

# Electrochemical Hydroboration of Alkynes

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**Abstract:** Herein we reported the electrochemical hydroboration of alkynes by using  $B_2Pin_2$  as the boron source. This unprecedented reaction manifold was applied to a broad range of alkynes, giving the hydroboration products in good to excellent yields without the need of a metal catalyst or a hydride source. This transformation relied on the possible electrochemical oxidation of an in situ formed borate. This anodic oxidation performed in an undivided cell allowed the formation of a putative boryl radical, which reacted on the alkyne.

In the realm of organic synthesis organoboron compounds play an important role to build up complex molecules.<sup>[1]</sup> In addition, boron-containing molecules found applications in medicinal chemistry, which culminated in the approval of boron-containing drugs (e.g. Dutogliptin).<sup>[2]</sup> These key building blocks showcase various and specific reactivities, which provide them a pivotal role in the arsenal of organic chemists to design retrosynthetic disconnections.<sup>[3]</sup> For instance, organoboron compounds have been widely employed in allylation, aldolisation, or homologation reactions and it is important to notice that the hydroboration and the Suzuki-Miyaura cross-coupling reactions were celebrated by the Nobel prize given to H. C. Brown and A. Suzuki in 1979 and 2010, respectively. Among these synthetically useful reactions, the hydroboration of an alkene or an alkyne is of paramount interest and has been widely studied for almost half a century.<sup>[4]</sup> These endeavors gave birth to noble and non-noble metal catalyzed processes.<sup>[5]</sup>

In parallel, the chemistry of boryl radicals was recently highlighted as a straightforward alternative to introduce a boron residue.<sup>[6]</sup> With that respect, Curran, Lacôte, Fensterbank and Malacria explored the formation and reactivity of these radicals from NHC-borane. They demonstrated the possibility to form the radical using usual initiators, such as peroxides or AIBN, for instance.<sup>[7]</sup> Among the studied reactions, the addition of the boryl radical to olefin and alkynes, pioneered by Lalevée and Curran,<sup>[8]</sup> has been less explored and the development of new protocols is still highly desirable to extend the portfolio of possible reactions. Very recently, the photocatalyzed formation of boryl radicals using iridium catalysts has been reported (Scheme 1). This new method was applied to the addition of NHC-boron residues on fluorinated olefins and aryls, according to an addition/fluoride elimination sequence<sup>[9]</sup> and to the hydroboration of imines,<sup>[10]</sup> alkenes<sup>[11]</sup> and electron poor aromatic derivatives.<sup>[12]</sup> Importantly, in contrast to the formation of boryl radicals from NHC-borane, their formation from diboron compounds remains scarce.<sup>[13]</sup> Within the last five years organic electrochemistry has known an impressive renewal of interest. Indeed, electrochemical synthesis, by replacing hazardous

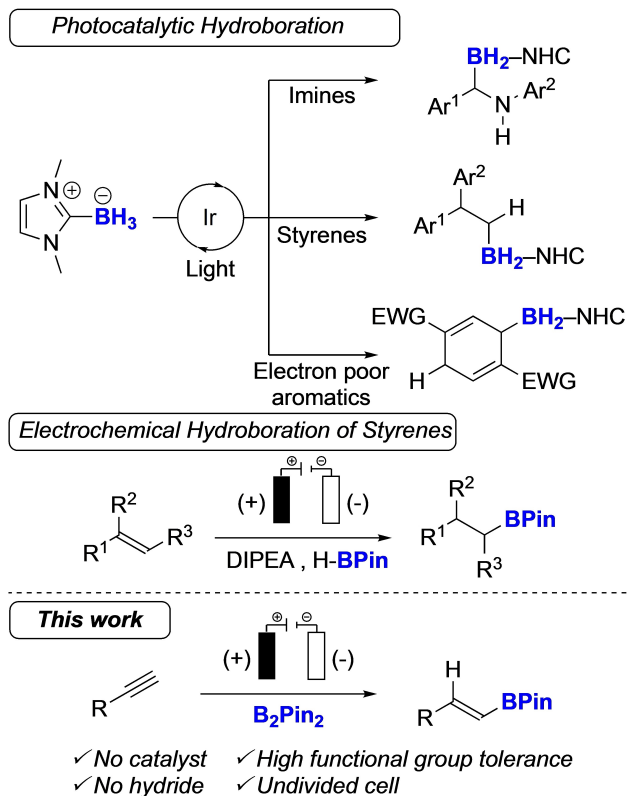
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Scheme 1. State of the art and present work.

chemical redox reagents by electrons, avoids the generation of wastes and if electricity is produced from renewable sources, it can be considered as a green process.<sup>[14]</sup> As part of our program to develop straightforward access to boron-containing molecules,<sup>[15]</sup> we sought to use organic electrochemistry to generate boryl radicals that would be used as an unprecedented reaction manifold in the hydroboration of alkynes. Worth of note, during the preparation of this manuscript, Qing and co-workers reported the electrochemical hydroboration of styrene using HBpin as the boron source and DIPEA as auxiliary.<sup>[16]</sup> Herein, we report an original electrochemical hydroboration of terminal alkyne formation from the readily available B<sub>2</sub>Pin<sub>2</sub> using electron as a green redox reagent.

