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## Zirconium-Catalyzed Atom-Economical Synthesis of 1,1-Diborylalkanes from Terminal and Internal Alkenes

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**Abstract:** A general and atom-economical synthesis of 1,1diborylalkanes from bulk alkenes with borane under H<sub>2</sub>-acceptorless conditions is reported for the first time. The key to our success is the use of an earth-abundant zirconium-based catalyst, which allows a balance of self-contradictory reactivities (dehydrogenative boration and hydroboration) to be achieved. Our methodology avoids using excess amount of another alkene as H<sub>2</sub>-acceptor that was otherwise required in the reported system. Furthermore, substrates such as simple long-chain aliphatic alkenes that did not work before also worked in our system. Significantly, the unprecedented 1,1diboration of internal alkenes for the preparation of 1,1diborylalkanes was also realized.

In recent years, 1,1-diborylalkanes have emerged as versatile building blocks and fundamental intermediates.<sup>[1]</sup> Traditionally, they were synthesized from bis(boryl)methane with alkylhalides<sup>[2]</sup> or the boration of geminal dihalides.<sup>[3]</sup> Approaches such as the dihydroboration of alkynes<sup>[4]</sup> and the hydroboration of vinyl boronates were also known,<sup>[1a, 1c, 5]</sup> but they are relatively less practical because of the accessibility of substrates. Hence, several other approaches have recently been developed, for instance, the insertion of diazoalkanes into diborons,<sup>[6]</sup> the Ir- or Co- catalyzed benzylic C–H diboration<sup>[7]</sup> and boryl group direct C–H borylation of alkyl boronic esters;<sup>[6]</sup> the deoxygenative diboration of carbonyls,<sup>[9]</sup> expanding the synthetic routes to 1,1-diborylalkanes.

Despite the above progress, the synthesis of 1,1diborylalkanes from readily available and bulk alkene has seldom been achieved. Actually, only two systems were reported to our knowledge. In 2017, a nickel-catalyzed 1,1diboration of alkenes with B<sub>2</sub>pin<sub>2</sub> as the boration reagent was developed.<sup>[10]</sup> On the other hand, the direct 1,1-diboration of alkenes using relatively inexpensive borane as the boration reagent has proven to be challenging because of the robust reduction ability of borane which, when reacting with alkenes, would preferably afford the saturated mono-hydroboration products and the reaction would be terminated.<sup>[11]</sup> To achieve the selective 1,1-diboration of alkenes with borane, a catalyst should fulfill the following criteria: 1) chemo-selective formation of the vinyl boronate ester instead of alkyl boronate ester (DHB a) challenges in the selective 1,1-diboration of alkenes with borane



b) 1,1-diboration of 1,1-disubstituted alkenes in the presence of  $\rm H_{2}$ -acceptor



c) unprecedented H<sub>2</sub>-acceptorless conditions and general alkenes: this work!



Scheme 1. Catalytic 1,1-diboration of alkenes with borane: a) challenges and possible side pathways; b) strategy by using excess amount H<sub>2</sub>-acceptor; c) our current H<sub>2</sub>-acceptorless methodology for the (remote) 1,1-diboration of terminal and internal alkenes.

over HB; DHB = dehydrogenative boration, HB = hydroboraiton);  $^{[11c,\ 12]}$  2) proceed chemo-selective HB over DHB of vinyl boronate ester, to produce diborylalkane rather than diborylalkene<sup>[10, 13]</sup>; 3) regio-selective HB of vinyl boronate ester at the  $\alpha$ -position of the bulky -Bpin group instead of at the  $\beta$ position (1,1-diboration over 1,2-diboration).<sup>[14]</sup> Thus, apart from selectivity issues, a catalyst must also possess self-contradictory reactivities (DHB and HB), which is difficult to balance (Scheme 1a). Indeed, it was not until 2018 when a Co(acac)<sub>2</sub>/phosphine system for the synthesis of 1,1-diborylalkane from alkenes and HBpin was reported, but 1.2 equiv. of norbornene or cyclooctene had to be added as  $H_2\mbox{-}acceptor$  (Scheme 1b).  $^{[15]}$  Besides, the substrates were limited to 1,1-disubstituted alkenes. Moreover, no system was known to be applicable to the bulkier and industrially favored internal alkenes.[16] Thus, a general and direct H<sub>2</sub>-acceptorless 1,1-diboration of bulk alkenes with borane

