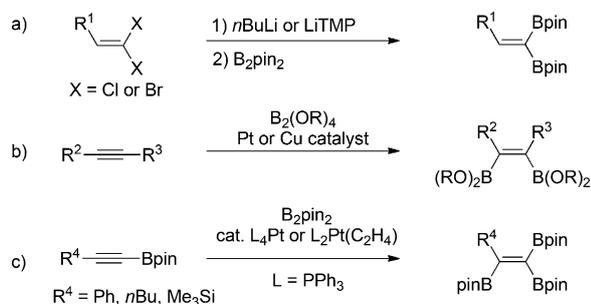


# Synthesis of Triborylalkenes from Terminal Alkynes by Iridium-Catalyzed Tandem C–H Borylation and Diboration

Chun-I Lee, Wei-Chun Shih, Jia Zhou, Joseph H. Reibenspies, and Oleg V. Ozerov\*

**Abstract:** A two-step reaction to convert terminal alkynes into triborylalkenes is reported. In the first step, the terminal alkyne and pinacolborane (HBpin) are converted into an alkynylboronate, which is catalyzed by an iridium complex supported by a SiNN pincer ligand. In the second step, treatment of the reaction mixture with CO generates a new catalyst which mediates dehydrogenative diboration of alkynylboronate with pinacolborane. The mechanism of the diboration remains unclear but it does not proceed via intermediacy of hydroboration products or via  $B_2pin_2$ .

Polysubstituted olefins are important structural motifs in drugs, natural products, and functional materials.<sup>[1,2]</sup> Among the many methodologies<sup>[1,2]</sup> developed for stereocontrolled synthesis of polysubstituted olefins, selective Suzuki–Miyaura coupling and other reactions of polyborylated alkenes appear to be an especially attractive route.<sup>[3–6]</sup> 1,1-Diborylalkenes can be made from either 1,1-dichloro- or 1,1-dibromoalkenes through lithium–halide exchange and subsequent reaction with bis(pinacolato)diboron ( $B_2pin_2$ ; Figure 1 a).<sup>[7,8]</sup> Alternatively, they can be accessed by hydroboration of alkynylboronates,<sup>[9]</sup> or by dehydrogenative borylation of alkenes with diboron reagents.<sup>[10]</sup> Metal-catalyzed addition of diboron reagents to terminal or internal alkynes leads to 1,2-*cis*-diborylalkenes (Figure 1 b).<sup>[11,12]</sup> These reactions are usually



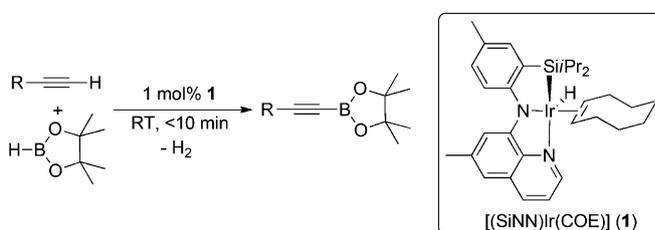
**Figure 1.** Syntheses of 1,1-diborylalkenes (top), 1,2-*cis*-diborylalkenes (middle), and triborylalkenes (bottom). TMP = 2,2,6,6-tetramethylpiperidine.

[\*] Dr. C.-I. Lee, W.-C. Shih, Dr. J. H. Reibenspies, Prof. O. V. Ozerov  
 Department of Chemistry, Texas A&M University  
 TAMU - 3255, College Station, TX 77843 (USA)  
 E-mail: ozerov@mail.chem.tamu.edu  
 Homepage: <http://www.chem.tamu.edu/rgroup/ozerov/>  
 Prof. J. Zhou  
 Department of Chemistry, Harbin Institute of Technology  
 Harbin 150001 (China)

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201507372>.

catalyzed by platinum<sup>[13–19]</sup> or copper<sup>[20–22]</sup> complexes. Only three examples have been reported for the synthesis of triborylalkenes and they employed platinum-catalyzed diboration of alkynylboronates (Figure 1 c).<sup>[15,23]</sup> Interestingly, in the example from Marder and co-workers,<sup>[15]</sup>  $Me_3SiC\equiv CBpin$  was formed by desilylative borylation of  $Me_3SiC\equiv CSiMe_3$  with  $B_2pin_2$ .