As a model reaction we chose phenylacetylene as the substrate and B<sub>2</sub>Pin<sub>2</sub> as the boron source. After extensive optimization, we found that the open-air reaction performed in MeOH using *n*-Bu<sub>4</sub>NBF<sub>4</sub> as the electrolyte (0.05 M), stainless steel electrodes (SST) at both the cathode and anode along with a constant current of 10 mA and a total charge of 2 F mol<sup>-1</sup> were required to ensure the formation of **1** in 84% yield (Table 1, entry 1).

Indeed, the use of EtOH or *i*-PrOH did not afford **1** with decent yields (entry 2, < 25%), while the use of other electrodes was deleterious for the reaction outcome (entries 3 and 4). Then, a total charge of 1 F mol<sup>-1</sup> or a decrease of the electrolyte concentration gave lower yields (entries 5 and 6). Finally, control experiments revealed that *i*) the reaction did not occur when B<sub>2</sub>Pin<sub>2</sub> was replaced by H-BPin (entry 7), *ii*) the reaction did not occur in the absence of current (entry 8)

and *iii*) no reaction occurred with MeONa in the absence of current (entry 9), precluding a base assisted hydroboration reaction.<sup>[17]</sup> Then, to ascertain the versatility and to ensure the reproducibility of our electrochemical hydroboration reaction, a sensitivity assessment regarding the reaction parameters was performed (Table 1).<sup>[18]</sup> This hydroboration protocol was found sensitive to the presence of water and to the temperature, while the yield slightly decreased (*c.a.* 25% less) when the scale of the reaction was increased.<sup>[19]</sup>

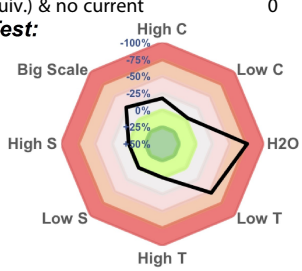
Having optimized the reaction conditions, we explored the scope of this catalyst- and hydride-free hydroboration reaction (Scheme 2). First, a large panel of aryl substituted terminal alkynes was tested. Aryls substituted with a methyl group provided the corresponding vinyl boronate derivatives (**2–4**) in good to excellent yields, whatever the substitution pattern. Other electron donating groups like methoxy, phenyl, *N,N*-dimethyl and non-protected amines were suitable affording the products (**6–11**) in good to excellent yields. Interestingly, the reaction was tolerant to the presence of a BPin group, a benzylic alcohol as well as an acetal, furnishing the synthetically useful hydroborated products **12**, **13** and **14**. Halogens and CF<sub>3</sub> substituents on the aromatic did not affect the efficiency of the reaction, offering an access to compounds **15–20** in good to excellent yields. Regarding the presence of electron-withdrawing on the aromatic, the aldehyde **21** and the ester **22** were synthesized in moderate to good yields, at the cost of an increase of the charge from 2.0 to 2.5 F mol<sup>-1</sup> for **22**. Similarly, naphthyl derivatives **23** and **24** were readily obtained using 2.5 F mol<sup>-1</sup>. This methodology was applied to pyridine derivative, giving **25** in 63% isolated yield. Then, alkyl substituted terminal alkynes were tested. The presence of a primary, secondary and tertiary alcohols, as well as a phthalimide did not affect the outcome of the reaction and the hydroborated products **26–31** were isolated in moderate to excellent yields. The reaction was selective to alkyne, since an enyne was selectively functionalized on the alkyne residue (**32**). Interestingly, the cyclopropyl derivative **33** was obtained with an excellent 70% NMR yield and a modest 39% isolated yield, due to a tedious purification. Surprisingly, the vinyl boronates **34–39** were isolated as a mixture of  $\alpha$ - and  $\beta$ -isomers in moderate yields, the  $\beta$ -isomer being the major one in all cases.<sup>[20]</sup> Pleasingly, the scope of this electrochemical hydroboration reaction was extended to internal alkynes. Using one equivalent of K<sub>2</sub>CO<sub>3</sub> as an additive, the boronic esters **40** and **41** were isolated in 49% and 58% yield, respectively. Note that in the case of **40**, a 70:30 mixture of  $\alpha$ - and  $\beta$ -isomers were obtained. Finally, this methodology was applied to complex molecules to demonstrate the synthetic utility of the reaction. The steroids derivatives **42** and **43** were obtained in 66% and 37% isolated yields. Regarding **43**, the low efficiency of the process was explained by the poor solubility of the starting material in the solvent of the reaction. Finally, the  $\alpha$ -tocopherol derivative **44** was isolated in 27% yield.

