

Transition Metal-Free 1,2-Carboration of Unactivated Alkenes

Ying Cheng, Christian Mück-Lichtenfeld,^{id} and Armido Studer*^{id}

Institute of Organic Chemistry, University of Münster, Corrensstrasse 40, 48149 Münster, Germany

S Supporting Information

ABSTRACT: A method for transition metal-free 1,2-carboration of unactivated alkenes with bis-(catecholato)diboron as the boron source in combination with alkyl halides as the alkyl component is introduced. The three-component reaction proceeds via a radical pathway on a broad range of unactivated alkenes, and the 1,2-carboration products serve as valuable synthetic building blocks. Density functional theory calculations provide insights into the mechanism.

Difunctionalization of carbon–carbon double bonds, forming two new C–X (X = C or other atoms) bonds in a single operation, is a very powerful and valuable transformation in organic chemistry.¹ Along these lines, alkene difunctionalization comprising a borylation step in combination with another C–X bond-forming process² is highly attractive due to the fact that the installed C–B bond offers a range of highly useful follow-up transformations.³

In recent decades, transition metal catalyzed carboration of alkenes has matured to an efficient approach for the construction of functionalized alkylboranes,² which serve as important reagents and building blocks in chemical synthesis. In contrast, only few reports on transition metal-free 1,2-carboration of alkenes have appeared to date. For example, 1,2-carboration of allenyl ketones and esters using the strong Lewis acid B(C₆F₅)₃ was disclosed in which B(C₆F₅)₃ regioselectively reacts with the allene moiety (Scheme 1A).^{4,5} Woerpel reported a carboration

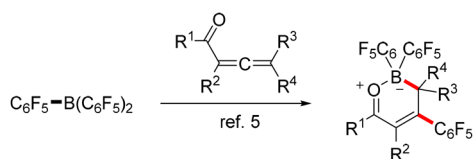
of seven-membered cyclic alkenes with triethylborane, which was suggested to proceed via a concerted process (Scheme 1B).⁶ A radical pathway, albeit less likely, could not be fully excluded. To our knowledge, a general transition metal-free intermolecular radical 1,2-carboration of unactivated alkenes is unknown.⁷ We present herein highly regioselective three-component alkene 1,2-carboration with a commercial diboron reagent as a chain carrying boron source and alkyl halides as radical precursors (Scheme 1C).

Encouraged by our recent work on transition metal-free 1,2-bifunctionalization of alkenes through radical processes,⁸ we decided to study unprecedented intermolecular alkene 1,2-carboration employing alkyl halides in combination with commercial diboron reagents. Tetraalkoxydiboron reagents are known to react with reactive aryl radicals⁹ and vinyl radicals¹⁰ via homolytic substitution at boron, and more recently, it was shown that alkyl radicals engage in radical borylation with this type of reagent.^{11,12}

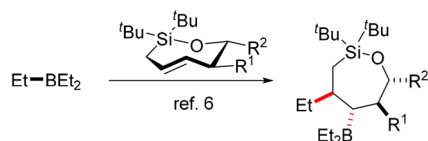
At first, we examined the reaction of 2-allylnaphthalene (**1a**), perfluorobutyl iodide (**2a**) as a C-radical precursor, and bis(catecholato)diboron (**3a**) as a trapping reagent at room temperature for 24 h in different solvents (Table 1, entries 1–8). Since alkyl iodides are known to generate C-radicals upon irradiation, initiation was attempted with a 10 W blue LED. In acetonitrile, the methanol and tetrahydrofuran reaction did not work (Table 1, entries 1–3). In 1,3-dimethyl-2-imidazolidinone (DMI) after transesterification with pinacol, the carboration product **4a** was formed in 19% yield (Table 1, entry 4), and dimethylacetamide (DMAc) provided a slightly lower yield (Table 1, entry 5). Since the corresponding catechol boronate was not stable during purification, the crude product was transesterified with pinacol to the pinacol boronate **4a** that could be readily isolated. In hexamethylphosphoramide (HMPA) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) as solvents the product **4a** was obtained in 21% and 40% yield, respectively (Table 1, entries 6 and 7). Pleasingly, upon switching to dimethylformamide (DMF), yield significantly increased to 70% (Table 1, entry 8). Other diboron reagents, such as bis(pinacolato)diboron (**3b**) and bis(neopentyl glycolato)diboron (**3c**), did not provide the corresponding carboration products (Table 1, entries 9 and 10). Perfluorobutyl bromide (**2b**) as a radical precursor afforded a worse result (Table 1, entry 11). Decreasing the amount of **1a** or **3a** to 1.0 equiv each led to lower yields (Table 1, entries 12 and 13) and yield dropped to 6% in the absence of blue LED irradiation indicating the importance of the light for the initiation step (Table 1, entry 14). Irradiation for 1 h followed by stirring for 23