Recently, we demonstrated the first example of dehydrogenative borylation<sup>[24]</sup> of terminal alkynes (DHBTA) catalyzed by the SiNN pincer cyclooctene iridium complex **1** (Figure 2)<sup>[25]</sup> Tsuchimoto et al. described DHBTA catalysis

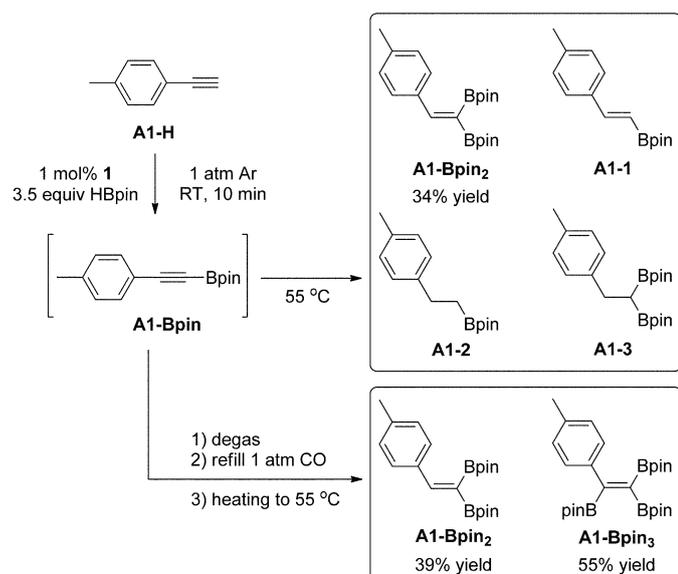


**Figure 2.** DHBTA catalyzed by **1**. COE = *cis*-cyclooctene.

by  $Zn(OTf)_2$ /pyridine using 1,8-naphthalenediamidoborane.<sup>[26]</sup> Very recently, we showed that iridium complexes supported by various PNP ligands are very effective catalysts for DHBTA.<sup>[27]</sup> The reaction was highly chemoselective, thus leading to alkynylboronates in excellent yields. This result motivated us to explore the potential to further borylate alkynylboronates in a one-pot reaction. Herein we report the discovery of a new selective dehydrogenative diboration of alkynylboronates.

The DHBTA reaction catalyzed by  $[(SiNN)Ir]$  complexes produces alkynylboronate in high yield and purity, and does so in minutes at ambient temperature. Because our protocol utilizes an excess of pinacolborane (HBpin), one or more equivalents of HBpin per alkynylboronate remains in the reaction mixture at the end of DHBTA catalysis. We became interested in the potential of a one-pot synthesis that would combine DHBTA and hydroboration in one sequence. It was envisaged that ideally, hydroboration might be performed at more forcing conditions by the same DHBTA catalyst or its decomposition products, or by modifying the DHBTA catalyst in the mixture by a simple additive. *syn*-Addition of HBpin to alkynylboronates would yield 1,1-diborylalkenes or 1,2-*trans*-diborylalkenes.

The complex **1** cleanly catalyzed DHBTA of 4-ethynyltoluene (**A1-H**) to **A1-Bpin** with 3.5 equivalents of HBpin. Thermolysis of the resultant mixture at 55 °C for 24 hours yielded multiple hydrogenation and hydroboration products

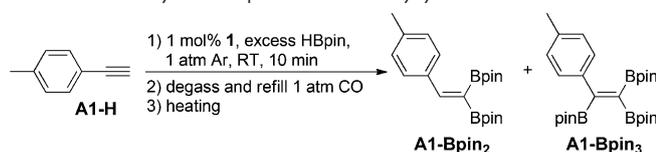


**Scheme 1.** Attempts at additional borylation of alkynylboronates.

(Scheme 1), including 34% yield of the 1,1-diborylalkene **A1-Bpin<sub>2</sub>**, thus indicating that iridium compounds present in the mixture do not give rise to effective hydroboration catalysis. Degassing the reaction mixture after DHBTA and refilling with 1 atm Ar before heating resulted in a similar product distribution. However, treatment of the post-DHBTA mixture with 1 atm of CO prior to heating at 55 °C led to a different and unexpected outcome. After 8 hours, only two products were observed: 34% of **A1-Bpin<sub>2</sub>** and 55% yield of a new triborylalkene product, **A1-Bpin<sub>3</sub>** (Scheme 1). The product ratio did not change after additional heating overnight at 55 °C. To the best of our knowledge, this is the first example of a dehydrogenative diboration of an alkyne using a dialkoxyboron reagent, as opposed to the additive diboration with diboron reagents.<sup>[12]</sup>

