. The catalytic cycle should be initiated upon generation of borylcopper **12** from LCuOt-Bu (**11**) and B₂(pin)₂. The borylcupration of aliphatic alkenes would then afford β -borylalkylcopper species **9** and **9'**. The transmetalation of such β -borylalkylcopper species and arylpalladium (II) (**7**), generated *via* the oxidative addition of aryl bromides (**2**) to LPd(0) (**6**), would afford LCuBr (**10**) and alkyl(aryl)palladium (II) species **8** and **8'**. *sec*-Alkyl(aryl)palladium **8'** should isomerize to more stable *n*-alkyl(aryl)palladium **8** *via* a β -boryl elimination and subsequent reductive elimination from **8** should afford the aryloboration product **3** as the major product [19].

In summary, we have developed an intermolecular 1,2-arylboration of aliphatic alkenes with aryl bromides and B₂(pin)₂ by cooperative Pd/Cu catalysis. The reaction proceeds under mild conditions and affords a variety of alkylboronic esters with high regio- and chemoselectivity. The regioselectivity of the aryloboration

**Scheme 1.** Plausible mechanism for the aryloboration of aliphatic alkenes by cooperative Pd/Cu catalysis.

seems to be controlled by the β -boryl elimination from β -borylalkyl(aryl)palladium(II) and not by the borylcupration of the alkenes. This unique mechanism should thus facilitate the development of new carboboration reactions of alkenes by cooperative Pd/Cu catalysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.tetlet.2021.153059>.