Scheme 1. Metal-Free 1,2-Carboration of C=C Bonds

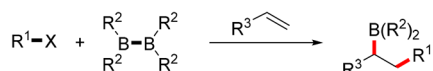
A) Two-component ionic allene 1,2-carboration



B) Two-component concerted alkene 1,2-carboration

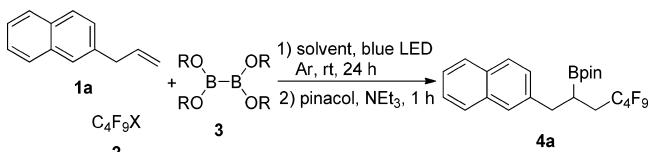


C) Three-component radical alkene 1,2-carboration (this work)



Received: March 27, 2018

Published: May 9, 2018

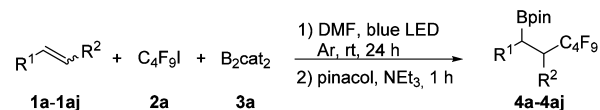
Table 1. Optimization of Reaction Conditions^a

entry	X	3	solvent	yield (%) ^b
1	I	3a	MeCN	0
2	I	3a	MeOH	0
3	I	3a	THF	0
4	I	3a	DMI	19
5	I	3a	DMAc	14
6	I	3a	HMPA	21
7	I	3a	DMPU	40
8	I	3a	DMF	70
9	I	3b	DMF	0
10	I	3c	DMF	0
11	Br	3a	DMF	29
12 ^c	I	3a	DMF	43
13 ^d	I	3a	DMF	44
14 ^e	I	3a	DMF	6
15 ^f	I	3a	DMF	16
16 ^g	I	3a	THF	40
17 ^h	I	3a	THF	0
18 ⁱ	I	3a	THF	0

^aReaction condition: **1a** (0.50 mmol, 2.5 equiv), **2** (0.20 mmol, 1.0 equiv), **3** (0.40 mmol, 2.0 equiv), solvent (0.40 mL), 10 W blue LED, Ar, rt, 24 h; pinacol (0.80 mmol, 4.0 equiv), NEt₃ (0.70 mL), 1 h. ^bIsolated yields. ^c**1a** (0.20 mmol, 1.0 equiv). ^d**3a** (0.20 mmol, 1.0 equiv). ^eIn the dark. ^f**1** h irradiated by 10 W blue LED followed by 23 h in the dark. ^g2.0 equiv of pyridine was used. ^h2.0 equiv of DABCO was used. ⁱ2.0 equiv of MeOK was used.

h in the dark afforded **4a** in only 16%, as expected for a radical chain reaction that needs continuous initiation. Using tetrahydrofuran as solvent, we tested several Lewis bases as additives (Table 1, entries 16–18). In the presence of pyridine (2.0 equiv), **4a** was isolated in 40% yield (Table 1, entry 16), and 1,4-diazabicyclo[2.2.2]octane (DABCO) or potassium methoxide (MeOK) as additives did not provide any product (Table 1, entries 17 and 18).

To document substrate scope, various alkenes **1b–1aj** were tested under optimized conditions keeping perfluorobutyl iodide as the C-radical precursor (Table 2). Allyl arenes bearing *para*-, *ortho*-, and *meta*-substituents at the arene ring performed well in the carboboration (**4b–k**). The reaction of 1-naphthyl- and 2-thienyl-substituted alkenes **1l** and **1m** provided **4l** and **4m** in 71% and 60% yields, respectively. Transformations with linear, branched, and cyclic aliphatic alkenes proceeded in good yields (**4n–r**). Ester- (**4s–v**), imide- (**4w**), sulfonamide- (**4x**), nitrile- (**4y**), and ether-functionalities (**4z**) were compatible with the reaction conditions. The alkene **1aa** containing a tosyloxy group participated in the reaction to give **4aa**. However, iodide **4aa'** derived from iodination of **4aa** was formed as a major product. Furthermore, alkenes containing heterocyclic rings, such as carbazole, coumarin, and chromone, could be converted to the corresponding products **4ab–ae** in moderate to good yields. *O*-Alkyl *D*-glucose derivative **1af** provided **4af** in a good yield. With 1,5-diene **1ag** containing both an internal and a terminal double bond, the carboboration occurred regioselectively at the terminal double bond to give **4ag** in 65% yield. The reaction of norbornene (**1ah**) afforded **4ah** in good yield and excellent