After this fortuitous discovery, we attempted to optimize the yield of triborylalkene and the results are summarized in Table 1. Some variation in the ratio of the **A1-Bpin<sub>2</sub>** and **A1-Bpin<sub>3</sub>** products was observed in either C<sub>6</sub>D<sub>6</sub>, fluorobenzene,

**Table 1:** Summary of the optimization of alkynylboronates diboration.

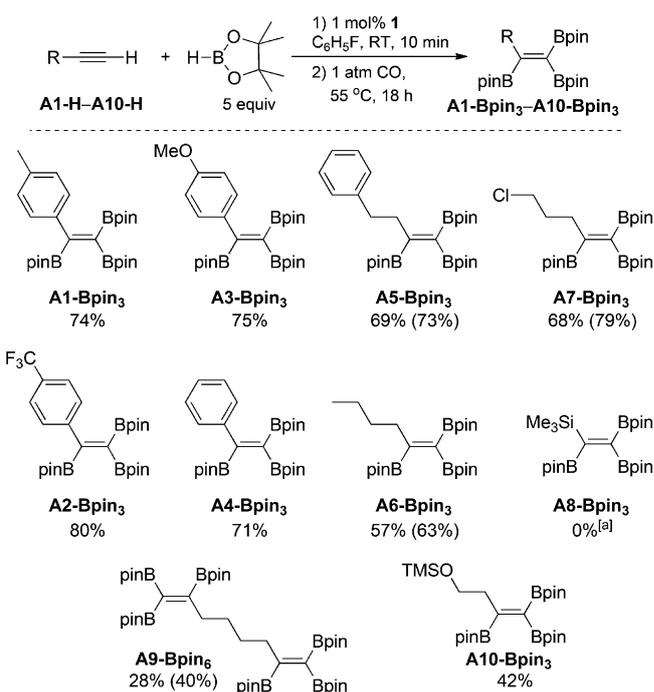


Entry	HBpin (equiv)	Solvent	Yield [%]	
			A1-Bpin <sub>2</sub>	A1-Bpin <sub>3</sub>
1 <sup>[a]</sup>	3.5	C <sub>6</sub> D <sub>6</sub>	39	55
2 <sup>[a]</sup>	3.5	PhF	45	50
3 <sup>[ab]</sup>	3.5	THF	26	43
4 <sup>[cd]</sup>	3.5	C <sub>6</sub> D <sub>6</sub>	52	32
5 <sup>[e]</sup>	5.0	PhF	7	88
6 <sup>[e]</sup>	10	neat	5	91

[a] Thermolysis stage: 55 °C, 8 h. [b] 26% A1-Bpin. [c] 3rd stage: 80 °C, 3 h. [d] 5% A1-1. [e] Thermolysis stage: 55 °C, 18 h.

or THF as the solvent at 55 °C (entries 1–3), or when the reaction was carried out in C<sub>6</sub>D<sub>6</sub> at 80 °C (entry 4), but practical selectivity for either product was not attained. Increasing the amount of HBpin to 5 equivalents and reducing the solvent volume led to substantial improvement in the selectivity for **A1-Bpin<sub>3</sub>** (88%, entry 5). The in situ fraction of **A1-Bpin<sub>3</sub>** was only slightly increased when the reaction was carried out in neat HBpin (entry 6), so we focused on the reaction conditions of entry 5 for the subsequent examination of the substrate scope.

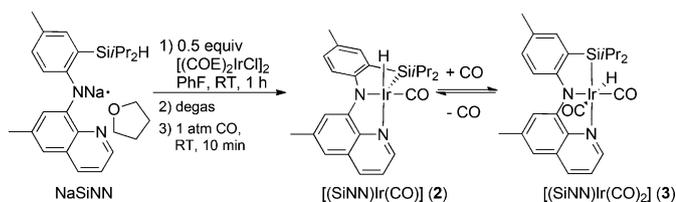
Several aryl- and alkyl-substituted terminal alkynes were subjected to a two-stage procedure whereby treatment with 5 equivalents of HBpin and 1 mol% **1** at ambient temperature was followed by degassing of the reaction mixture, introduction of CO (1 atm), and thermolysis at 55 °C for 18 hours (Scheme 2). The triborylalkenes derived from aryl alkynes (**A1-H** to **A4-H**) were easily isolated as pure solids in 70–80% yields by removing the volatiles at the end of the reaction, suspending the residue in *n*-pentane at ambient temperature, and filtering off the products. For alkyl-substituted triborylalkenes (**A5-Bpin<sub>3</sub>** to **A7-Bpin<sub>3</sub>**), 60–80% yields (NMR) were observed in situ. However, the yields of the isolated products were significantly lower since the solubility of alkyl-substituted triborylalkenes in *n*-pentane proved to be much higher. The yield of the isolated product was significantly improved by using cold isooctane in the work



