A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
GDCh
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Accepted Article

Title: Cobalt-Catalyzed Regio- and Stereoselective Hydroboration of Allenes

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201915716
Angew. Chem. 10.1002/ange.201915716

Link to VoR: http://dx.doi.org/10.1002/anie.201915716
http://dx.doi.org/10.1002/ange.201915716

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Angewandte Chemie International Edition 10.1002/anie.201915716

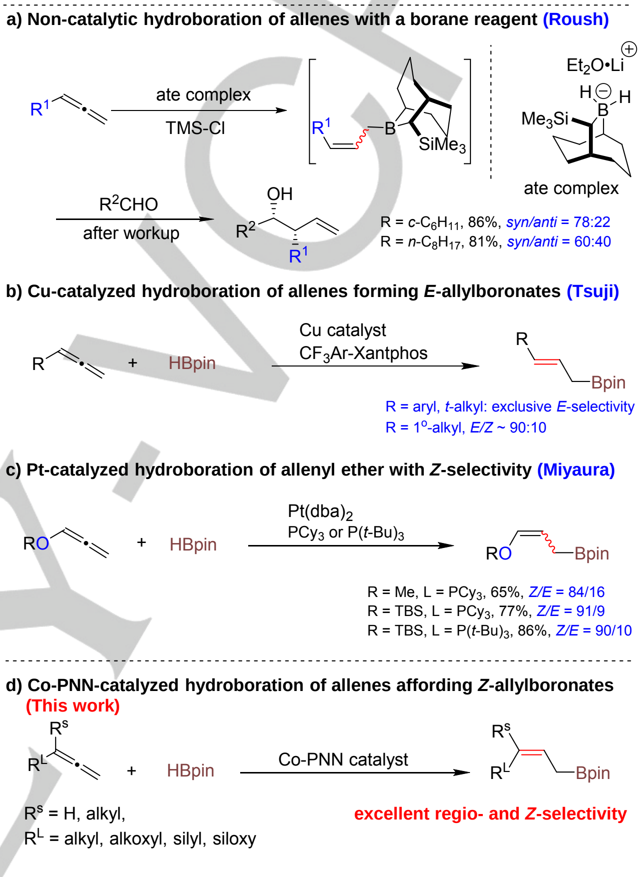
Cobalt-Catalyzed Regio- and Stereoselective Hydroboration of Allenes

Can Li,[a,b]§ Zheng Yang,[a]§ Lei Wang,[a] Yinlong Guo,*[a] Zheng Huang,*[a] and Shengming Ma*[a,c]

Dedication ((optional))

Abstract: An efficient pincer ligand-based cobalt complex-catalyzed allene hydroboration affording *Z*-allylic boronates is described. The reaction enjoys an excellent regio- as well as *Z*-stereoselectivity and a wide substrate scope tolerating many functional groups. Based on SAESI/MS studies, a rationale for the cobalt-catalyzed hydroboration involving the highly selective insertion of allene into the Co-H bond to form *Z*-allylic cobalt intermediates is proposed.

Organic boronic acid derivatives are of low toxicity and decent stability, and thus serve as versatile intermediates for many synthetic transformations.[1,2] Of particular interest is the stereo-defined allylic boronic acid derivatives, which may provide a synthetically attractive allylic entity into organic skeletons. Compared to previous approaches to allylic boronic acid derivatives,[3] transition metal-catalyzed hydroboration of readily available allenes with pinacolborane (HBpin) would be, in principle, a very efficient method featuring excellent atom economy. However, compared with the well-established catalytic hydroboration of alkenes,[4] alkynes,[5] and 1,3-dienes,[6] the hydroboration of allenes has remained underdeveloped.[7,8] In 2009, a one-pot two-step reaction to form homoallylic alcohols involving non-catalytic hydroboration of alkyl-substituted terminal allenes with a chiral borane reagent has been reported, however, the stereoselectivity is rather poor (Scheme 1a).[9] In 2013, Tsuji et al. reported a copper-catalyzed hydroboration of mono-substituted terminal allenes to form linear *E*-allylic boronates as the major products, although the *E*/*Z* selectivity is subject to the steric effect of the R group (Scheme 1b).[10] In 1999, Miyaura and coworkers reported the preparation of linear *Z*-allylic boronates as major products via platinum-catalyzed hydroboration of 2,3-propadienyl TBS or methyl ether with *Z*/*E* ratios ranging from 84:16~91:9 (Scheme 1c).[11] Herein, we report a cobalt-catalyzed hydroboration of allenes with pinacolborane (HBpin) to provide *Z*-allylboronates with an excellent regio- and stereoselectivity (Scheme 1d).