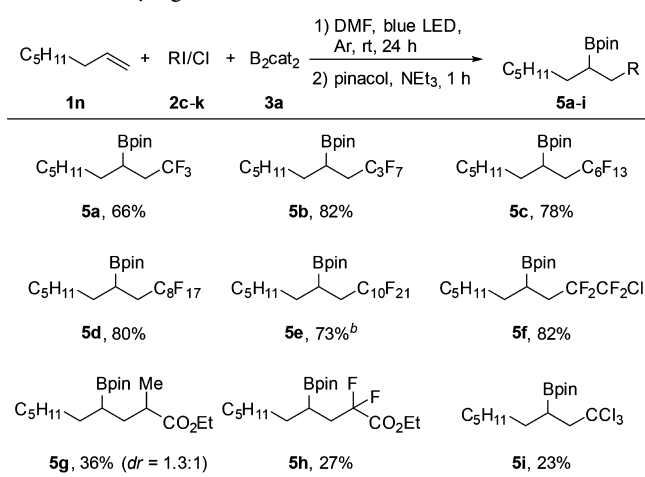
Table 2. Varying the Alkene Radical Acceptor^a

4b , R = H, 70%	4l , R = 1-Naphthyl, 71%
4c , R = 4-OMe, 80%	4m , R = 2-Naphthyl, 70%
4d , R = 4-Me, 79%	4n , R = C ₅ H ₁₁ , 91%
4e , R = 4-Cl, 75%	4o , R = C ₇ H ₁₅ , 84%
4f , R = 4-Br, 69%	4p , R = ^t Pr, 83%
4g , R = 4-CF ₃ , 71%	4q , R = ⁱ Bu, 88%
4h , R = 2-Me, 72%	4r , R = Cy, 86%
4i , R = 2-OAc, 63%	
4j , R = 3-Me, 77%	
4k , R = 3-OMe, 4-OMe, 75%	
	4s , R = Ph, 62%
	4t , R = PhCH ₂ CH ₂ , 59%
4u , R = H, 62%	4w , 50%
4v , R = Me, 66%, dr = 1.6:1	4x , 71%
4y , 47%	4aa , 27% (X = OTos)
4z , 40%	4aa' , 31% (X = I)
4ab , 70%	4ad , 78%
4ac , 74%	4af , 71% (dr = 1:1)
4ae , 51%	4ag , 65%
4ah , 87% (dr > 98:2)	4ai , 30% (dr > 98:2)
	4aj , 20% (dr = 10:1)

^aReaction conditions: **1** (0.50 mmol, 2.5 equiv), **2a** (0.20 mmol, 1.0 equiv), **3a** (0.40 mmol, 2.0 equiv), DMF (0.40 mL), 10 W blue LED, Ar, rt, 24 h; pinacol (0.80 mmol, 4.0 equiv), NEt₃ (0.70 mL), 1 h, isolated yields.

diastereoselectivity. Internal unstrained alkenes such as cyclohexene and (*E*)-4-octene gave the carboboration products **4ai** and **4aj** in significantly lower yields. Unfortunately, styrene did not react under optimized conditions.