**Scheme 2.** Substrate scope of one-pot diboration of alkynylboronates. Reaction conditions: **1** (0.020 mmol) and HBpin (10 mmol) were dissolved in PhF in a PTFE-valved gas-tight flask. Alkyne (2.00 mmol for monoynes [1.00 mmol for 1,7-octadiyne]) was then added in 4 portions with 1 min intervals at RT. After 10 min, the mixture was degassed, refilled with 1 atm of CO, and heated at 55 °C for 18 h (see experimental for details). Yields are those of isolated products. Values within parentheses are yields determined by <sup>1</sup>H NMR spectroscopy. [a] 87% **A8-Bpin**.

up instead.<sup>[28]</sup> The reaction with  $\text{Me}_3\text{SiC}\equiv\text{CH}$  (**A8-H**) stopped at the alkynylboronate stage, with no di- or triborylalkene products observed, perhaps owing to steric hindrance. The hexaborylated diene **A9-Bpin**<sub>6</sub> and the homoallyl ether **A10-Bpin**<sub>3</sub> were obtained from 1,7-octadiyne and trimethylsilyl homopropargyl ether, respectively, albeit in modest yields.

To examine the nature of possible SiNN-ligated iridium species under CO-rich conditions, we treated the in situ generated **1** with 1 atm CO at ambient temperature. This treatment led to an equilibrium mixture of the monocarbonyl adduct **2** and dicarbonyl adduct **3** (Scheme 3). We were able

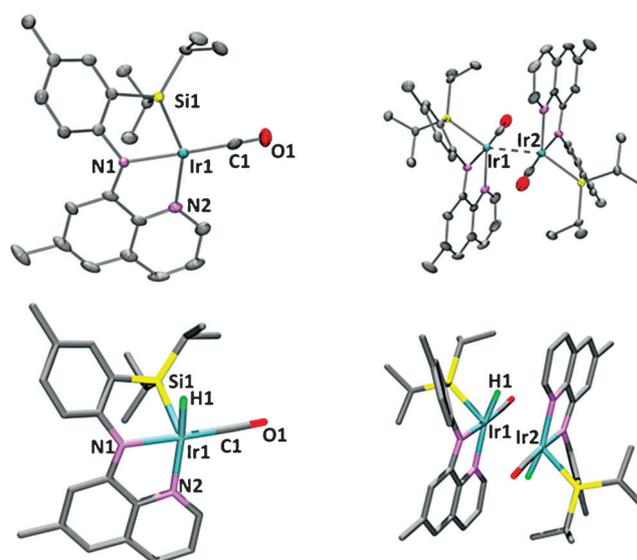


**Scheme 3.** Synthesis of the carbonyl adducts **2** and **3**.

to isolate pure **2** as a brown solid in 92% yield. The <sup>1</sup>H NMR resonances corresponding to Ir-H in **2** ( $\delta$ –15.52 ppm) and **3** ( $\delta$ –6.10 ppm) showed little to no coupling to <sup>29</sup>Si.<sup>[29]</sup> The more downfield chemical shift for **3** is consistent with a hydride *trans* to CO and not a nitrogenous ligand. The identification of **2** and **3** as mono- and dicarbonyl complexes, respectively, is supported by the corresponding single band at 1977  $\text{cm}^{-1}$  for **2**, and two bands at 2057 and 2007  $\text{cm}^{-1}$ , in about a 1:1 intensity ratio (indicating a *cis*-dicarbonyl), for **3** in the IR spectra.

The result of the determination of solid-state structure of **2** by single-crystal X-ray diffractometry is shown in Figure 3 (top). In addition, density functional theory (DFT) calculations were carried out on **2** in the gas phase using the M06 functional (Figure 3, bottom). The positions of nonhydrogen atoms from the experimental XRD determination were closely reproduced in the DFT-calculated structure. The longer calculated Si-H distance in **2** (2.183 Å) versus that in **1** (2.007 Å) and the diboryl complex [(SiNN)Ir(Bpin)<sub>2</sub>] (**4**; 1.889 Å), is in agreement with the lack of observable Si-H coupling in **2**, and the  $J_{\text{Si-H}}$  values of 8 and 32 Hz for **1** and **4**, respectively.<sup>[25]</sup> Both the calculated Si-H distance and the  $J_{\text{Si-H}}$  value of **2** are outside the range for a Si-H bonding interaction, hence **2** should be viewed as a d<sup>6</sup>-iridium(III) silyl hydride complex.<sup>[30,31]</sup> The coordination environment about iridium in **2** can be viewed as derived from square-pyramidal where the ligand *trans* to the empty site (silyl) is displaced towards the base plane, presumably in part because of the inability of the SiNN ligand to adopt an idealized facial geometry.