Scheme 1. Hydroboration of allenes affording alkenyl or allylic boronates.

Based on the pincer ligand-based iron and cobalt complexes developed in Huang's group,[12] initially, ($^{tBu}P^ONN^{iPr}$)$FeCl_2$ (**1**) was chosen as the precatalyst for the hydroboration of 1,2-undecadiene (**3a**) with HBpin in toluene. Unfortunately, only a complicated mixture was formed. Subsequently, a series of complexes of Fe and Co supported by various P^CNN ligands[12] were investigated. To our delight, using ($^{tBu}P^CNN^{iPr}$)$FeCl_2$ (**2a**) as the precatalyst, the reaction afforded *Z*-**4a** in a high yield together with small amounts of regioisomers **5a** and **6a** as determined by ^1H NMR analysis of the crude reaction mixture (Table 1, entry 2). The difference between **1** and **2a** is largely due to the increased steric hindrance around the metal center. Interestingly, using the cobalt complex with the same pincer ligand **2b** with its structure established by X-ray diffraction (Table 1),[13] the reaction afforded *Z*-**4a** exclusively, albeit with 40% of **3a** being recovered. Further screening of the precatalysts revealed that Fe complex **2c** with a less hindered $^{iPr}P^CNN^{iPr}$ ligand is more active than the Co variant **2d** with the same ligand, but the former is much less selective (Table 1, compare entry 5 with entry 6). The Co complex **2e** with the least sterically demanding ligand among the PNN ligands investigated here is less efficient than **2b**, albeit with an excellent selectivity

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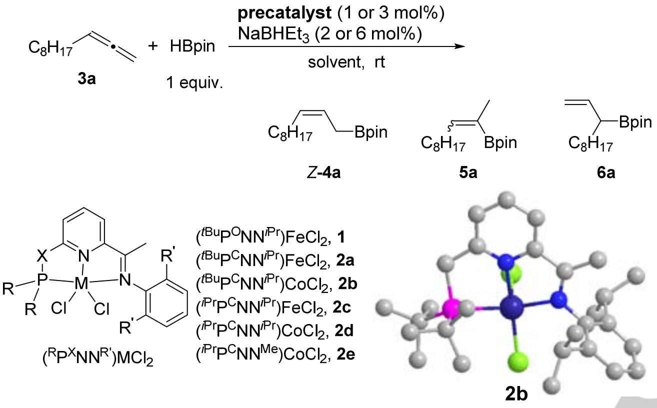
(Table 1, entry 8 vs. entry 2). Further optimization led to the observation that increasing the loading of precatalyst **2b** from 1 to 3 mol% afforded the hydroboration product *Z*-**4a** in 90% yield without the detection of other isomers (Table 1, entry 4). The yield dropped when the reaction was conducted in ethyl ether, hexane, or THF, although the selectivity remained unaffected (Table 1, entries 9-11). No conversion was observed in the absence of the metal complex or the catalyst activator $NaBHEt_3$ (Table 1, entries 12 and 13). Therefore, the conditions used in entry 4 were chosen as the optimized reaction conditions for further study.