<sup>[</sup>c] X. Wang

 $\label{eq:table_$ 



Entry	Catal.	Bases -	Yields [%] <sup>[b]</sup>			
			3	4	5	6
1	$Cp_2ZrCl_2$	-	0	0	6	0
2	Cp <sub>2</sub> ZrHCl	-	0	73	0	0
3	$Cp_2ZrCl_2$	MeONa	29	47	11	1
4	Cp <sub>2</sub> ZrCl <sub>2</sub>	MeOLi	88	2	6	1
5	Cp <sub>2</sub> ZrMe <sub>2</sub>	MeOLi	63	0	34	2
6	CpZrCl₃	MeOLi	3	1	84	12
7	Cp <sub>2</sub> ZrHCl	MeOLi	87	1	7	1
8 <sup>[c]</sup>	$Cp_2ZrCl_2$	MeOLi	81	4	8	1
9 <sup>[d]</sup>	$Cp_2ZrCl_2$	MeOLi	69	1	24	3
10	-	MeOLi	0	0	83	12

<sup>[a]</sup>Reaction conditions: 0.2 mmol 1, 0.6 mmol HBpin, 1 equiv. of bases, 5 mol% catal, 1 mL of toluene in 15 mL pressure tube and heated at 100 °C for 8 h; <sup>[b]</sup>yields were determined by GC-MS using *n*-dodecane as internal standard; <sup>[c]</sup>reaction was performed at 80 °C; <sup>[d]</sup>reaction was performed with 2 mol% of catalyst loading.

for the preparation of 1,1-diborylalkanes remains underdeveloped. Herein, we report our application of a zirconium-based catalyst that allows the first example of H2acceptorless 1,1-diboration of alkenes with borane to be realized. Our system is operationally simple, cost-efficient, and suitable for a series of different alkenes ranging from aryl alkenes to long-chain aliphatic alkenes. Most significantly, the unprecedented remote 1,1-diboration of internal alkenes was also achieved (Scheme 1c).

Early transition metals often have different structures and orthogonal reactivities compared with late ones.<sup>[17]</sup> Moreover. several of them are earth-abundant, e.g., zirconium, which is almost as abundant as carbon. In addition, zirconocene complexes were reported to be able to catalyze the hydroboration of alkynes<sup>[18]</sup> and alkenes.<sup>[19]</sup> We then became interested in exploring the possibility of using zirconocene complexes to achieve the unreported H<sub>2</sub>-acceptorless 1,1diboration of alkenes. In a model reaction, 0.2 mmol styrene (1) and 0.6 mmol HBpin (2) in 1 mL toluene was reacted with 5 mol% of different zirconocene complexes at 100 °C. First, the reaction with Cp2ZrCl2 was carried out, but only 6% mono hydroboration product 5 was obtained (Table 1, entry 1). Then, the reaction with  $\mbox{Cp}_2\mbox{ZrHCI}$  was performed and 73% of the dehydrogenative boration product 4 was observed (Table 1, entry 2). Interestingly, we found that the addition of MeONa promoted the formation of 1,1-diborylalkane 3 in 29% yield (Table 1, entry 3). Changing the base from MeONa to MeOLi largely improved the yield of 3 to 88% (Table 1, entry 4). The use of other zirconium-catalysts such as Cp<sub>2</sub>ZrMe<sub>2</sub> and CpZrCl<sub>3</sub> gave inferior results (Table 1, entries 5-6). While the use of



5 mol% Cp2ZrCl2

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Cp<sub>2</sub>ZrHCl in the presence of MeOLi gave almost similar results to Cp<sub>2</sub>ZrCl<sub>2</sub> (Table 1, entry 7). In addition, the reaction temperature and catalyst loading could be further reduced, albeit slightly lower yields of **3** were obtained (Table 1, entries 8-9). It is noted that when the reaction was performed with MeOLi alone, only the hydroboration products **5** and **6** were obtained (Table 1, entry 10). It is also noted that product **5** was not the intermediate of **3** as submitting it to the catalytic conditions with HBpin did not lead any reactions.