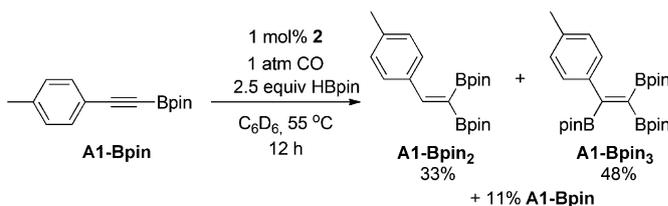
Interestingly, two molecules of **2** approach each other closely in the solid state, with about a 2.91 Å distance between two iridium centers. The gas-phase DFT calculation results in a similar approach with about a 3.05 Å distance between iridium atoms. No  $\pi$ - $\pi$  stacking is observed and the hydrides are clearly terminal (calculated values: Ir1-H1, 1.592 Å; Ir2-H1, 3.117 Å), thus ruling out the possibility of a hydride-



**Figure 3.** ORTEP drawing<sup>[32]</sup> (thermal ellipsoids shown at 50% probability) of **2** (top) showing selected atom labeling, and drawing of the DFT-calculated structures of **2** (bottom). Hydrogen atoms are omitted for clarity, except for the hydride on the Ir atom. Selected bond distances (Å) and angles (deg) for **2**, with DFT-derived metrics in square brackets: Ir1-Si1, 2.3366(15) [2.376]; Si1-H1, [2.183]; Ir1-H1, [1.592]; Ir2-H1, [3.117]; Ir1-Ir2, 2.9074(8) [3.046]; Si1-Ir1-N2, 124.89(11) [127.51]; Si1-Ir1-H1, [63.17]; Ir1-C1-O1, 176.1(5) [177.75].

bridged dimer. This arrangement appears to be a rare case of a d<sup>6</sup>-d<sup>6</sup> metallophilic interaction. Metallophilic interactions are quite common for d<sup>10</sup>-d<sup>10</sup> (Ag, Au) and d<sup>8</sup>-d<sup>8</sup> (square-planar Pd, Pt), with M-M distances around 2.8–3.1 Å being rather typical for unbridged dimers.<sup>[33–36]</sup> The lack of steric bulk projecting from the base of the square pyramid in **2** is atypical for five-coordinate d<sup>6</sup> complexes and likely contributes to permitting close contact.

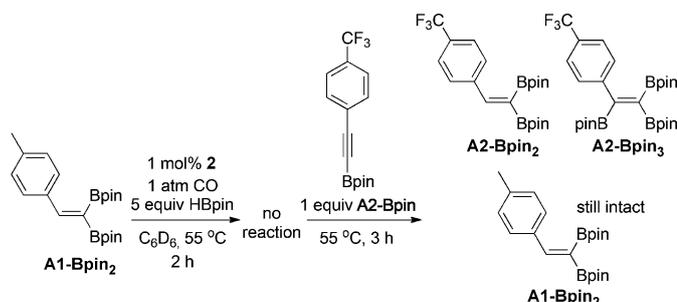
To examine the possible role of **2** in the diboration of alkynylboronates, we first tested **2** in the reaction between isolated **A1-Bpin** and HBpin under 1 atm CO (Scheme 4). The product ratio was consistent with the results observed from the one-pot synthesis reactions, but with a slightly slower reaction rate. This result suggested **2** acts as the actual entry point into the catalytic cycle of the diboration. Performing the reaction under the same reaction conditions except under 1 atm Ar instead of CO, interestingly, led to a much slower rate (36% conversion) and higher product ratio of **A1-Bpin**<sub>2</sub> to **A1-Bpin**<sub>3</sub> (16%:12%). Catalysis of the diboration step can utilize less iridium than DHBTA, as evidenced by a 61% yield of **A1-Bpin**<sub>3</sub>, within 28 hours, when 0.1% of **2** was used (NMR evidence in situ, ca. 600 TON) under reaction conditions



**Scheme 4.** Borylation of **A1-Bpin** catalyzed by **2**.

analogous to those in Scheme 4. For the tandem process, DHBTA is thus limiting with respect to the required iridium catalyst loading.