To get further insight into the mechanism, the reaction was carried out in the presence of CD<sub>3</sub>OD instead of CH<sub>3</sub>OH (Scheme 3, Eq. (1)).<sup>[19]</sup> This control experiment furnished the deuterated product [**D**]-**1** in 42% yield with a complete

**Table 1.** Optimization of the reaction and sensitivity tests.

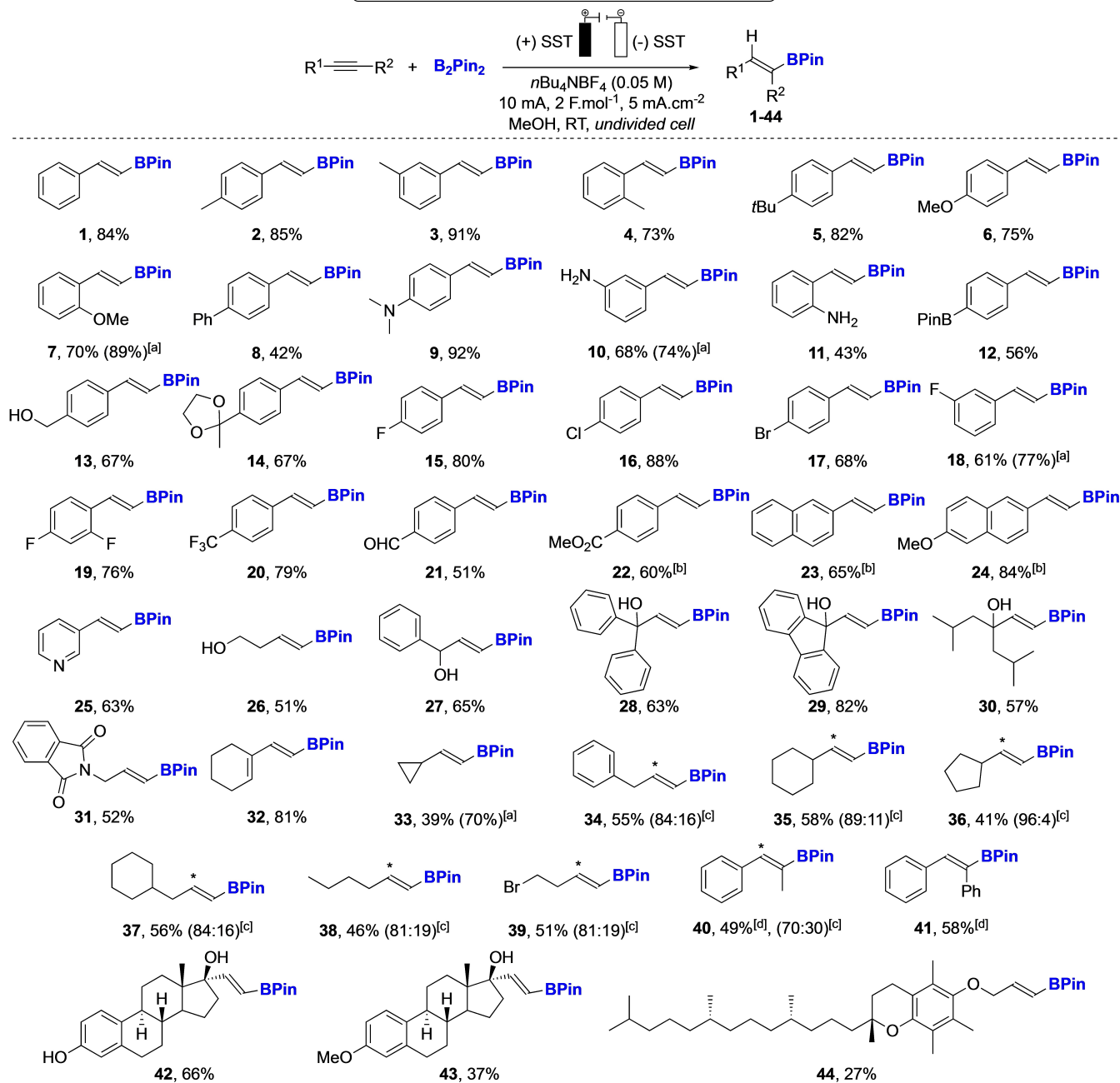
Entry	Variation from standard conditions	Yield [%] <sup>[a]</sup>
1	none	84 <sup>[b]</sup>
2	EtOH or <i>i</i> -PrOH instead of MeOH	< 25
3	graphite electrodes instead of SST	0
4	platinum electrodes instead of SST	< 30
5	1 F mol <sup>-1</sup> instead of 2 F mol <sup>-1</sup>	51
6	<i>n</i> -Bu <sub>4</sub> NBF <sub>4</sub> : 0.025 M instead of 0.05 M	75
7	H-BPin instead of B <sub>2</sub> Pin <sub>2</sub>	0
8	no current	0
9	NaOMe (1 equiv.) & no current	0