We then investigated the generality of different alkenes under the optimized reaction conditions (Table 1, entry 4). We were pleased to find that our methodology worked well with numerous aryl alkenes with electronically and sterically varied substituents (Scheme 2). Thus, substrates with -Me, -*t*Bu, -Ph, -OMe, -NMe<sub>2</sub>, -CF<sub>3</sub> groups at various positions on the phenyl ring reacted well in our system (65-82% isolated yields, **3**, **7–12**, **17– 18**, **22–23**). In addition, halogen-substituted aryl alkenes selectively produced the corresponding 1,1-diborylalkanes without side reactions from C–X bonds (X = F, Cl, Br), and yields up to 80% were obtained (**13–15**, **19–21**, **24–25**). Notably, the -NH<sub>2</sub> group which was supposed to react with HBpin was survived in our system (**16**). Moreover, the reaction also worked



Scheme 3. Proposed reaction mechanism.

well with poly-substituted alkenes, for example, 1,4-dimethyl and pentafluoro-substituted aryl alkenes afforded their products **26** and **27** in up to 80% yields. Vinyl naphthalene and  $\alpha$ -methyl styrene yielded **28** and **29** in 83% and 40% yields. Starting from vinyl ferrocene, ferrocenyl-substituted 1,1-diborylalkane **30** was also obtained. Further extending the substrates' scope to heteroatom-containing alkenes were also successful: 2-vinylthiophene, 5-vinylbenzofuran, and 3-vinyl-9*H*-carbazole underwent efficient 1,1-diboration in yields up to 85% (**31–33**). Of note was that the -NH group on the carbazole moiety remained intact (**33**).

Next, we turned our attention to validate the generality of our methodology to long-chain aliphatic alkenes. We were pleased to find that our protocol worked for a series of bulk aliphatic alkenes with different carbon lengths albeit with reduced yields due to the presence of alkane and monohydroboration side-products: thus **34–36** were obtained in up to 65% yields. In addition, our diboration process was also applicable to aliphatic alkenes with various substituents: cyclohexyl-, cyclopentyl-, and phenyl-substituted aliphatic alkenes all worked well to give the corresponding products in yields up to 72% (**37–43**). *N*-Allylaniline was one exception, in which case, only 14% of **44** was obtained. Fortunately, other *N*and *O*-containing moieties, such as methyl benzylamine and benzyl ether, all survived the 1,1-diboration process, with yields ranging from 61% to 73% (**45–47**).

Then, in order to gain insights into the reaction mechanism, we carried out the following experiments: analyzing the stoichiometric reaction of Cp<sub>2</sub>ZrCl<sub>2</sub>, MeOLi, and HBpin (molar ratio 1:2:2) revealed the formation of MeO-Bpin, which was also detected in the catalytic reaction with or without styrene (Figure S1-S3). In addition, Zr-H was detected on <sup>1</sup>H NMR spectrum by trapping with acetone (Figure S4). Furthermore, H<sub>2</sub> and vinyl boronate ester 4 was observed on <sup>1</sup>H NMR spectrum in the catalytic reaction with styrene (Figure S5). Moreover, the sequential addition of MeOLi followed by HBpin to the Cp<sub>2</sub>ZrCl<sub>2</sub> solution in d<sub>8</sub>-toluene showed obvious color change from colorless to dark brown and the chemical shift changes of the Cp and MeO- peaks as detected by <sup>1</sup>H NMR spectroscopy (Figure S6). On the basis of those observations and literature precedents,<sup>[20]</sup> we proposed the following reaction mechanism: Cp<sub>2</sub>ZrCl<sub>2</sub> first interacts with 2 equiv. MeOLi to yield Cp<sub>2</sub>Zr(OMe)<sub>2</sub>. and then further reacts with HBpin to form Cp<sub>2</sub>ZrH<sub>2</sub> (A) and MeO-Bpin.  $Cp_2ZrH_2$  (A) enters into the catalytic cycle by reaction with HBpin and forms Cp<sub>2</sub>Zr(H)Bpin species (**B**) with release of H<sub>2</sub>. Then, insertion of alkene into the Zr-B bond forms the zirconium boryl alkyl species (**C**) which gives the vinyl boronate ester intermediate **4** after  $\beta$ -H elimination. Addition of Cp<sub>2</sub>Zr(H)Bpin (**B**) to vinyl boronate ester **4** affords zirconium diboryl alkyl species (**D**), which then reacts with another HBpin via  $\sigma$ -bond metathesis to give 1,1-diborylalkane **3** (Scheme 3).