During the optimization of diboration, we found that the ratio of 1,1-diborylalkene to triborylalkene products remained constant once the alkynylboronate had been fully consumed. To expand on this observation, we treated **A1-Bpin**<sub>2</sub><sup>[9]</sup> with 5 equivalents of HBpin and 3 mol % **2** under 1 atm CO, but no change in the <sup>1</sup>H NMR spectrum was evident after 2 hours at 55 °C (Scheme 5). In contrast, when



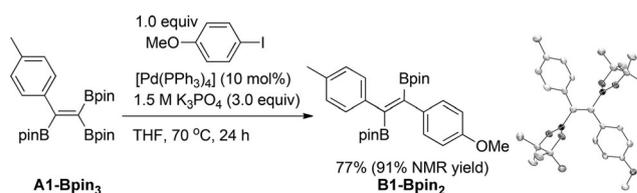
**Scheme 5.** Borylation of **A1-Bpin**<sub>2</sub> catalyzed by **2**.

one equivalent of **A2-Bpin** was added to this mixture (with restoration of CO atmosphere) and it was subjected to further heating at 55 °C, **A2-Bpin** was fully converted into **A2-Bpin**<sub>2</sub> and **A2-Bpin**<sub>3</sub> after 3 hours, while **A1-Bpin**<sub>2</sub> remained intact. These results unambiguously show that a 1,1-diborylalkene is not an intermediate en route to a triborylalkene. No significant yield changes were observed for either **A1-Bpin**<sub>3</sub> or the major side-product **A1-Bpin**<sub>2</sub> in the presence of mercury,<sup>[37]</sup> whereas [Ir<sub>4</sub>(CO)<sub>12</sub>], iridium powder, and [(COE)<sub>2</sub>IrCl]<sub>2</sub>, with or without CO, were all unable to catalyze the diboration of **A1-Bpin** to **A1-Bpin**<sub>3</sub>. This result suggests homogeneous catalysis that relies on the SiNN ligated or at least derived iridium species. **A1-Bpin** did not react with B<sub>2</sub>pin<sub>2</sub> in the presence of **2**, and B<sub>2</sub>pin<sub>2</sub> was not observed when HBpin was thermolyzed in the presence of **2** under a CO atmosphere at 55 °C for 8 hours. Diboration via the intermediate B<sub>2</sub>pin<sub>2</sub> formation can thus be ruled out.

In a very generic sense, we anticipate that the triborylalkene is formed by insertion of alkynylboronate into an Ir–B bond and subsequent reductive C–B elimination, whereas the diborylalkene product is formed by insertion of the alkynylboronate into Ir–B and reductive C–H elimination (or insertion into Ir–H and C–B reductive elimination). Increased triborylalkene formation would then be assisted by conversion of Ir–H bonds into Ir–B bonds, which may explain the beneficial role of increased HBpin content. Nonetheless, the detailed mechanistic picture remains rather obscure. We are especially challenged to explain the beneficial role of excess CO in the diboration step and how a polydentate SiNN ligand, CO, and two substrates all ostensibly coordinate to the iridium center in some order.

In-depth exploration of the utility of triborylalkenes as substrates for further transformation and functionalization is outside the scope of this report. However, we were pleased to find that **A1-Bpin**<sub>3</sub> underwent stereoselective Suzuki–

Miyaura coupling with one equivalent of 4-iodoanisole to afford **B1-Bpin**<sub>2</sub> in 77 % yield upon isolation (Scheme 6). The *E* stereochemistry of **B1-Bpin**<sub>2</sub> was confirmed by an X-ray diffraction study of a suitable single crystal.<sup>[28]</sup> Only a few examples have been demonstrated for *trans*-selective alkyne diboration, but they required propargyl alcohols or alkyne nitrates as substrates.<sup>[38,39]</sup> Small quantities of the *trans*-diboration product were observed by Lin, Marder, and co-workers in the predominantly *cis*-selective catalysis of diboration of a diarylalkyne by [Co(PMe<sub>3</sub>)<sub>4</sub>].<sup>[40]</sup> The reaction in Scheme 6 points to a potential complementary synthetic strategy for *trans*-diaryldiborylalkenes.



**Scheme 6.** Selective monoarylation of **A1-Bpin**<sub>3</sub> and ORTEP drawing<sup>[32]</sup> of **B1-Bpin**<sub>2</sub>. The crystallographic disorder of the aryl groups and hydrogen atoms is not shown. Thermal ellipsoids shown at 50 % probability.