**Sensitivity Test:**



Reaction conditions: phenylacetylene (0.2 mmol), B<sub>2</sub>Pin<sub>2</sub> (0.4 mmol), MeOH (4 mL), r.t. [a] NMR yield. [b] Isolated yield. C: concentration, T: temperature, S: electrodes surface.

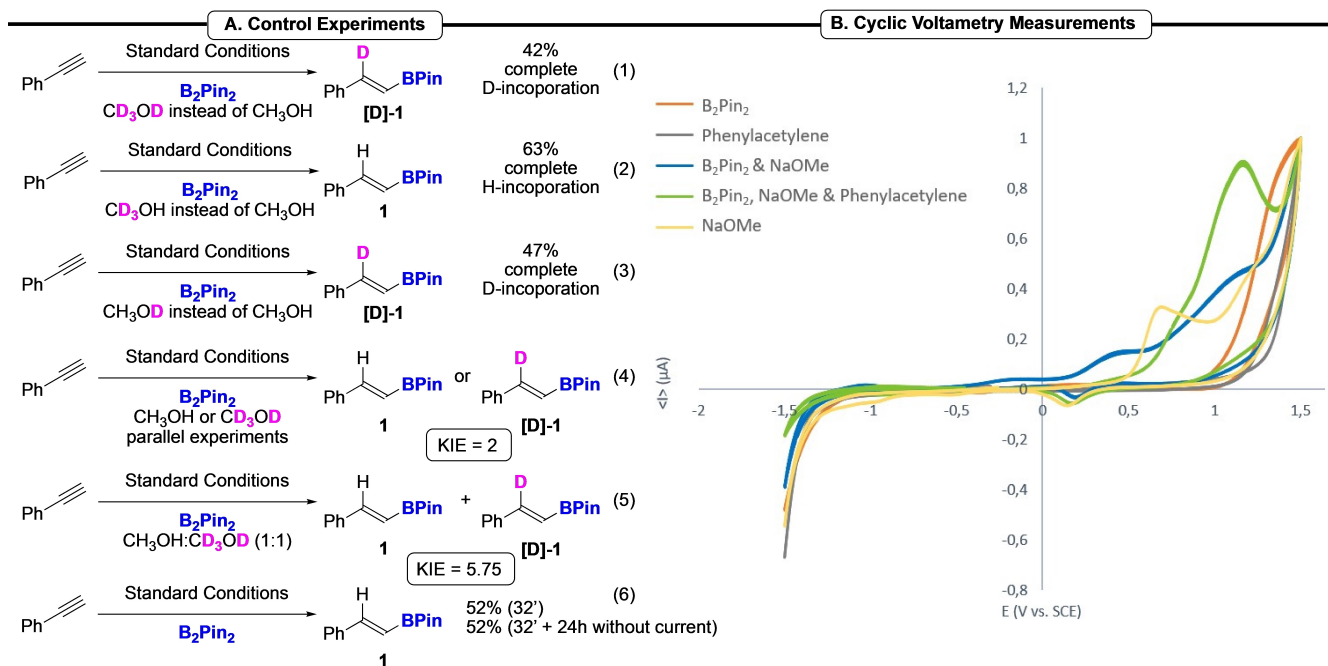
## Electrochemical Hydroboration of Alkynes



**Scheme 2.** Exploration of the scope of the electrochemical hydroboration of alkynes. All data are the average of two runs. [a] Yield determined by  $^1\text{H}$  NMR by using DMF as an internal standard. [b]  $2.5 \text{ F mol}^{-1}$  instead of  $2 \text{ F mol}^{-1}$ . [c] Determined by  $^1\text{H}$  NMR on the crude reaction mixture. [d] 1 equiv. of  $\text{K}_2\text{CO}_3$  was added.