Table 1. Optimization of the reaction conditions.[a]



Entry	**Precatalyst**	Solvent	NMR yield (%)[b] *Z*-**4a**:**5a**:**6a**	Recovery of **3a** (%)
1	**1**	toluene	-	-
2	**2a**	toluene	85:7:6	-
3	**2b**	toluene	57:0:0	40
4[c]	**2b**	toluene	90 (87):0:0	-
5	**2c**	toluene	41:12:12	-
6	**2d**	toluene	40:0:0	45
7	**2d**	toluene	66:13:0	22
8	**2e**	toluene	38:0:0	45
9[c]	**2b**	Et_2O	88:0:0	-
10[c]	**2b**	hexane	87:0:0	-
11[c]	**2b**	THF	60:0:0	-
12[c]	**-**	toluene	-	89
13[c,d]	**2b**	toluene	-	93

[a] Reaction conditions: **3a** (0.2 mmol), HBpin (0.2 mmol), 2 μmol of precatalyst, and 4 μmol of $NaBHEt_3$ in toluene (0.5 mL) for 4 h. [b] Determined by ^1H NMR analysis of the crude product with CH_3NO_2 as the internal standard. The value in parentheses is the isolated yield of product *Z*-**4a**. [c] **3a** (0.2 mmol), HBpin (0.2 mmol), 3 mol% of precatalyst, and 6 mol% of $NaBHEt_3$ in solvent (1 mL) for 24 h. [d] $NaBHEt_3$ was not added.

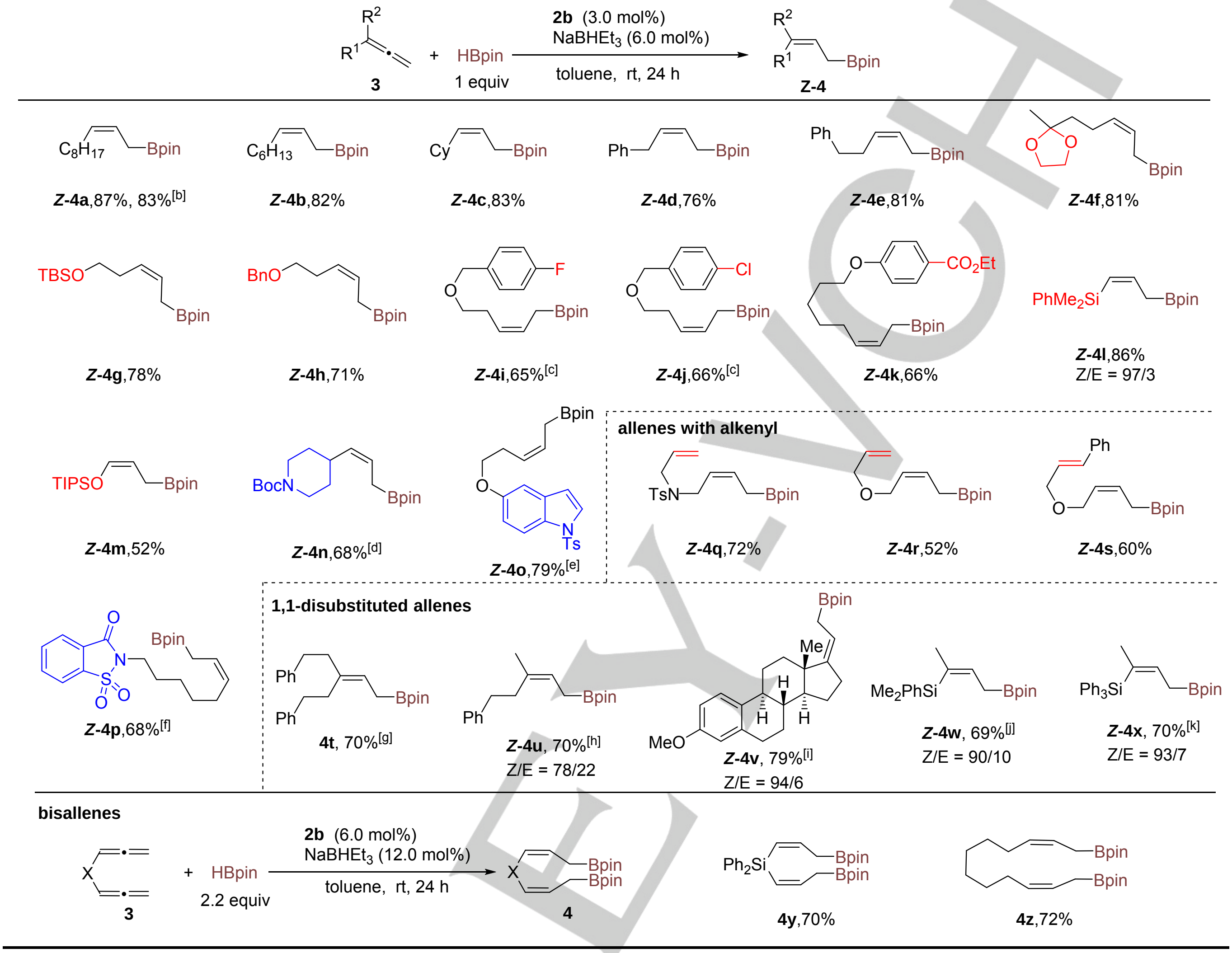
Next, we investigated the scope of cobalt-catalyzed allene hydroboration. Various functionalized allenes underwent hydroboration with HBpin in high yields and excellent regio- and stereoselectivity at ambient temperature (Table 2). Hydroboration of alkyl substituted allenes proceeded smoothly under the standard reaction conditions (**4a**-**4e**). The gram-scale reaction of **3a** with HBpin (5 mmol) afforded **4a** in 83% yield. Synthetically useful functional groups such as ketal (**4f**), OTBS (**4g**), benzyloxy (**4h**), halogen (**4i** and **4j**), ester (**4k**), and *N*-heterocycles (**4n**, **4o,** and **4p**) could be tolerated. Even the very bulky silyl-substituted allene **3l** could also be accommodated, affording the corresponding *Z*-allylboronate **4l** containing both C-B and C-Si bonds with a 97:3 *Z/E* selectivity. Exclusive *Z*-selectivity was observed even for product **4m**, which showed a *Z/E* selectivity of ~90:10 as reported in the literature.[11] The high selectivity for the formation of allylic boronate *Z*-**4c** from cyclohexylpropadiene is also noteworthy since it afforded vinylic boronates under the conditions reported by Tsuji et al.[10]