We described the development of a convenient one-pot, two-step synthesis of triborylalkenes directly from terminal alkynes. The process combines DHBTA, which uses a [(SiNN)Ir] catalyst, and a subsequent novel dehydrogenative diboration initiated by the carbonylation of the DHBTA catalyst. Good yields of the isolated products were obtained for a variety of alkynes. The carbonyl complex **2** has been independently synthesized from **1** and has been shown to possess the ability to catalyze diboration. Preliminary mechanistic studies suggested that triborylalkenes are not obtained from borylation of free diborylalkenes. Further work will be aimed at the elucidation of the mechanism of dehydrogenative diboration and the exploration of synthetic use of triborylalkenes.

## Experimental Section

Complete experimental details are available online as Supporting Information.

Supporting Information for this article in the form of descriptions of experiments, characterization data, computational details is available on the WWW under <http://www.angewandte.org>. CCDC 1417117 and 1417149 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

## Acknowledgements

We are grateful to the US National Science Foundation (grant CHE-1310007 to O.V.O.) and the Welch Foundation (grant A-1717 to O.V.O.) for the support of this research. W.-C.S. is thankful for the Studying Abroad Scholarship from Ministry of Education, Taiwan. J.Z. thanks the Fundamental Research

Funds for the Central Universities of China (Grant No. AUGA5710013115). We are also grateful to Dr. Yohannes Rezenom and Ms. Vanessa Santiago for assistance with mass spectrometry and Ms. Linda Redd for assistance with manuscript preparation.