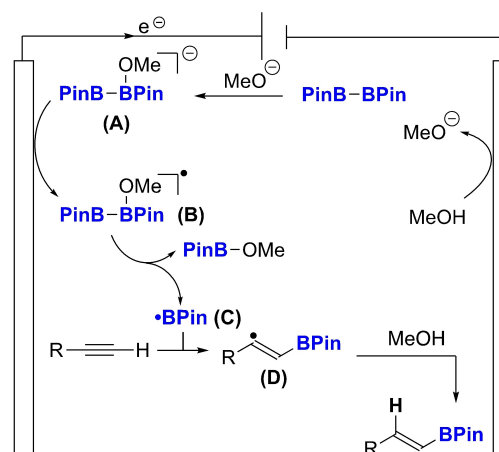
incorporation of deuterium, which demonstrates that the hydrogen atom comes from the solvent. Then, to determine if the H abstraction results from the cleavage of the C–H or O–H bond of the solvent, reactions were carried out with  $\text{CD}_3\text{OH}$  and  $\text{CH}_3\text{OD}$ , independently (Scheme 3, Eqs. (2) & (3)). These results clearly highlight that the H results from the cleavage of the O–H bond, despite its higher BDE compared to the C–H bond. Finally, we studied the kinetic isotopic effect (KIE). Parallel reactions in  $\text{CH}_3\text{OH}$  or  $\text{CD}_3\text{OD}$  revealed a  $\text{KIE} = 2$ , while a KIE of

5.75 was measured in a 1:1 mixture of  $\text{CH}_3\text{OH}/\text{CD}_3\text{OD}$ , suggesting that the hydrogen abstraction from the solvent after the addition of the boryl radical might be the rate determining step (Scheme 3, Eqs. (4) & (5)). Finally, to ascertain the reaction does not result from the presence of metallic salts released from the electrodes, the electrochemical reaction was stopped after 32 minutes ( $1 \text{ F mol}^{-1}$ ) and the reaction mixture was stirred within the electrochemical cell for an additional 24 h (Scheme 3, Eq. (6)). Pleasingly, we did not observe an increase



**Scheme 3.** Mechanistic study: control experiments, CV measurements.  $n\text{Bu}_4\text{NBF}_4$  was used as the electrolyte for the cyclic voltammetry measurements (see Supporting Information for details). All potentials are reported vs. SCE.

of the reaction yield after this additional stirring. This observation precluded a background hydroboration reaction catalyzed by metallic salts released from the SST electrodes. Then, since we surmised a possible oxidation of a transient borate species, we carried out cyclic voltammetry (CV) experiments to depict a possible reaction mechanism. The CV measurements of  $\text{B}_2\text{Pin}_2$  (orange), NaOMe (yellow),  $\text{B}_2\text{Pin}_2$  and NaOMe (blue), phenylacetylene (grey) and the mixture of  $\text{B}_2\text{Pin}_2$ , NaOMe and phenylacetylene (green) in MeOH were carried out.<sup>[19]</sup> To mimic the formation of the alkoxide, which is unlikely during the CV measurement due to the tiny surface of the anode, NaOMe was added to the  $\text{B}_2\text{Pin}_2$  species. The CV analysis of the mixture  $\text{B}_2\text{Pin}_2/\text{NaOMe}$  (blue) demonstrated an irreversible oxidation wave at +1.2 V vs. SCE, that is not observed on the CV measurement of the  $\text{B}_2\text{Pin}_2$  (orange). Moreover, a similar oxidation wave was observed on the mixture of all reagents (green). Finally, no oxidation nor reduction of  $\text{B}_2\text{Pin}_2$  or phenylacetylene was observed, while a completely different oxidation wave was witnessed with NaOMe (yellow). Hence, with these experimental data in hand, we suggested the following plausible mechanism (Scheme 4). First, we surmised the formation of the boryl radical from the oxidation of an in situ formed borate **A**.<sup>[21]</sup> Indeed, the coordination of an alkoxide, here generated by the reduction of the solvent at the cathode (i.e. MeOH), to the empty orbital of a boron atom of  $\text{B}_2\text{Pin}_2$  might give birth to this species.<sup>[17]</sup> Then, the anodic oxidation of the latter would generate **B**, that would quickly collapse into the boryl radical **C** (i.e.  $\bullet\text{BPin}$ ) and  $\text{MeOBPin}$ . This boryl radical is probably a 7-electrons centered one, rather than a less stable 5-electrons, thanks to the coordination of the solvent to the empty orbital of the boron atom.<sup>[6b]</sup> This radical would then