References

- [1] a) R. Jana, T.P. Pathak, M.S. Sigman, *Chem. Rev.* 111 (2011) 1417;
b) T. Ohishi, L. Zhang, M. Nishiura, Z. Hou, *Angew. Chem., Int. Ed.* 50 (2011) 8114;
c) S.N. Mlynarski, A.S. Karns, J.P. Morken, *J. Am. Chem. Soc.* 134 (2012) 16449;
d) H.K. Scott, V.K. Aggarwal, *Chem. Eur. J.* 17 (2011) 13124;
e) S.P. Thomas, R.M. French, V. Jheengut, V.K. Aggarwal, *Chem. Rec.* 9 (2009) 24.
- [2] a) For reviews on non-catalyzed and catalyzed hydroborations, see: H.C. Brown *Pure. Appl. Chem.* 47 (1976) 49;
b) I. Beletskaya, A. Pelter, *Tetrahedron* 53 (1997) 4957;
c) C.M. Crudden, D. Edwards, *Eur. J. Org. Chem.* (2003) 4695.
- [3] a) A.S. Dudnik, G.C. Fu, *J. Am. Chem. Soc.* 134 (2012) 10693;
b) C.-T. Yang, Z.-Q. Zhang, H. Tajuddin, C.-C. Wu, J. Liang, J.-H. Liu, Y. Fu, M. Czystowska, P.G. Steel, T.B. Marder, L. Liu, *Angew. Chem., Int. Ed.* 51 (2012) 528;
c) H. Ito, K. Kubota, *Org. Lett.* 14 (2012) 890.
- [4] a) H. Chen, S. Schlecht, T.C. Semple, J.F. Hartwig, *Science* 2000 (1995) 287;
b) S. Kawamorita, R. Murakami, T. Iwai, M. Sawamura, *J. Am. Chem. Soc.* 135 (2013) 2947;
c) C.W. Liskay, J.F. Hartwig, *J. Am. Chem. Soc.* 134 (2012) 12422.
- [5] a) For reviews and pioneering reports on the carboboration of unsaturated carbon-carbon bonds, see: M. Sugimoto *Chem. Rec.* 10 (2010) 348;
b) G. Kehr, G. Erker, *Chem. Commun.* 48 (2012) 1839;
c) Y.N. Bubnov, O.A. Nesmeyanova, T.Y. Rudashevskaya, B.M. Mikhailov, B.A. Kazansky, *Tetrahedron Lett.* 12 (1971) 2153;
d) F.-Y. Yang, M.-Y. Wu, C.-H. Cheng, *J. Am. Chem. Soc.* 122 (2000) 7122;
e) M. Sugimoto, A. Yamamoto, M. Murakami, *J. Am. Chem. Soc.* 125 (2003) 6358;
f) M. Sugimoto, A. Yamamoto, M. Murakami, *Angew. Chem., Int. Ed.* 44 (2005) 2380.
- [6] a) C. Zhong, S. Kunii, Y. Kosaka, M. Sawamura, H. Ito, *J. Am. Chem. Soc.* 132 (2010) 11440;
b) H. Ito, T. Toyoda, M. Sawamura, *J. Am. Chem. Soc.* 132 (2010) 5990;
c) H. Yoshida, I. Kageyuki, K. Takaki, *Org. Lett.* 15 (2013) 952;
d) I. Kageyuki, H. Yoshida, K. Takaki, *Synthesis* 2014 (1924) 46;
e) K. Semba, Y. Nakao, *J. Am. Chem. Soc.* 136 (2014) 7567;
f) K. Semba, Y. Ohtagaki, Y. Nakao, *Org. Lett.* 18 (2016) 3956;
g) K.B. Smith, K.M. Logan, Y.W. Brown, *Chem. Eur. J.* 20 (2014) 12032;
h) K.M. Logan, K.B. Smith, K.M. Brown, *Angew. Chem., Int. Ed.* 54 (2015) 5228;
i) T. Jia, P. Cao, B. Wang, Y. Lou, X. Yin, M. Wang, J. Liao, *J. Am. Chem. Soc.* 137 (2015) 13760;
j) K.M. Logan, K.M. Brown, *Angew. Chem., Int. Ed.* 56 (2017) 851;
k) K. Yang, Q. Song, *Org. Lett.* 18 (2016) 5460;
l) B. Chen, P. Cao, X. Yin, Y. Liao, L. Jiang, J. Ye, M. Wang, J. Liao, *ACS Catal.* 7 (2017) 2425;
m) J.J. Smith, D. Best, H.W. Lam, *Chem. Commun.* 52 (2016) 3770.
- [7] F. Meng, F. Haefner, A.H. Hoveyda, *J. Am. Chem. Soc.* 136 (2014) 11304.
- [8] a) K.B. Smith, K.M. Brown, *J. Am. Chem. Soc.* 139 (2017) 7721;
b) S.R. Sardini, K.M. Brown, *J. Am. Chem. Soc.* 139 (2017) 9823;
c) L. Jiang, P. Cao, M. Wang, B. Chen, B. Wang, J. Liao, *Angew. Chem., Int. Ed.* 55 (2016) 13854.
- [9] a) Ref. 6e;
b) A. Welle, V. Cirriez, O. Riant, *Tetrahedron* 68 (2012) 3435.
- [10] a) Ref. 5d;
b) F. Meng, H. Jang, B. Jung, A.H. Hoveyda, *Angew. Chem., Int. Ed.* 52 (2013) 5046;
c) K. Yeung, R.E. Ruscoe, J. Rae, A.P. Pulis, D.J. Procter, *Angew. Chem., Int. Ed.* 55 (2016) 11912;