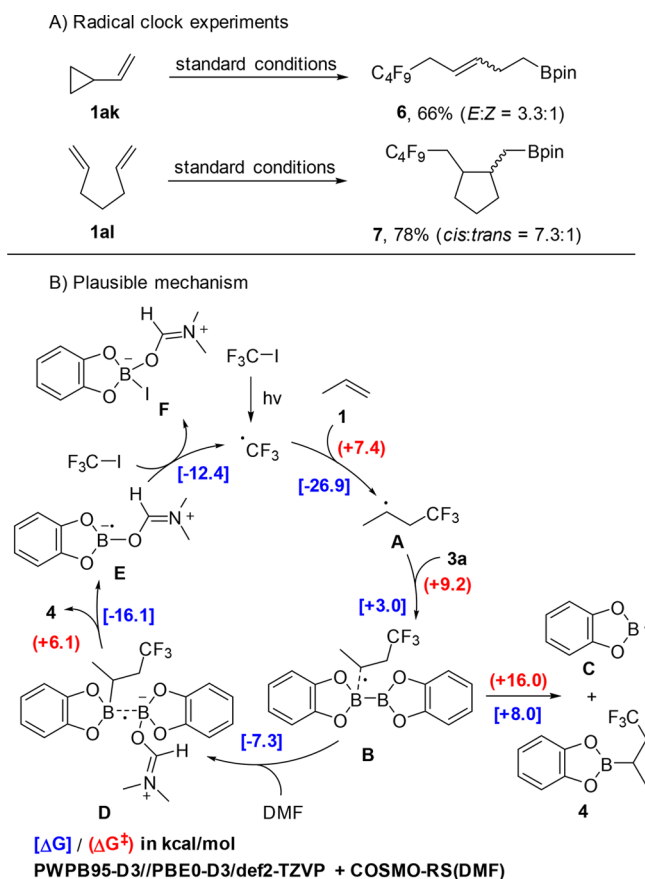
Variation of the C-radical precursor was studied next with 1-octene (**1n**) as the radical acceptor (Table 3). Using perfluoroalkyl iodides (CF₃(CF₂)_n-I) with *n* = 0, 2, 5, 7, and 9, the corresponding pinacolboronates **5a–e** were obtained in good yields. 1-Chlorotetrafluoro-2-iodoethane reacted chemoselectively by cleavage of the C–I bond to give **5f** in 82% yield. Lower yields for the carboboration were achieved with ethyl 2-iodopropanoate and ethyl difluoroiodoacetate as substrates (**5g**, **5h**). Carbon tetrachloride also engaged in the carboboration, albeit a lower yield was achieved (**5i**).

Table 3. Varying the Radical Precursor^a

^aReaction conditions: **1n** (0.50 mmol, 2.5 equiv), **2** (0.20 mmol, 1.0 equiv), **3a** (0.40 mmol, 2.0 equiv), DMF (0.40 mL), 10 W blue LED, Ar, rt, 24 h; pinacol (0.80 mmol, 4.0 equiv), NEt₃ (0.70 mL), 1 h, isolated yields. ^b1 mL of DMF was used.

To address the mechanism, radical clock experiments were conducted (Scheme 2A). Reaction of vinyl cyclopropane **1ak** with perfluorobutyl iodide (**2a**) and **3a** gave exclusively the ring-opening product **6**, indicating the radical nature of the carboboration.¹³ The radical mechanism was further supported by the carboboration of 1,6-heptadiene **1al**, which afforded the cyclic boronate **7** in 78% yield.

Scheme 2. Mechanistic Studies and Suggested Mechanism



A plausible mechanism exemplified for the reaction of propene, CF₃I, and bis(catecholato)diboron, which is supported by DFT calculations, is depicted in Scheme 2 (for details on the DFT calculations, see SI). The trifluoromethyl radical, generated by light-mediated C–I bond homolysis, adds with low barrier (7.4 kcal/mol) to propene to give the secondary alkyl radical A. The critical step is the subsequent formal homolytic substitution at boron of bis(catecholato)diboron (**3a**). Our DFT calculations reveal that alkyl radical A adds with a low barrier of 9.2 kcal/mol to the boron atom in **3a** to generate the adduct radical B. Addition is endothermic by 3.0 kcal/mol. The adduct B could then fragment with a barrier of 16.0 kcal/mol to the product boronic ester **4** along with the reactive boryl radical C. C would then be immediately trapped by the solvent DMF in a strongly exothermic step (–31.4 kcal/mol) to provide the DMF-stabilized boryl radical E.^{11c} However, considering the endothermic (+8 kcal/mol) fragmentation of B to C and **4**, radical B would rather fragment back to **3a** and A in a degenerate process. We therefore looked for alternative decomposition paths of intermediate B and found that it can be readily trapped without an enthalpic barrier by DMF to provide D (ΔG = –7.3 kcal/mol). Intermediate D is an interesting structure where the B/B interaction is best described as a B–B one-electron σ-bond (Figure 1).¹⁴ Fragmentation of D by cleavage of this B–B one-

