Synthetic Methods

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A Cobalt-Catalyzed Alkene Hydroboration with Pinacolborane**

*Lei Zhang, Ziqing Zuo, Xuebing Leng, and Zheng Huang**

Abstract: *An extremely efficient cobalt catalyst for the hydroboration of both vinylarenes and aliphatic α-olefins with pinacolborane is described, providing the anti-Markovnikov products with excellent regio- and chemoselectivity, broad functional-group tolerance, and high turnover numbers (up to 19800). The alkene hydroboration route is further extended to a two-step, one-pot hydroboration and cross-coupling of alkylboronates with aryl chlorides.*

Alkylboronic acid derivatives are versatile intermediates for organic synthesis, as they are utilized in the construction of various C−C, C−O, and C−N bonds.[1] In the context of the transition-metal-catalyzed $C(sp^3)-C(sp^2)$ and $C(sp^3)-C(sp^3)$ bond-forming reactions, the Suzuki–Miyaura coupling using $C(sp^3)$ organoboron compounds has emerged as a powerful protocol because of the thermal stability of the nucleophiles, nontoxic nature of the inorganic by-products, operational simplicity, and wide functional-group compatibility.[2] Traditionally, alkylboronic acid derivatives are synthesized by addition of alkyllithium or alkylmagnesium reagents to suitable boron compounds.[3] However, the use of reactive organometallic reagents is restricted to substrates without sensitive functional groups. Recently, transition-metal-catalyzed borylations have been developed for the preparation of alkylboronic acid derivatives. For example, Hartwig and co-workers reported a direct alkylboronate synthesis involving Rh-catalyzed alkane borylation with B_2Pin_2.[4] In 2012, Liu, Marder, Steel, and co-workers reported a Cu-catalyzed borylation of alkyl halides with B_2Pin_2 to form alkylboronates with diverse functionalities.[5]

With respect to atom economy, alkene hydroboration is a more attractive approach to alkylboronate esters.[1b,6] Although dialkylboranes react readily with alkenes, the addition of dialkoxyboranes to alkenes occurs sluggishly in the absence of catalyst. Most catalytic alkene hydroborations involve complexes of precious metals, such as Rh[7] and Ir.[7k,8] However, the low abundance, economic constrains, and environmental concerns over noble metals have inspired the investigation of earth-abundant and inexpensive base–metal alternatives. In 2009, Ritter described iminopyridine iron catalysts that show high regio- and stereoselectivity in the hydroboration of 1,3-dienes with pinacolborane (HBpin).[9] In 2013, we reported that a [(^{tBu}PNN)$FeCl_2$] pincer complex **1** (Figure 1) is even more efficient than the well-documented Rh and Ir catalysts in the hydroboration of α-olefins with HBpin.[10] However, the Fe catalyst is unreactive toward internal olefins. In a subsequent report, Obligacion and Chirik demonstrated that bis(imino)pyridine iron dinitrogen complexes are effective for hydroboration of α-olefins and cycloalkenes.[11] More recently, Greenhalgh and Thomas showed that a combination of $FeCl_2$ and a bis(imino)pyridine ligand, upon activation with EtMgBr, is also active for alkene hydroborations.[12] There are limitations to the scope of iron catalysts: preliminary studies in our group showed that α-olefins containing allyl ethers and ketones cannot be efficiently hydroborated.[13]

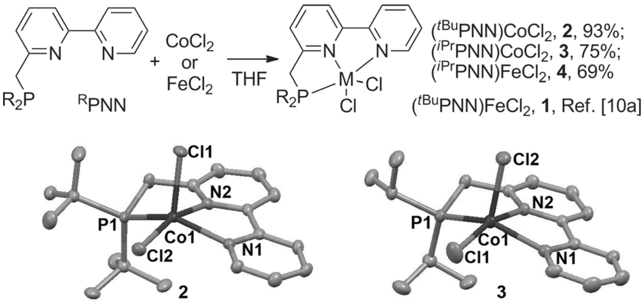

Figure 1. Synthesis of [(^{tBu}PNN)$CoCl_2$] (**2**), [(^{iPr}PNN)$CoCl_2$] (**3**), and [(^{iPr}PNN)$FeCl_2$] (**4**), and the solid-state structures of the cobalt complexes **2** and **3**.