**Scheme 4.** Plausible Mechanism.

undergo an addition reaction onto the alkyne to form the corresponding highly reactive vinyl radical **D**. Then, taking into account the above-mentioned results from the labelling experiments, a plausible pathway to explain the abstraction of the H from the stronger O–H bond is suggested.<sup>[22]</sup> The coordination of a boron species, which can act as a Lewis acid, to MeOH might decrease the O–H bond dissociation energy and allow the H abstraction by the vinyl radical. Then, the resulting O radical could be reduced at the cathode to complete the redox cycle.<sup>[23]</sup> Alternatively, the methoxide anion, generated at the cathode, might act as a hydrogen donor as well. Although its concentration in the reaction media is much lower than MeOH this pathway can be productive as well.<sup>[24]</sup>

In conclusion, we developed the first electrochemical hydroboration of alkynes. This catalyst- and hydride-free methodology provides a greener alternative for the synthesis of borylated alkenes. Furthermore, the use of stainless steel electrodes makes the process cost-effective. According to a possible anodic oxidation of an in situ formed borate species, a putative boryl radical derived from the cleavage of the B–B bond of  $B_2Pin_2$  was added to a large panel of alkynes, including complex molecules such as steroids. The resulting products were obtained in good to excellent yields.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** alkynes · anodic oxidation · boryl radical · electrochemistry · hydroboration