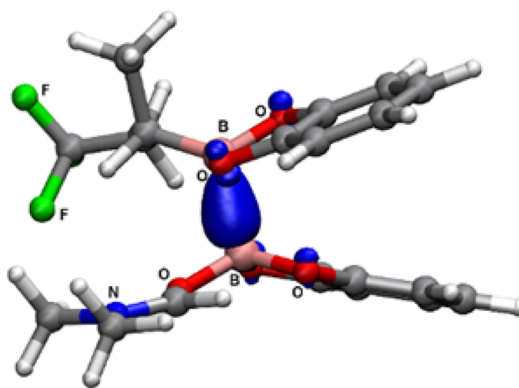


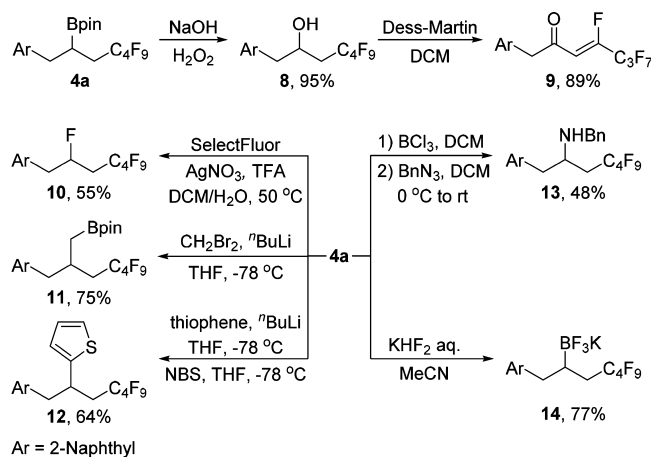
Figure 1. Spin density (PBE0/def2-TZVP, isosurface value = 0.02 au) of radical D, revealing the B–B single electron bond.

electron σ-bond has a low barrier of 6.1 kcal/mol and leads to product **4** and the DMF-complexed boryl radical E, which further reacts via SET reduction¹⁵ of CF₃I to F and the chain carrying trifluoromethyl radical.¹⁶ Hence, the radical cascade belongs to an electron-catalyzed process.¹⁷

Finally, to demonstrate the synthetic value of the difunctionalized adducts, we investigated follow-up chemistry using alkylboronate **4a** as a substrate (Scheme 3). Oxidation of **4a** afforded hydroxylated product **8** in 95% yield. Further oxidation of **8** with Dess–Martin periodinane and subsequent HF elimination gave the fluorinated enone **9**¹⁸ in excellent yield. Silver-catalyzed radical deboronofluorination of **4a** in aqueous solution provided the alkyl fluoride **10**.¹⁹ Other successful transformations of **4a** include homologation,²⁰ oxidative coupling with thiophene,²¹ and amination²² to afford functionalized products **11–13**. Treatment of **4a** with an aqueous KHF₂ solution gave the trifluoroborate salt **14** in 77% yield.

In summary, a new method for transition metal-free radical carboboration of unactivated alkenes was introduced. The three-component reaction proceeds on a broad range of unactivated alkenes under mild conditions and is experimentally easy to

Scheme 3. Follow-up Chemistry



conduct. The boron reagent and the starting alkyl iodides are commercially available. Control experiments and DFT calculations support the suggested radical mechanism. Importantly, the synthetic potential of the novel method was convincingly documented by a series of valuable follow-up transformations.

■ ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b03333.

Experimental procedures and analytical data for all compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*studer@uni-muenster.de

ORCID

Christian Mück-Lichtenfeld: 0000-0002-9742-7400

Armido Studer: 0000-0002-1706-513X

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the WWU Münster and the European Research Council (ERC Advanced Grant Agreement no. 692640) for financial support.

■ REFERENCES

- (1) For reviews, see: (a) McDonald, R. I.; Liu, G.; Stahl, S. S. *Chem. Rev.* **2011**, *111*, 2981. (b) Zeng, X. *Chem. Rev.* **2013**, *113*, 6864. (c) Greenhalgh, M. D.; Jones, A. S.; Thomas, S. P. *ChemCatChem* **2015**, *7*, 190. (d) Hoffmann, R. W. *Chem. Soc. Rev.* **2016**, *45*, 577. (e) Coombs, J. R.; Morken, J. P. *Angew. Chem., Int. Ed.* **2016**, *55*, 2636.
- (2) For reviews, see: (a) Shimizu, Y.; Kanai, M. *Tetrahedron Lett.* **2014**, *55*, 3727. (b) Neeve, E. C.; Geier, S. J.; Mkhallid, I. A. I.; Westcott, S. A.; Marder, T. B. *Chem. Rev.* **2016**, *116*, 9091. (c) Cuenca, A. B.; Shishido, R.; Ito, H.; Fernández, E. *Chem. Soc. Rev.* **2017**, *46*, 415. (d) Fyfe, J. W. B.; Watson, A. J. B. *Chem.* **2017**, *3*, 31. (e) Collins, B. S. L.; Wilson, C. M.; Myers, E. L.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2017**, *56*, 11700. For recent examples, see: (f) Daini, M.; Suginome, M. *J. Am. Chem. Soc.* **2011**, *133*, 4758. (g) Yoshida, H.; Kageyuki, I.; Takaki, K. *Org. Lett.* **2013**, *15*, 952. (h) Semba, K.; Nakao, Y. *J. Am. Chem. Soc.* **2014**, *136*, 7567. (i) Smith, K. B.; Logan, K. M.; You, W.; Brown, M. K. *Chem. - Eur. J.* **2014**, *20*, 12032. (j) Jia, T.; Cao, P.; Wang, B.; Lou, Y.; Yin, X.; Wang, M.; Liao, J. *J. Am. Chem. Soc.* **2015**, *137*, 13760. (k) Logan, K. M.; Smith,