Very recently, there has been noteworthy progress in the development of cobalt catalysts for alkene hydrogenations[14] and hydrosilylations.[15] For example, Hanson and co-workers reported a novel aliphatic PNP pincer Co^{II} alkyl catalyst for the hydrogenation of olefins, ketones, aldehydes, and imines.[14a,b] Chirik and co-workers developed an enantiopure Co complex of a bis(imino)pyridine ligand for the asymmetric hydrogenation of *gem*-disubstituted alkenes.[14c] They also showed that a Co complex of an biscarbene pyridine ligand is an effective precatalyst for the hydrogenation of sterically hindered alkenes.[14d] However, examples of cobalt-catalyzed alkene hydroborations are very rare.[16]

Herein, we report the preparation of PNN pincer Co complexes and their application in Co-catalyzed alkene hydroborations. This system is remarkably efficient for the anti-Markovnikov hydroboration of both vinylarenes and aliphatic α-olefins with HBpin. Most reactions proceeded to completion with 0.005–0.05 mol % of catalyst with or without solvent. Beyond high activity, the new base–metal system offers broad functional-group tolerance and excellent chemo-

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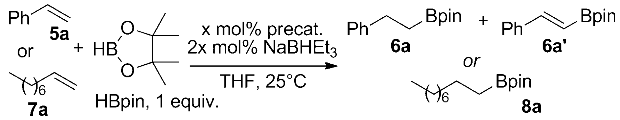
selectivity. In addition, we describe a two-step, one-pot protocol comprising a Co-catalyzed hydroboration and a Pd-catalyzed cross-coupling of alkylboronates with aryl chlorides.

The synthesis of the [(^{R}PNN)CoCl$_2$] (**2**: R = *t*Bu; **3**: R = *i*Pr) complexes is outlined in Figure 1. Treatment of Milstein's PNN ligands, which contain phosphino *tert*-butyl and phosphino isopropyl groups, with CoCl$_2$ resulted in the Co pincer complexes **2** and **3**, respectively, in good yields. The iron analogue **4**, which is supported by the ^{iPr}PNN ligand, was also prepared in a similar procedure.[17] Figure 1 includes the solid-state structures of **2** and **3**, which show a distorted square-pyramidal geometry at the mononuclear Co site.[18]

Our initial experiments focused on assessing the activity of the Co and Fe precatalysts for the hydroboration of vinylarenes and aliphatic α-olefins with HBpin. In our previous report, we showed that the Fe precatalyst **1**, upon activation with NaBHEt$_3$, is efficient in the hydroboration of aliphatic α-olefins (Table 1, entry 2). For vinylarenes, however, the hydroboration process was accompanied by a dehydrogenative borylation to form vinylboronate (Table 1, entry 1).[10a] The catalysis with the new Fe complex [(^{iPr}PNN)FeCl$_2$] (**4**) led to similar results. The reaction with 1-nonene (**7a**) occurred smoothly (Table 1, entry 4), but the reaction with styrene (**5a**) gave the hydroboration product **6a** in 48 % and vinylboronate ester **6a′** in 52 % yield (entry 3). In sharp contrast, the use of the Co complex **2** engendered **6a** in a high yield (93 %) in the hydroboration of **5a**. No dehydrogenative borylation product was observed in this reaction (Table 1, entry 5). However, this precatalyst is less efficient for the hydroboration of **7a**, giving **8a** in 75 % yield after one hour and 78 % yield after five hours. To our delight, the less sterically hindered Co complex **3** proved highly effective in the hydroboration of both vinylarenes and aliphatic α-olefins. The reaction of **5a** with only 0.05 mol % of **3** in THF at 25 °C afforded isolated product **6a** in 91 % yield after 15 minutes (Table 1, entry 8). Under the "solvent-free" conditions, the reaction proceeded to completion within three minutes, corresponding to a turnover frequency of 40 000 h^{-1} (Table 1, entry 9). In the reaction with **7a**, the catalyst loading could be reduced to 0.01 mol % and isolated product **8b** was obtained in nearly quantitative yield (95 %) after one hour (Table 1, entry 11). The desired hydroboration products were detected as the sole products in each instance (Table 1, entries 7–11).