Although cobalt complexes have been reported to catalyze the hydroboration of alkenes,[4e,4g,4h] under the optimized conditions, allenes exhibit a much higher reactivity than both terminal and internal alkenes as demonstrated by the formation of *Z*-**4q**, *Z*-**4r**, and *Z*-**4s** in high yields with an exclusive chemoselectivity.

Hydroboration of 1,1-disubstituted allenes also worked well allowing for the construction of trisubstituted (*Z*)-allylic boronates **4t-4x**. The stereoselectivity is determined by the steric effect of these two substituents as shown by the *Z*/*E* ratios of **4u, 4w,** and **4x.** Even an estrone 3-methyl ether derived product *Z*-**4v** was formed and isolated in a high yield and an excellent *Z/E* selectivity. Double hydroboration of Si- or C-tethered bisallenes **3y** and **3z** afforded bisallylic boronates **4y** and **4z** in high yields and an excellent ***Z***-selectivity via the reaction with 2.2 equiv of HBpin, without formation of the monohydroboration products.

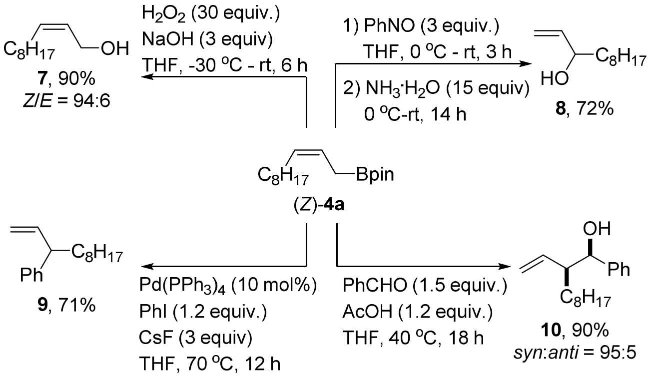
To demonstrate the synthetic utility of this methodology, synthetic transformations of (*Z*)-**4a** were conducted. Linear allylic alcohol **7** or branched allylic alcohol **8** could be obtained in high yields using H_2O_2[14] or PhNO[15] as the oxidant, respectively. Suzuki-Miyaura coupling reaction of (*Z*)-**4a** and iodobenzene afforded the corresponding branched allylbenzene derivative (**9**). Moreover, (*Z*)-**4a** could react with benzaldehyde,[16] furnishing homoallylic alcohol **10** with a high diastereoselectivity.