K. B.; Brown, M. K. *Angew. Chem., Int. Ed.* **2015**, *54*, 5228. (l) Yang, K.; Song, Q. *Org. Lett.* **2016**, *18*, 5460. (m) Yang, K.; Song, Q. *J. Org. Chem.* **2016**, *81*, 1000. (n) Semba, K.; Ohtagaki, Y.; Nakao, Y. *Org. Lett.* **2016**, *18*, 3956. (o) Huang, Y.; Smith, K. B.; Brown, M. K. *Angew. Chem., Int. Ed.* **2017**, *56*, 13314. (p) Logan, K. M.; Brown, M. K. *Angew. Chem., Int. Ed.* **2017**, *56*, 851. (q) Chen, B.; Cao, P.; Yin, X.; Liao, Y.; Jiang, L.; Ye, J.; Wang, M.; Liao, J. *ACS Catal.* **2017**, *7*, 2425. (r) Kim, N.; Han, J. T.; Ryu, D. H.; Yun, J. *Org. Lett.* **2017**, *19*, 6144. (s) Kageyuki, I.; Osaka, I.; Takaki, K.; Yoshida, H. *Org. Lett.* **2017**, *19*, 830. (t) Logan, K. M.; Sardini, S. R.; White, S. D.; Brown, M. K. *J. Am. Chem. Soc.* **2018**, *140*, 159. (u) Liu, Z.; Ni, H.; Zeng, T.; Engle, K. M. *J. Am. Chem. Soc.* **2018**, *140*, 3223.

(3) For reviews, see: (a) Leonori, D.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2015**, *54*, 1082. (b) Sandford, C.; Aggarwal, V. K. *Chem. Commun.* **2017**, *53*, 5481.

(4) For transition metal-free 1,2-carboboration of alkynes, see: (a) Cade, I. A.; Ingleson, M. J. *Chem. - Eur. J.* **2014**, *20*, 12874. (b) Devillard, M.; Brousses, R.; Miqueu, K.; Bouhadir, G.; Bourissou, D. *Angew. Chem., Int. Ed.* **2015**, *54*, 5722. (c) Roscales, S.; Csáky, A. G. *Org. Lett.* **2015**, *17*, 1605. (d) Yamazaki, A.; Nagao, K.; Iwai, T.; Ohmiya, H.; Sawamura, M. *Angew. Chem., Int. Ed.* **2018**, *57*, 3196.

(5) Melen, R. L.; Wilkins, L. C.; Kariuki, B. M.; Wadepohl, H.; Gade, L. H.; Hashmi, A. S. K.; Stephan, D. W.; Hansmann, M. M. *Organometallics* **2015**, *34*, 4127.

(6) Sanzone, J. R.; Hu, C. T.; Woerpel, K. A. *J. Am. Chem. Soc.* **2017**, *139*, 8404.

(7) 1,2-Carboration involving boryl radical addition and subsequent cyclization onto alkenes and alkynes was recently reported, see: (a) Ren, S.-C.; Zhang, F.-L.; Qi, J.; Huang, Y.-S.; Xu, A.-Q.; Yan, H.-Y.; Wang, Y.-F. *J. Am. Chem. Soc.* **2017**, *139*, 6050. (b) Watanabe, T.; Hirose, D.; Curran, D. P.; Taniguchi, T. *Chem. - Eur. J.* **2017**, *23*, 5404.

(8) (a) Hartmann, M.; Li, Y.; Studer, A. *J. Am. Chem. Soc.* **2012**, *134*, 16516. (b) Li, Y.; Studer, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 8221. (c) Li, Y.; Hartmann, M.; Daniliuc, C. G.; Studer, A. *Chem. Commun.* **2015**, *51*, 5706. (d) Hartmann, M.; Li, Y.; Mück-Lichtenfeld, C.; Studer, A. *Chem. - Eur. J.* **2016**, *22*, 3485. (e) Hartmann, M.; Li, Y.; Studer, A. *Org. Biomol. Chem.* **2016**, *14*, 206. (f) Kischkewitz, M.; Okamoto, K.; Mück-Lichtenfeld, C.; Studer, A. *Science* **2017**, *355*, 936. (g) Tang, X.; Studer, A. *Chem. Sci.* **2017**, *8*, 6888. (h) Tang, X.; Studer, A. *Angew. Chem., Int. Ed.* **2018**, *57*, 814. (i) Gerleve, C.; Kischkewitz, M.; Studer, A. *Angew. Chem., Int. Ed.* **2018**, *57*, 2441.