Table 1: Co- and Fe-catalyzed alkene hydroboration.[a]

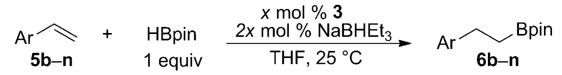


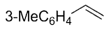
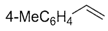
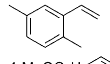
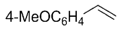
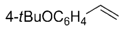
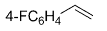
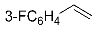
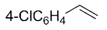
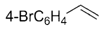
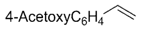
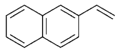
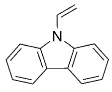
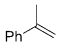
	Olefin	Precat. ([mol %])	*t* [min]	**6a** or **8a**, yield [%]	Yield [%] of **6a′**
1[b]	**5a**	**1** (2)	30	**6a**, 34[c]	65[c]
2[b]	**7a**	**1** (0.25)	10	**8a**, 95	–
3	**5a**	**4** (1)	60	**6a**, 48[c]	52[c]
4	**7a**	**4** (1)	60	**8a**, 95	–
5	**5a**	**2** (1)	60	**6a**, 93	–
6	**7a**	**2** (1)	60	**8a**, 75	–
7	**5a**	**3** (1)	60	**6a**, 92	–
8	**5a**	**3** (0.05)	15	**6a**, 91	–
9[d]	**5a**	**3** (0.05)	3	**6a**, > 99	–
10	**7a**	**3** (0.05)	15	**8a**, 95	–
11	**7a**	**3** (0.01)	60	**8a**, 95	–

[a] Reaction conditions: HBpin (0.5 mmol) and **5a** or **7a** (0.5 mmol) in THF (1 mL) at 25 °C. Unless otherwise specified, yields shown are of isolated products. [b] Results from Ref. [10a]. Reaction conditions: HBpin (0.5 mmol) and **5a** or **7a** (1 mmol) in THF (1 mL) at 25 °C. [c] Yield was determined by ^{1}H NMR analysis using an internal standard. [d] Under solvent-free conditions, HBpin (5.0 mmol) and **5a** (5.0 mmol).

To investigate the scope and limitation of the cobalt system, we used complex **3** as the precatalyst for the hydroboration of a diverse array of vinylarenes. The results are summarized in Table 2. All reactions were selective for the formation of the linear hydroboration products. Most reactions proceeded to completion within 15 minutes at 25 °C using only 0.05 mol % of **3**, and provided isolated products in yields higher than 90 %. The method worked efficiently for vinylarenes that bear electron-donating and electron-withdrawing groups. A methyl substituent is tolerated at all the positions on the aromatic ring (**6b–d**). Halogen-substituted vinylarenes are compatible with the reaction conditions (**6g–j**). Ester functionalities are also tolerated, as shown by the isolation of **6k** in 80 % yield. The hydroboration of *N*-vinylcarbazole gave **6m** in 92 % yield. However, α-methylstyrene (**5n**) was unreactive in the hydroboration, even though a higher catalyst loading was used.

Table 2: Hydroboration of vinylarenes (**5b–n**) with HBpin catalyzed by **3**.