Table 2. Z-selective hydroboration of various allenes.[a]

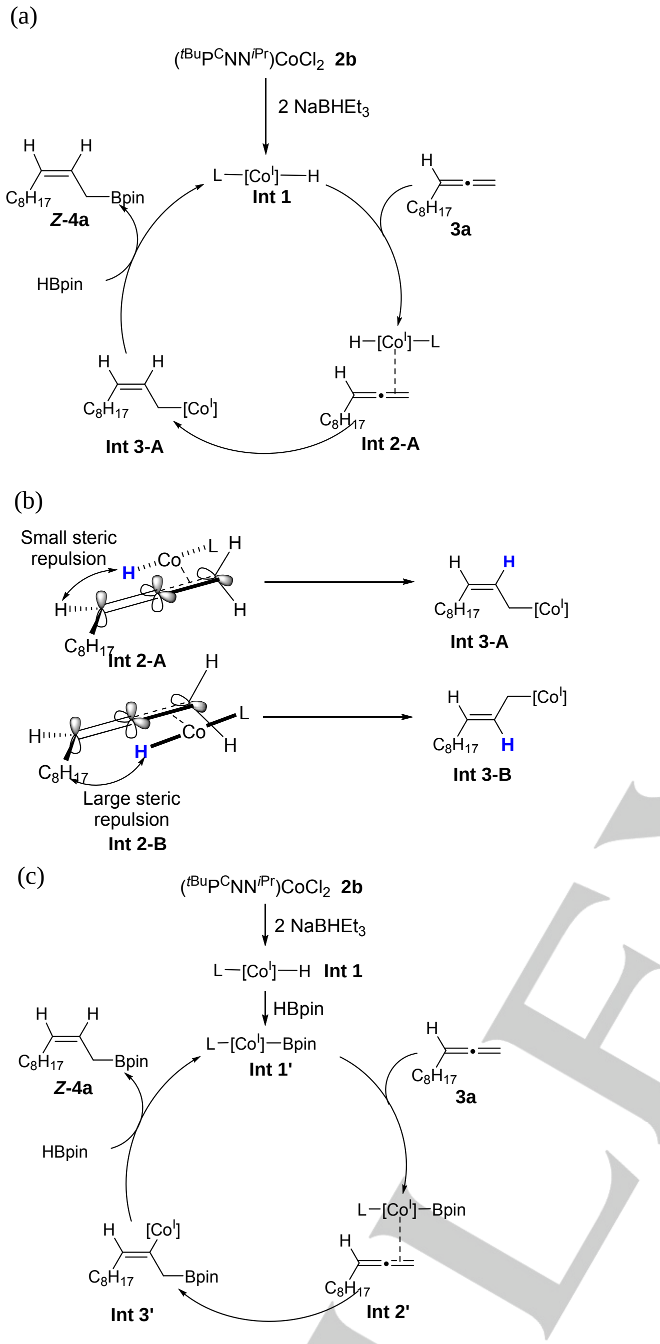


[a] The reaction was carried out with 1 equiv of **3**, 1 equiv of HBpin, 3 mol% of **2b**, and 6 mol% of $NaBHEt_3$ in toluene (0.2 M) at room temperature for 24 h on 1.0 or 0.5 mmol scale. Yields of isolated products were given. [b] The reaction was carried out on 5 mmol scale to afford 1.16 g of *Z*-**4a**. [c] 5 mol% of **2b** and 10 mol% of $NaBHEt_3$ were used. [d] The reaction was run for 43 h. [e] The reaction was run for 36 h. [f] The reaction was run for 35 h. [g] The reaction was run for 54 h. [h] The reaction was run for 22 h. [i]The reaction was run for 38.5 h. [j] The reaction was carried out at 50 °C for 48 h. [k] 5 mol% of **2b** and 10 mol% of $NaBHEt_3$ were used. The reaction was carried out at 50 °C for 48 h.