**Keywords:** boranes · C–C coupling · density functional calculations · homogeneous catalysis · iridium

**How to cite:** *Angew. Chem. Int. Ed.* **2015**, *54*, 14003–14007  
*Angew. Chem.* **2015**, *127*, 14209–14213

- [1] A. B. Flynn, W. W. Ogilvie, *Chem. Rev.* **2007**, *107*, 4698–4745.  
 [2] K. Itami, J.-i. Yoshida, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 811–824.  
 [3] T. Ishiyama, M. Yamamoto, N. Miyaura, *Chem. Lett.* **1996**, *25*, 1117–1118.  
 [4] M. Shimizu, C. Nakamaki, K. Shimono, M. Schelper, T. Kurahashi, T. Hiyama, *J. Am. Chem. Soc.* **2005**, *127*, 12506–12507.  
 [5] Y. Nishihara, M. Miyasaka, M. Okamoto, H. Takahashi, E. Inoue, K. Tanemura, K. Takagi, *J. Am. Chem. Soc.* **2007**, *129*, 12634–12635.  
 [6] N. Iwadata, M. Suginome, *J. Am. Chem. Soc.* **2010**, *132*, 2548–2549.  
 [7] T. Hata, H. Kitagawa, H. Masai, T. Kurahashi, M. Shimizu, T. Hiyama, *Angew. Chem. Int. Ed.* **2001**, *40*, 790–792; *Angew. Chem.* **2001**, *113*, 812–814.  
 [8] T. Kurahashi, T. Hata, H. Masai, H. Kitagawa, M. Shimizu, T. Hiyama, *Tetrahedron* **2002**, *58*, 6381–6395.  
 [9] H. E. Ho, N. Asao, Y. Yamamoto, T. Jin, *Org. Lett.* **2014**, *16*, 4670–4673.  
 [10] a) R. B. Coapes, F. E. S. Souza, R. L. Thomas, J. J. Hall, T. B. Marder, *Chem. Commun.* **2003**, 614–615; b) J. Takaya, N. Kirai, N. Iwasawa, *J. Am. Chem. Soc.* **2011**, *133*, 12980–12983; c) I. A. I. Mkhaliid, R. B. Coapes, S. N. Edes, D. N. Coventry, F. E. S. Souza, R. L. Thomas, J. J. Hall, S.-W. Bi, Z. Lin, T. B. Marder, *Dalton Trans.* **2008**, 1055–1064.  
 [11] T. Ishiyama, N. Matsuda, N. Miyaura, A. Suzuki, *J. Am. Chem. Soc.* **1993**, *115*, 11018–11019.  
 [12] J. Takaya, N. Iwasawa, *ACS Catal.* **2012**, *2*, 1993–2006.  
 [13] T. Ishiyama, N. Matsuda, M. Murata, F. Ozawa, A. Suzuki, N. Miyaura, *Organometallics* **1996**, *15*, 713–720.  
 [14] G. Mann, K. D. John, R. T. Baker, *Org. Lett.* **2000**, *2*, 2105–2108.  
 [15] G. Lesley, P. Nguyen, N. J. Taylor, T. B. Marder, A. J. Scott, W. Clegg, N. C. Norman, *Organometallics* **1996**, *15*, 5137–5154.  
 [16] R. L. Thomas, F. E. S. Souza, T. B. Marder, *J. Chem. Soc. Dalton Trans.* **2001**, 1650–1656.  
 [17] V. Lillo, J. Mata, J. Ramírez, E. Peris, E. Fernandez, *Organometallics* **2006**, *25*, 5829–5831.  
 [18] H. Prokopcová, J. Ramírez, E. Fernández, C. O. Kappe, *Tetrahedron Lett.* **2008**, *49*, 4831–4835.  
 [19] A. Grirrane, A. Corma, H. Garcia, *Chem. Eur. J.* **2011**, *17*, 2467–2478.  
 [20] V. Lillo, M. R. Fructos, J. Ramírez, A. A. C. Braga, F. Maseras, M. M. Díaz-Requejo, P. J. Pérez, E. Fernández, *Chem. Eur. J.* **2007**, *13*, 2614–2621.  
 [21] H. Yoshida, S. Kawashima, Y. Takemoto, K. Okada, J. Ohshita, K. Takaki, *Angew. Chem. Int. Ed.* **2012**, *51*, 235–238; *Angew. Chem.* **2012**, *124*, 239–242.  
 [22] K. Takahashi, T. Ishiyama, N. Miyaura, *J. Organomet. Chem.* **2001**, *625*, 47–53.  
 [23] H. A. Ali, A. E. A. A. Quntar, I. Goldberg, M. Srebnik, *Organometallics* **2002**, *21*, 4533–4539.  
 [24] For a comprehensive review on C–H borylation (of sp<sup>2</sup> and sp<sup>3</sup> C–H bonds), see: I. A. I. Mkhaliid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890–931.  
 [25] C.-I. Lee, J. Zhou, O. V. Ozerov, *J. Am. Chem. Soc.* **2013**, *135*, 3560–3566.  
 [26] T. Tsuchimoto, H. Utsugi, T. Sugiura, S. Horio, *Adv. Synth. Catal.* **2015**, *357*, 77–82.  
 [27] C.-I. Lee, J. C. DeMott, C. J. Pell, A. Christopher, J. Zhou, N. Bhuvanesh, O. V. Ozerov, *Chem. Sci.* **2015**, DOI: 10.1039/C5SC02161H.  
 [28] See the Supporting Information.  
 [29] From a <sup>1</sup>H-<sup>29</sup>Si DQF experiment:  $J_{\text{Si-H}}$  not detected for **2**,  $J_{\text{Si-H}} = 2$  Hz for **3**.  
 [30] J. Y. Corey, *Chem. Rev.* **2011**, *111*, 863–1071.  
 [31] G. I. Nikonov, *Adv. Organomet. Chem.* **2005**, *53*, 217–309.  
 [32] ORTEP plots were created using Ortep-3 for Windows. L. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565–565.  
 [33] H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2012**, *41*, 370–412.  
 [34] J. E. Bercaw, A. C. Durrell, H. B. Gray, J. C. Green, N. Hazari, J. A. Labinger, J. R. Winkler, *Inorg. Chem.* **2010**, *49*, 1801–1810.  
 [35] X. Yan, R. J. Batchelor, F. W. B. Einstein, X. Zhang, R. Nagelkerke, D. Sutton, *Inorg. Chem.* **1997**, *36*, 1237–1246.  
 [36] J. Luo, J. R. Khusnutdinova, N. P. Rath, L. M. Mirica, *Chem. Commun.* **2012**, *48*, 1532–1534.  
 [37] R. H. Crabtree, *Chem. Rev.* **2012**, *112*, 1536–1554.  
 [38] Y. Nagashima, K. Hirano, R. Takita, M. Uchiyama, *J. Am. Chem. Soc.* **2014**, *136*, 8532–8535.  
 [39] K. Nagao, H. Ohmiya, M. Sawamura, *Org. Lett.* **2015**, *17*, 1304–1307.  
 [40] C. J. Adams, R. A. Baber, A. S. Batsanov, G. Bramham, J. H. P. Charmant, M. F. Haddow, J. A. K. Howard, W. H. Lam, Z. Lin, T. B. Marder, N. C. Norman, A. G. Orpen, *Dalton Trans.* **2006**, *35*, 1370–1373.

Received: August 7, 2015

Published online: October 1, 2015