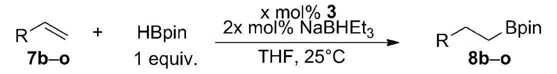


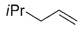
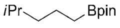
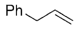
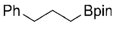
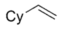
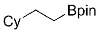
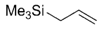
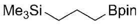
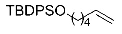
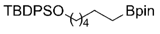
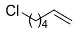
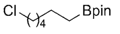
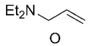
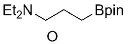
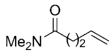
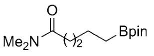
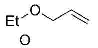
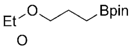
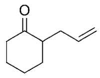
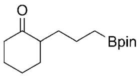
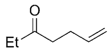
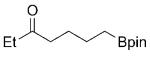
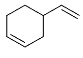
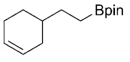
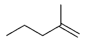
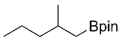
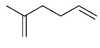
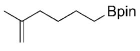
	Substrate		**3** [mol %]	*t* [min]	Yield [%][b]
1	 3-MeC$_6$H$_4$	**5b**	0.05	15	97
2	 4-MeC$_6$H$_4$	**5c**	0.05	15	93
3		**5d**	0.05	15	93
4	 4-MeOC$_6$H$_4$	**5e**	0.05	15	96
5	 4-*t*BuOC$_6$H$_4$	**5f**	0.1	15	93
6	 4-FC$_6$H$_4$	**5g**	0.05	15	97
7	 3-FC$_6$H$_4$	**5h**	0.05	15	89
8	 4-ClC$_6$H$_4$	**5i**	0.1	30	90
9	 4-BrC$_6$H$_4$	**5j**	0.05	15	92
10	 4-AcetoxyC$_6$H$_4$	**5k**	0.1	15	80
11		**5l**	0.1	15	93
12		**5m**	0.1	15	92
13	 Ph	**5n**	5	30	n.r.

Reaction conditions: HBpin (0.5 mmol) and alkenes (0.5 mmol) in THF (1 mL) at 25 °C. Yields shown are of isolated products. n.r. = no reaction.

Complex **3** was next investigated as a precatalyst for the hydroboration of aliphatic olefins that contain various func-

Table 3: Hydroboration of various aliphatic alkenes (**7a–o**) with HBpin catalyzed by **3**.



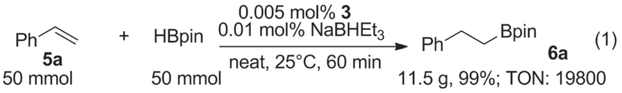
	Substrate		Product		**3** [mol %]	*t* [min]	Yield [%][b]
1		**7b**		**8b**	0.05	15	91
2		**7c**		**8c**	0.05	15	86
3		**7d**		**8d**	0.05	15	97
4		**7e**		**8e**	0.05	15	87
5		**7f**		**8f**	0.05	15	96
6		**7g**		**8g**	0.05	15	96
7		**7h**		**8h**	0.05	30	87
8		**7i**		**8i**	0.1	15	94
9[a]		**7j**		**8j**	1	15	72
10		**7k**		**8k**	1	15	92
11[a]		**7l**		**8l**	1	15	76
12		**7m**		**8m**	0.05	15	96
13		**7n**		**8n**	5	30	n.r.
14		**7o**		**8o**	0.05	15	94

Reaction conditions: HBpin (0.5 mmol) and alkenes (0.5 mmol) in THF (1 mL) at 25 °C. Yields shown are of isolated products. [a] HBpin (0.5 mmol) and **7** (0.75 mmol).

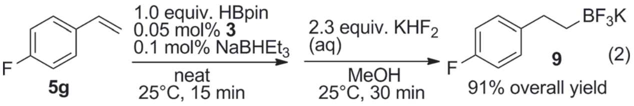
tional groups. The results are summarized in Table 3. Simple alkenes, such as 4-methyl-1-pentene, γ-phenylpropene, and cyclohexylethene were hydroborated in high yield. Functional groups, including silyl (**8e**, 87 %), silyl ether (**8f**, 96 %), halide (**8g**, 96 %), amine (**8h**, 87 %), and tertiary amide (**8i**, 94 %) were tolerated under the reaction conditions. Allyl ethers, which are challenging substrates, were also compatible, as shown by the isolation of **8j** in 72 % yield. It should be noted the Co system is highly chemoselective for the hydroboration of ketone-functionalized alkenes. The reaction of 2-allylcyclohexanone **7k** with HBpin exclusively formed the alkene hydroboration product **8k** in 92 % yield. No ketone hydroboration product was detected in this reaction. Similarly, the hydroboration of 6-hepten-3-one (**7l**) gave the desired product selectively in 76 % yield.