(9) (a) Mo, F.; Jiang, Y.; Qiu, D.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 1846. (b) Yu, J.; Zhang, L.; Yan, G. *Adv. Synth. Catal.* **2012**, *354*, 2625. (c) Qiu, D.; Jin, L.; Zheng, Z.; Meng, H.; Mo, F.; Zhang, X.; Zhang, Y.; Wang, J. *J. Org. Chem.* **2013**, *78*, 1923. (d) Qiu, D.; Zhang, Y.; Wang, J. *Org. Chem. Front.* **2014**, *1*, 422. (e) Qiu, D.; Meng, H.; Jin, L.; Tang, S.; Wang, S.; Mo, F.; Zhang, Y.; Wang, J. *Org. Synth.* **2014**, *91*, 106. (f) Ahammed, S.; Nandi, S.; Kundu, D.; Ranu, B. C. *Tetrahedron Lett.* **2016**, *57*, 1551. (g) Chen, K.; Zhang, S.; He, P.; Li, P. *Chem. Sci.* **2016**, *7*, 3676. (h) Mfuh, A. M.; Doyle, J. D.; Chhetri, B.; Arman, H. D.; Larionov, O. V. *J. Am. Chem. Soc.* **2016**, *138*, 2985. (i) Mfuh, A. M.; Nguyen, V. T.; Chhetri, B.; Burch, J. E.; Doyle, J. D.; Nesterov, V. N.; Arman, H. D.; Larionov, O. V. *J. Am. Chem. Soc.* **2016**, *138*, 8408. (j) Zhang, L.; Jiao, L. *J. Am. Chem. Soc.* **2017**, *139*, 607. (k) Candish, L.; Teders, M.; Glorius, F. *J. Am. Chem. Soc.* **2017**, *139*, 7440. (l) Liu, W.; Yang, X.; Gao, Y.; Li, C.-J. *J. Am. Chem. Soc.* **2017**, *139*, 8621. (m) Zhang, L.; Jiao, L. *Chem. Sci.* **2018**, *9*, 2711. With Ir-catalysis: (n) Jiang, M.; Yang, H.; Fu, H. *Org. Lett.* **2016**, *18*, 5248. With Zn-catalysis: (o) Bose, S. K.; Deifsenberger, A.; Eichhorn, A.; Steel, P. G.; Lin, Z.; Marder, T. B. *Angew. Chem., Int. Ed.* **2015**, *54*, 11843. (p) Qi, X.; Jiang, L.-B.; Zhou, C.; Peng, J.-B.; Wu, X.-F. *ChemistryOpen* **2017**, *6*, 345. For a review, see: (q) Mo, F.; Qiu, D.; Zhang, Y.; Wang, J. *Acc. Chem. Res.* **2018**, *51*, 496.

(10) (a) Yoshimura, A.; Takamachi, Y.; Han, L.-B.; Ogawa, A. *Chem. - Eur. J.* **2015**, *21*, 13930. (b) Yoshimura, A.; Takamachi, Y.; Mihara, K.; Saeki, T.; Kawaguchi, S.-i.; Han, L.-B.; Nomoto, A.; Ogawa, A. *Tetrahedron* **2016**, *72*, 7832.

(11) For cyclization of an alkyl radical onto boron, see (a) Batey, R. A.; Smil, D. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 1798. Intermolecular trapping of alkyl radicals with diboron compounds: (b) Bose, S. K.;