- [1] a) *Synthesis and Applications of Organoboron Compounds.*, Eds. E. Fernandez, A. Whiting, Springer **2015**; For selected reviews, see: b) J. Carreras, A. Caballero, P. J. Pérez, *Chem. Asian J.* **2019**, *14*, 329–343; c) J. W. B. Fyfe, A. J. B. Watson, *Chem* **2017**, *3*, 31–55; d) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483; e) L. Xu, S. Zhang, P. Li, *Chem. Soc. Rev.* **2015**, *44*, 8848–8858; f) A. J. J. Lennox, G. C. Lloyd-Jones, *Chem. Soc. Rev.* **2014**, *43*, 412–443; g) G. Duret, R. Quinlan, P. Bissere, N. Blanchard, *Chem. Sci.* **2015**, *6*, 5366–5382; h) C. Ollivier, P. Renaud, *Chem. Rev.* **2001**, *101*, 3415–3434; i) S. Namirembe, J. P. Morken, *Chem. Soc. Rev.* **2019**, *48*, 3464–3474.
- [2] F. Yang, M. Zhu, J. Zhang, H. Zhou, *MedChemComm* **2018**, *9*, 201–211.
- [3] a) F. W. Friese, A. Studer, *Chem. Sci.* **2019**, *10*, 8503–8518; b) E. C. Neeve, S. J. Geier, I. A. I. Mkhallid, S. A. Westcott, T. B. Marder, *Chem. Rev.* **2016**, *116*, 9091–9161; c) T. Ishiyama, N. Miyaura, *Chem. Rec.* **2004**, *3*, 271–280; d) I. A. I. Mkhallid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890–931; e) A. Ros, R. Fernández, J. M. Lassaletta, *Chem. Soc. Rev.* **2014**, *43*, 3229–3243; f) V. Snieckus, *Chem. Rev.* **1990**, *90*, 879–933.
- [4] a) K. Burgess, M. J. Ohlmeyer, *Chem. Rev.* **1991**, *91*, 1179–1191; b) C. M. Crudden, D. Edwards, *Eur. J. Org. Chem.* **2003**, *2003*, 4695–4712; c) C. M. Vogels, S. A. Westcott, *Curr. Org. Chem.* **2005**, *9*, 687–699; d) J.-B. Chen, A. Whiting, *Synthesis* **2018**, *50*, 3843–3861.
- [5] J. V. Obligacion, P. J. Chirik, *Nat. Chem. Rev.* **2018**, *2*, 15–34.
- [6] a) D. P. Curran, A. Solovyev, M. Makhlof Brahmī, L. Fensterbank, M. Malacria, E. Lacôte, *Angew. Chem. Int. Ed.* **2011**, *50*, 10294–10317; *Angew. Chem.* **2011**, *123*, 10476–10500; b) T. Taniguchi, *Eur. J. Org. Chem.* **2019**, 6308–6319.
- [7] a) S.-H. Ueng, M. M. Brahmī, E. Derat, L. Fensterbank, E. Lacôte, M. Malacria, D. P. Curran, *J. Am. Chem. Soc.* **2008**, *130*, 10082–10083; b) S.-H. Ueng, A. Solovyev, X. Yuan, S. J. Geib, L. Fensterbank, E. Lacôte, M. Malacria, M. Newcomb, J. C. Walton, D. P. Curran, *J. Am. Chem. Soc.* **2009**, *131*, 11256–11262.
- [8] a) J. Lalevé, N. Blanchard, A.-C. Chany, M.-A. Tehfe, X. Allonas, J.-P. Fouassier, *J. Phys. Org. Chem.* **2009**, *22*, 986–993; b) J. Lalevé, M.-A. Tehfe, X. Allonas, J.-P. Fouassier, *Macromolecules* **2008**, *41*, 9057–9062; c) T. Watanabe, D. Hirose, D. P. Curran, T. Taniguchi, *Chem. Eur. J.* **2017**, *23*, 5404–5409; d) T. Watanabe, S. J. Geib, D. P. Curran, T. Taniguchi, *J. Org. Chem.* **2017**, *82*, 13034–13042; e) M. Shimoī, T. Watanabe, K. Maeda, D. P. Curran, T. Taniguchi, *Angew. Chem. Int. Ed.* **2018**, *57*, 9485–9490; *Angew. Chem.* **2018**, *130*, 9629–9634; For recent examples, see: f) J.-K. Jin, W.-X. Zheng, H.-M. Xia, F.-L. Zhang, Y.-F. Wang, *Org. Lett.* **2019**, *21*, 8414–8418; g) X. Liu, E. E. Lin, G. Chen, J.-L. Li, P. Liu, H. Wang, *Org. Lett.* **2019**, *21*, 8454–8458; h) M. Shimoī, K. Maeda, S. J. Geib, D. P. Curran, T. Taniguchi, *Angew. Chem. Int. Ed.* **2019**, *58*, 6357–6361; *Angew. Chem.* **2019**, *131*, 6423–6427; i) Y.-S. Huang, J. Wang, W.-X. Zheng, F.-L. Zhang, Y.-J. Yu, M. Zheng, X. Zhou, Y.-F. Wang, *Chem. Commun.* **2019**, *55*, 11904–11907; j) S.-C. Ren, F.-L. Zhang, A.-Q. Xu, Y. Yang, M. Zheng, X. Zhou, Y. Fu, Y.-F. Wang, *Nat. Commun.* **2019**, *10*, 1934; k) J.-K. Jin, F.-L. Zhang, Q. Zhao, J.-A. Lu, Y.-F. Wang, *Org. Lett.* **2018**, *20*, 7558–7562.
- [9] a) W. Xu, H. Jiang, J. Leng, H. W. Ong, J. Wu, *Angew. Chem. Int. Ed.* **2020**, *59*, 4009–4016; *Angew. Chem.* **2020**, *132*, 4038–4045; b) J. Qi, F.-L. Zhang, J.-K. Jin, Q. Zhao, B. Li, L. X. Liu, Y.-F. Wang, *Angew. Chem. Int. Ed.* **2020**, *59*, 12876–12884; *Angew. Chem.* **2020**, *132*, 12976–12984; c) G. Chen, L. Wang, X. Liu, P. Liu, *Adv. Synth. Catal.* **2020**, *362*, 2990–2996.