The catalytic activity of the Co system is very sensitive to the olefin substitution pattern. In 4-vinyl-cyclohexene (**7m**), the hydroboration of the terminal olefin occurred selectively without the hydroboration of the internal olefin (**8m**, 96 %). Even more noteworthy, *gem*-disubstituted alkenes, such as 2-methyl-1-pentene (**7n**) and **5n** (see Table 2) are unreactive under the Co-catalyzed hydroboration conditions. The high sensitivity of the Co catalyst to the steric effects of alkene substrates enables for chemoselective hydroboration of monosubstituted alkenes in the presence of *gem*-disubstituted alkenes. For example, the reaction of 2-methylhexa-1,5-diene (**7o**) afforded exclusively the product resulting from the hydroboration of the less sterically hindered double bond (**8o**, 94 %).

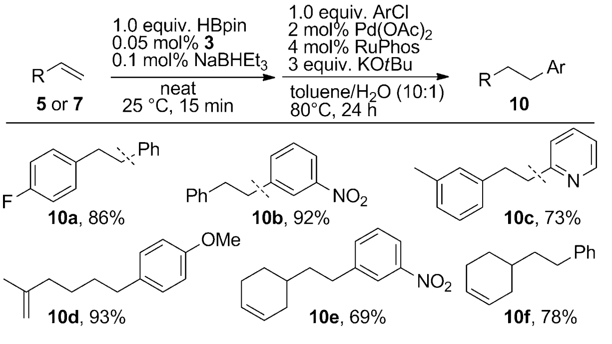
With a remarkably active catalyst for the alkene hydroboration in hand, we sought to develop procedures to conduct this transformation on a large scale. Using only 50 ppm (0.005 mol %) of **3**, the hydroboration of **5a** (50 mmol) with HBPin (50 mmol) occurred at 25 °C under neat conditions to afford isolated product **6a** in 99 % yield after one hour [Eq. (1)]. The result corresponds to a turnover number (TON) of 19800, which represents the highest turnover number observed for any metal-catalyzed alkene hydroboration with HBpin.



Given the quantitative conversion of alkenes to alkylboronates and the extremely low loading of the Co catalyst in most reactions, we anticipated that the crude products could be used for sequential transformations without purification. Organotrifluoroborates are valuable synthetic intermediates in Suzuki cross-couplings.[2c,19] Treatment of alkylboronate **6g**, generated in situ from 5g, with aqueous KHF_2, afforded the corresponding trifluoroborate in a high yield [Eq. (2)].



More interestingly, the hydroboration products could react in situ with aryl chlorides to afford the Suzuki–Miyaura cross-coupling products in good yields by using a Pd/RuPhos catalyst system (Scheme 1; RuPhos = 2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl).[20] This method represents the first one-pot process for the direct synthesis of alkyl–aryl coupling compounds from alkenes and aryl chlorides with HBpin as the hydroboration reagent. These reactions highlight several advantages compared to the conventional method utilizing *B*-alkyl-9-BBN (9-BBN = 9-borabicyclo-[3.3.1]nonane) reagents as the coupling partners. First, the handling of the robust alkylboronates is very simple, whereas



Scheme 1. One-pot Co-catalyzed hydroboration and Pd-catalyzed cross-coupling of alkylboronates with aryl chlorides. Yields shown are of isolated products.

the air-sensitive *B*-alkyl-9-BBN compounds are difficult to handle. Second, the alkylboronate approach can be used to prepare compounds containing *gem*-disubstituted alkenes (e.g., **10d**, 93%), whereas this functional group is readily hydroborated when alkylborane cross-coupling reactions are carried out.[21]

In conclusion, we have disclosed an unprecedented cobalt-catalyzed alkene hydroboration with pinacolborane. Featuring the use of sustainable, cost-efficient, and environmentally benign cobalt catalysts with loadings in the ppm range, 100% atom economy, mild reaction conditions, high conversion, excellent regio- and chemoselectivity, broad functional-group compatibility, and operational simplicity, the cobalt-catalyzed alkene hydroboration is a practical route to alkylboronates. We have also reported a convenient one-pot protocol for the Suzuki–Miyaura coupling of alkylboronates generated in situ with aryl chlorides. Mechanistic investigations of the cobalt-catalyzed hydroboration are in progress and will be reported in due course.

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Keywords: alkenes · cobalt · cross-coupling · hydroboration · synthetic methods

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