Fucke, K.; Liu, L.; Steel, P. G.; Marder, T. B. *Angew. Chem., Int. Ed.* **2014**, *53*, 1799. (c) Fawcett, A.; Pradeilles, J.; Wang, Y.; Mutsuga, T.; Myers, E. L.; Aggarwal, V. K. *Science* **2017**, *357*, 283. (d) Hu, D.; Wang, L.; Li, P. *Org. Lett.* **2017**, *19*, 2770. Mn-catalyzed: (e) Atack, T. C.; Cook, S. P. *J. Am. Chem. Soc.* **2016**, *138*, 6139. Cu-mediated radical borylation, see: (f) Yang, C.-T.; Zhang, Z.-Q.; Tajuddin, H.; Wu, C.-C.; Liang, J.; Liu, J.-H.; Fu, Y.; Czyzewska, M.; Steel, P. G.; Marder, T. B.; Liu, L. *Angew. Chem., Int. Ed.* **2012**, *51*, 528. (g) Ito, H.; Kubota, K. *Org. Lett.* **2012**, *14*, 890. (h) Kim, J. H.; Chung, Y. K. *RSC Adv.* **2014**, *4*, 39755. (i) Bose, S. K.; Brand, S.; Omoregie, H. O.; Haehnel, M.; Maier, J.; Bringmann, G.; Marder, T. B. *ACS Catal.* **2016**, *6*, 8332. Ni-mediated radical borylation, see: (j) Dudnik, A. S.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, *134*, 10693. (k) Yi, J.; Liu, J.-H.; Liang, J.; Dai, J.-J.; Yang, C.-T.; Fu, Y.; Liu, L. *Adv. Synth. Catal.* **2012**, *354*, 1685. (l) Li, C.; Wang, J.; Barton, L. M.; Yu, S.; Tian, M.; Peters, D. S.; Kumar, M.; Yu, A. W.; Johnson, K. A.; Chatterjee, A. K.; Yan, M.; Baran, P. S. *Science* **2017**, *356*, eaam7355.

(12) Review on boron in radical chemistry: Ollivier, C.; Renaud, P. *Chem. Rev.* **2001**, *101*, 3415.

(13) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

(14) (a) Hoefelmeyer, J. D.; Gabbai, F. G. *J. Am. Chem. Soc.* **2000**, *122*, 9054. (b) Hübner, A.; Diehl, A. M.; Diefenbach, M.; Endeward, B.; Bolte, M.; Lerner, H.-W.; Holthausen, M.; Wagner, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 4832.

(15) Alternatively, the DMF-boryl radical adduct **E** can react with CF₃I via I-abstraction, see (a) Tehfe, M.-A.; Monot, J.; Makhoulf Brahmī, M.; Bonin-Dubarle, H.; Curran, D. P.; Malacria, M.; Fensterbank, L.; Lacote, E.; Lalevéé, J.; Fouassier, J.-P. *Polym. Chem.* **2011**, *2*, 625. (b) Pan, X.; Lacôte, E.; Lalevéé, J.; Curran, D. P. *J. Am. Chem. Soc.* **2012**, *134*, 5669. Review: (c) Curran, D. P.; Solovye, A.; Makhoulf Brahmī, M.; Fensterbank, L.; Malacria, M.; Lacote, E. *Angew. Chem., Int. Ed.* **2011**, *50*, 10294.

(16) We also looked at the possible reaction of the DMF complexed diborane **3a**–DMF with the secondary alkyl radical **A**. However, we could not locate an intermediate with a covalent DMF–boron bond but only a noncovalent complex, which is formed with a positive ΔG .

(17) (a) Studer, A.; Curran, D. P. *Nat. Chem.* **2014**, *6*, 765. (b) Studer, A.; Curran, D. P. *Angew. Chem., Int. Ed.* **2016**, *55*, 58.

(18) (a) Kurykin, M. A.; Vol'pin, I. M.; German, L. S. *J. Fluorine Chem.* **1996**, *80*, 9. (b) Sato, K.; Higashinagata, M.; Yuki, T.; Tarui, A.; Omote, M.; Kumadaki, I.; Ando, A. *J. Fluorine Chem.* **2008**, *129*, 51. (c) Sato, K.; Yamazoe, S.; Akashi, Y.; Hamano, T.; Miyamoto, A.; Sugiyama, S.; Tarui, A.; Omote, M.; Kumadaki, I.; Ando, A. *J. Fluorine Chem.* **2010**, *131*, 86.

(19) Li, Z.; Wang, Z.; Zhu, L.; Tan, X.; Li, C. *J. Am. Chem. Soc.* **2014**, *136*, 16439.

(20) Sonawane, R. P.; Jheengut, V.; Rabalakos, C.; Larouche-Gauthier, R.; Scott, H. K.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2011**, *50*, 3760.

(21) Bonet, A.; Odachowski, M.; Leonori, D.; Essafi, S.; Aggarwal, V. K. *Nat. Chem.* **2014**, *6*, 584.

(22) Hupe, E.; Marek, I.; Knochel, P. *Org. Lett.* **2002**, *4*, 2861.