Mixtures of internal alkenes, commonly obtained from cracking processes, are substantially cheaper and more easily accessible.<sup>[16, 21]</sup> However, the selective remote 1,1-diboration of simple and bulk internal alkenes has not yet been reported. It was well known that stoichiometric amount of zirconium-reagent could mediate the isomerization of double bonds<sup>[22]</sup> and one catalytic system has recently been reported.<sup>[23]</sup> Then, we became interested to explore whether the isomerization of internal alkenes to terminal alkenes and the subsequent selective 1,1-diboration could be achieved using our system. To our delight, a variety of internal alkenes with different chain lengths and positions of the double bond worked well in our system (Scheme 4).



Scheme 4. Zirconium-catalyzed remote 1,1-diboration of various internal alkenes. Reaction conditions: 0.2 mmol internal alkenes, 0.6 mmol HBpin, 5 mol% Cp<sub>2</sub>ZrCl<sub>2</sub>, 0.2 mmol MeOLi and 1 mL toluene in 15 mL pressure tube, heated at 100 °C for 8 - 16 h; isolated yields are given.

With 2-octene, 2-heptene, and 2-pentene, the corresponding 1,1-diborylalkanes were obtained in 51-73% yields. A yield comparable to that with 2-octene was also gained from 4octene, illustrating the efficiency of our catalytic system. Ethylidenecyclohexane afforded 37 in 65% yield, and β-methyl styrene, which was reluctant to isomerize, underwent efficient remote 1,1-diboration and gave the terminal 1,1-diboration product 41 in 66% isolated yield. Moreover, internal alkenes with a benzyl ether group undertook the 1,1-dibroation without problems and afforded the corresponding product 47 in 63% yield. In addition, sterically hindered (E)-1-isopropyl-4-(2methylpent-3-en-1-yl)benzene, and an alkene derived from helional produced 48 and 49 in yields up to 69%. In the case of (E)-2,6-dimethylundeca-2,8-diene, which contains two internal double bonds, selective reaction at the less hindered double bond was achieved, with an acceptable yield of product 50.

In summary, we have developed an earth-abundant zirconiumbased catalytic system that enabled the first selective H<sub>2</sub>acceptorless 1,1-diboration of bulk and inexpensive alkenes with borane to be realized. Our methodology avoids the requirement of excess amount of another alkene as H<sub>2</sub>-acceptor, thereby, making our strategy both atom-economical and cost-efficient. Compared to the limited substrates scope of the existing H<sub>2</sub>acceptor system, many aryl alkenes, as well as long-chain aliphatic alkenes, converted smoothly into various 1,1diborylalkanes, which are excellent platforms for complex molecules. More importantly, using our methodology, the unprecedented remote 1,1-diboration of internal alkenes were also realized.

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#### **Conflict of interest**

The authors declare no conflict of interest

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# COMMUNICATION

#### Entry for the Table of Contents



A general and atom-economical synthesis of 1,1-diborylalkanes from various alkenes with borane under  $H_2$ -acceptorless conditions is reported for the first time. Many aryl alkenes and bulk long-chain aliphatic alkenes that did not work in other systems also worked here. Significantly, the unprecedented 1,1-diboration of internal alkenes for the preparation of 1,1-diborylalkanes is also realized.