Based on previous reports of cobalt-catalyzed hydroborylation reactions,[4e,18] a rationale for the cobalt-catalyzed hydroboration of allenes is proposed as shown in Scheme 3. The precatalyst **2b** would react with $NaBHEt_3$, affording the catalytically active Co(I) hydride species **Int 1**, followed by the coordination with the terminal C=C double bond of substrate **3a** from the less hindered side to form **Int 2-A** (Scheme 3b shows that **Int 2-A** is sterically more favorable than **Int 2-B**). Following the insertion of double bond into the Co-H bond, a *Z*-allylic cobalt intermediate **Int 3-A** is formed. Subsequent reaction with HBpin, via either σ-bond metathesis or oxidative addition and reductive elimination, would furnish the hydroboration product *Z*-**4a** and regenerate **Int 1** (Scheme 3a). Alternatively, the Co(I) hydride species **Int 1** may react with HBpin to cobalt(I)-Bpin intermediate **Int 1'**.[17] **Int 1'** then undergoes coordination and insertion processes to yield the vinyl cobalt intermediate **Int 3'** through **Int 2'**. Subsequently the reaction of **Int-3'** with HBpin affords the hydroboration product *Z*-**4a** and regenerates **Int-1'** (Scheme 3c).



Scheme 2. Synthetic applications.



Scheme 3. Proposed mechanisms.

In order to distinguish between these two pathways, we sought to identify the catalytic intermediates of the catalytic reaction by solvent-assisted electrospray ionization−mass spectrometry (SAESI-MS) and SAESI-MS/MS analysis. Two species with molecular weight matching those of Co(I)-H **Int-1** **(***m/z* 497, [M-H]$^+$**)** and *Z*-allylic cobalt **Int 3-A** **(***m/z* 650, [M]$^{\bullet+}$) were detected (Figure 1 and see Supporting Information for details),[18] while the species corresponding to Co(I)-Bpin intermediate **Int-1'** **(***m/z* 624) and vinyl cobalt intermediate **Int 3'** **(***m/z* 776) were not observed. The structures of **Int 1** and **Int 3-A** were further confirmed by SAESI-MS/MS experiment (Figure 1c and 1d). Such SAESI-MS data provide evidence in support of the catalytic cycle involving the intermediacies of Co(I)-H **Int 1** and *Z*-allyl-cobalt **Int 3-A**, as shown in Scheme 3a.