- [10] N. Zhou, X.-A. Yuan, Y. Zhao, J. Xie, C. Zhu, *Angew. Chem. Int. Ed.* **2018**, *57*, 3990–3994; *Angew. Chem.* **2018**, *130*, 4054–4058.
- [11] P.-J. Xia, D. Song, Z.-P. Ye, Y.-Z. Hu, J.-A. Xiao, H.-Y. Xiang, X.-Q. Chen, H. Yang, *Angew. Chem. Int. Ed.* **2020**, *59*, 6706–6710; *Angew. Chem.* **2020**, *132*, 6772–6776.
- [12] W. Dai, S. J. Geib, D. P. Curran, *J. Am. Chem. Soc.* **2020**, *142*, 6261–6267.
- [13] a) G. Wang, H. Zhang, J. Zhao, W. Li, J. Cao, C. Zhu, S. Li, *Angew. Chem. Int. Ed.* **2016**, *55*, 5985–5989; *Angew. Chem.* **2016**, *128*, 6089–6093; b) R. Xu, G.-P. Lu, C. Cai, *New J. Chem.* **2018**, *42*, 16456–16459.
- [14] For recent reviews, see: a) C. Kingston, M. D. Palkowitz, Y. Takahira, J. C. Vantourout, B. K. Peters, Y. Kawamata, P. S. Baran, *Acc. Chem. Res.* **2020**, *53*, 72–83; b) D. Pollok, S. R. Waldvogel, *Chem. Sci.* **2020**, *11*, 12386–12400; c) M. Yan, Y. Kawamata, P. S. Baran, *Chem. Rev.* **2017**, *117*, 13230–13319; d) K. Yamamoto, M. Kuriyama, O. Onomura, *Acc. Chem. Res.* **2020**, *53*, 105–120; e) K. Mitsudo, Y. Kurimoto, K. Yoshioka, S. Suga, *Chem. Rev.* **2018**, *118*, 5985–5999; f) S. R. Waldvogel, S. Lips, M. Selt, B. Riehl, C. J. Kampf, *Chem. Rev.* **2018**, *118*, 6706–6765; g) Y. Yuan, A. Lei, *Acc. Chem. Res.* **2019**, *52*, 3309–3324.
- [15] A. Nitelet, D. Thevenet, B. Schiavi, C. Hardouin, J. Fournier, R. Tamion, X. Pannecoucke, P. Jubault, T. Poisson, *Chem. Eur. J.* **2019**, *25*, 3262–3266.
- [16] Y. Zhang, X. Zhao, C. Bi, W. Lu, M. Song, D. Wang, G. Qing, Y. Zhang, *Green Chem.* **2021**, *23*, 1691–1699.
- [17] For a review, see: a) Z. Kuang, K. Yang, Y. Zhou, Q. Song, *Chem. Commun.* **2020**, 56, 6469–6479; b) A. Bonet, C. Pubill-Ulldemolins, C. Bo, H. Gulyás, E. Fernandez, *Angew. Chem. Int. Ed.* **2011**, *50*, 7158–7161; *Angew. Chem.* **2011**, *123*, 7296–7299; c) S. Hong, W. Zhang, M. Liu, Z.-J. Yao, W. Deng, *Tetrahedron Lett.* **2016**, *57*, 1–4; d) C. M. Deng, Y. F. Ma, Y. M. Wen, *ChemistrySelect* **2018**, *3*, 1202–1204.
- [18] L. Pitzer, F. Schäfers, F. Glorius, *Angew. Chem. Int. Ed.* **2019**, *58*, 8572–8576; *Angew. Chem.* **2019**, *131*, 8660–8664.
- [19] See Supporting Information for details.
- [20] The presence of the  $\alpha$ -isomer has not been so far explained and is in contrast to the previous reports of hydroboration reaction of alkyne with boryl radicals, see: a) M. Shimoī, T. Watanabe, K. Maeda, D. P. Curran, T. Taniguchi, *Angew. Chem. Int. Ed.* **2018**, *57*, 9485–9490; b) M. Zhong, Y. Gagné, T. Hope, X. Pannecoucke, M. Frenette, P. Jubault, T. Poisson, *Angew. Chem. Int. Ed.* **2021**, <https://doi.org/10.1002/anie.202101874>.
- [21] For selected examples of electrochemical oxidation of borates, see: a) D. H. Geske, *J. Phys. Chem.* **1959**, *63*, 1062–1070; b) D. H. Geske, *J. Phys. Chem.* **1962**, *66*, 1743–1744; c) S. B. Beil, S. Möhle, P. Enders, S. R. Waldvogel, *Chem. Commun.* **2018**, *54*, 6128–6131; d) A. Music, A. N. Baumann, P. Spieß, A. Plantefol, T. C. Jagau, D. Didier, *J. Am. Chem. Soc.* **2020**, *142*, 4341–4348; e) A. N. Baumann, A. Music, J. Dechent, N. Müller, T. C. Jagau, D. Didier, *Chem. Eur. J.* **2020**, *26*, 8382–8387; f) H. Yan, M.

- Chen, D. Zhao, J. Xu, C. Li, C. Lu, *Angew. Chem. Int. Ed.* **2021**, *60*, 7838–7844; *Angew. Chem.* **2021**, *133*, 7917–7923.
- [22] H-CH<sub>2</sub>OH, BDE = 96 kcal.mol<sup>-1</sup> and CH<sub>3</sub>O-H BDE = 104 kcal.mol<sup>-1</sup>.
- [23] The reduction of the vinyl radical **D** into the corresponding vinyl anion followed by protonation to afford the hydroborated product is unlikely, since no reduction has been witnessed during the CV measurement with all reaction partners, see Scheme 3B.
- [24] W. J. Boyle, J. F. Bunnett, *J. Am. Chem. Soc.* **1974**, *96*, 1418–1422.

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