d) F. Meng, K.P. McGrath, A.H. Hoveyda, *Nature* 513 (2014) 367;
e) K. Semba, N. Bessho, T. Fujihara, J. Terao, Y. Tsuji, *Angew. Chem., Int. Ed.* 53 (2014) 9007;
f) T. Fujihara, A. Sawada, T. Yamaguchi, Y. Tani, J. Terao, Y. Tsuji, *Angew. Chem., Int. Ed.* 56 (2017) 1539;
g) Y. Zhou, W. You, K.B. Smith, K.M. Brown, *Angew. Chem., Int. Ed.* 53 (2014) 3475.
- [11] K. Yang, Q. Song, *J. Org. Chem.* 81 (2016) 1000.
- [12] a) H.M. Nelson, B.D. Williams, J. Miró, F.D. Toste, *J. Am. Chem. Soc.* 137 (2015) 3213;
b) W. Su, T.-J. Gong, X. Lu, M.-Y. Xu, C.-G. Yu, Z.-Y. Xu, H.-Z. Yu, B. Xiao, Y. Fu, *Angew. Chem., Int. Ed.* 54 (2015) 12957;
c) Z. Liu, H.-Q. Ni, T. Zeng, K.M. Engle, *J. Am. Chem. Soc.* 140 (2018) 3223;
d) Z. Liu, X. Li, T. Zeng, K.M. Engle, *ACS Catal.* 9 (2019) 3260;
e) Z. Bai, S. Zheng, Z. Bai, F. Song, H. Wang, Q. Peng, G. Chen, G. He, *ACS Catal.* 9 (2019) 6502;
f) K.M. Logan, S.R. Sardini, S.D. White, K.M. Brown, *J. Am. Chem. Soc.* 140 (2018) 159;
g) S.R. Sardini, A.L. Lambright, G.L. Trammel, H.M. Omer, P. Liu, K.M. Brown, *J. Am. Chem. Soc.* 141 (2019) 9391;
h) Y. Li, H. Pang, D. Wu, Z. Li, W. Wang, H. Wei, Y. Fu, G. Yin, *Angew. Chem., Int. Ed.* 58 (2019) 8872;
i) W. Wang, C. Ding, Y. Li, Z. Li, Y. Li, L. Peng, G. Yin, *Angew. Chem., Int. Ed.* 58 (2019) 4612;
j) Y. Chen, C. Mück-Lichtenfeld, A. Studer, *J. Am. Chem. Soc.* 140 (2018) 6221;
k) H. Pang, D. Wu, H. Cong, G. Yin, *ACS Catal.* 9 (2019) 8555;
l) S. Joung, A.M. Bergman, K.M. Brown, *Chem. Sci.* 10 (2019) 10944.
- [13] K.D. Collins, F. Glorius, *Nat. Chem.* 5 (2013) 597.
- [14] See the Supporting Information for details.
- [15] For the borylcupration of alkenes, see: D.S. Laitar, E.Y. Tsui, J.P. Sadighi *Organometallics* 25 (2006) 2405.
- [16] a) For the β -boryl elimination from β -borylalkylpalladium(II) species, see: N. Miyauchi, A. Suzuki *J. Organomet. Chem.* 213 (1981);
b) For the β -boryl elimination from β -borylalkylruthenium species, see: B. Marciniak, M. Jankowska, C. Pietraszuk, *Chem. Commun.* (2005) 663;
c) K.C. Lam, Z. Lin, T.B. Marder, *Organometallics* 26 (2007) 3149.
- [17] a) For the Lewis-base-catalyzed diboration of alkenes and allenes, see: A. Bonet, C. Pubill-Ulldemolins, C. Bo, H. Gulyás, E. Fernández *Angew. Chem., Int. Ed.* 50 (2011) 7158;
b) For the Cu-catalyzed diboration of alkynes and arynes, see: H. Yoshida, S. Kawashima, Y. Takemoto, K. Okada, J. Ohshita, K. Takaki, *Angew. Chem., Int. Ed.* 51 (2012) 235;
c) For the Pd-catalyzed diboration of allenes, see: F.-Y. Yang, C.-H. Cheng, *J. Am. Chem. Soc.* 123 (2001) 761.
- [18] S.N. Mlynarski, C.H. Schuster, J.P. Morken, *Nature* 505 (2014) 386.
- [19] a) Isomerization between *sec*-alkylpalladium and *n*-alkylpalladium is often observed in the cross-coupling with *sec*-alkylmetal reagents. See: T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi, K. Hirotsu *J. Am. Chem. Soc.* 106 (1984) 158;
b) C. Han, S.L. Buchwald, *J. Am. Chem. Soc.* 131 (2009) 7532;
c) S. Calimsiz, M.G. Organ, *Chem. Commun.* 47 (2011) 5181;
d) Organ and co-workers have reported that (IPr)PdPh(*n*-Pr) is more stable than (IPr)PdPh(*i*-Pr), and that the reductive elimination from (IPr)PdPh(*n*-Pr) is more favorable than that of (IPr)PdPh(*i*-Pr). For details, see: M. Pompeo, R.D.J. Froese, N. Hadei, M.G. Organ, *Angew. Chem., Int. Ed.* 51 (2012) 11354.