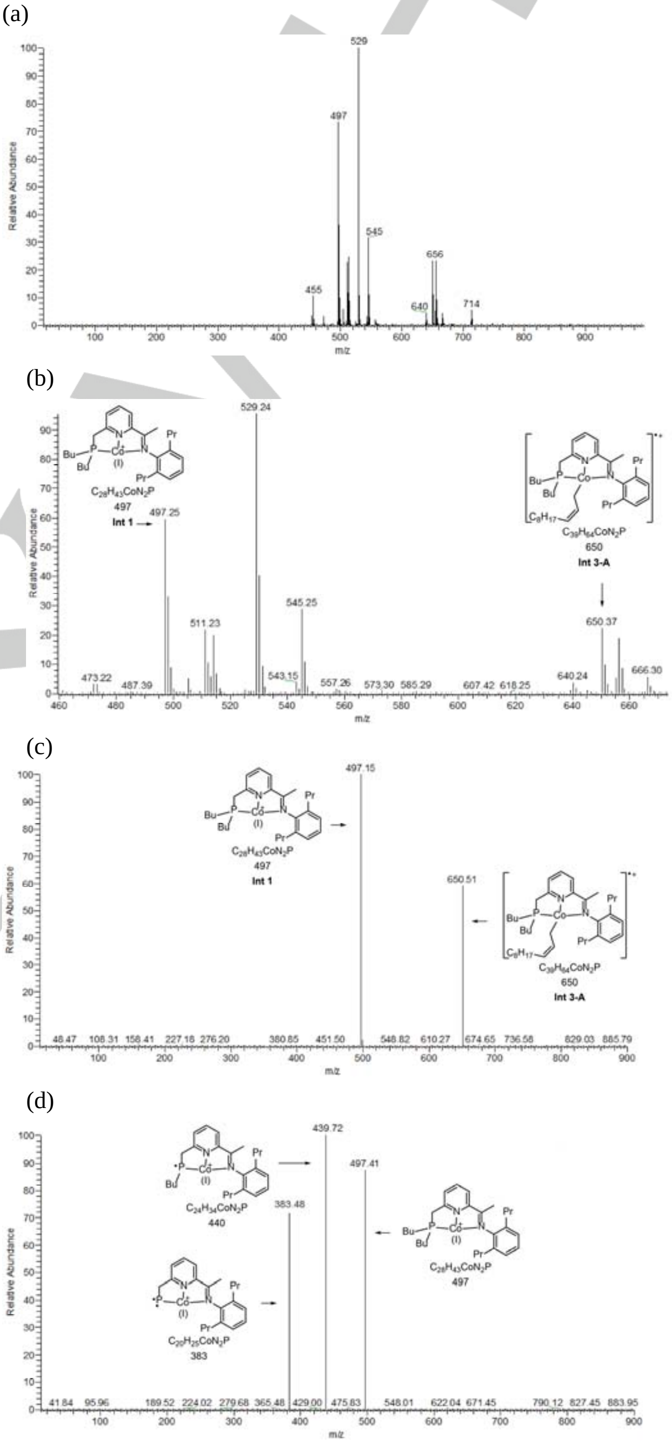


Figure 1. SAESI-MS studies. (a) SAESI-MS spectrum of the solution. (b) Expanded SAESI-MS spectrum, showing the major signal of **Int 1** [C$_{28}$H$_{43}$CoN$_2$P]$^+$ at *m/z* 497 and **Int 3-A** [C$_{39}$H$_{64}$CoN$_2$P]$^{\bullet+}$ at *m/z* 650. (c) SAESI-MS/MS spectrum of complex ion **Int 1** [C$_{28}$H$_{43}$CoN$_2$P]$^{\bullet+}$ at *m/z* 497. (d) SAESI-MS/MS spectrum of complex ion **Int 3-A** [C$_{39}$H$_{64}$CoN$_2$P]$^{\bullet+}$ at *m/z* 650.

In summary, we have developed a highly efficient hydroboration of allenes catalyzed by P^{C}NN-cobalt complex **2b** and identified two of the catalytic intermediates using SAESI-MS and SAESI-MS/MS analyses. This reaction features excellent regio- and *Z*-stereoselectivity, 100% atom economy, and a broad substrate scope with functionalized mono- and bisallenes. In addition, for the reaction of enallenes, the exclusive hydroboration of the allene moiety was observed, leaving alkene moiety untouched. (*Z*)-Allylboronate products could be transformed into different allylic alcohols, or underwent Suzuki-Miyaura coupling reaction to form C-C bonds.

Acknowledgements

Financial support from National Natural Science Foundation of China (21690063 for S. Ma; 21825109 for Z. Huang) is greatly appreciated. We thank Mr. Penglin Wu in this group for reproducing the results for (*Z*)-**4e**, (*Z*)-**4i**, and (*Z*)-**4q** as presented in this study.

Keywords: Allene • Hydroboration • Cobalt-catalyzed • (*Z*)-allylboronate

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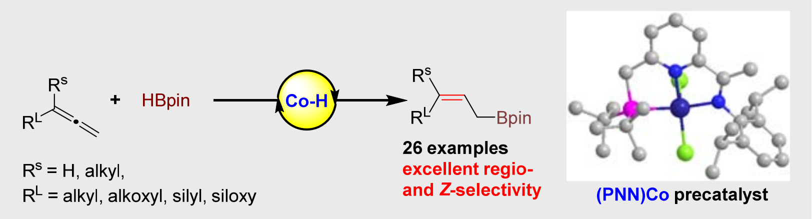

An efficient **(PNN)Co**-catalyzed allene hydroboration affording *Z*-allylic boronates is described. The reaction enjoys an excellent regio- as well as *Z*-selectivity and a wide substrate scope.

Can Li, Zheng Yang, Lei Wang, Yinlong Guo, Zheng Huang,* and Shengming Ma**

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Cobalt-Catalyzed Regio- and Stereoselective Hydroboration of Allenes