

Hydroboration of Alkynes Catalyzed by Pyrrolide-Based PNP Pincer-Iron Complexes

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Supporting Information

ABSTRACT: To utilize iron complexes as catalysts, the application of a well-designed ligand is critical to control the reactivity of the iron center. Recently, our group has succeeded in the synthesis of iron complexes bearing a pyrrolide-based PNP pincer ligand and their application to the catalytic transformation of dinitrogen into ammonia under mild reaction conditions. As an extensive study, we report the iron-catalyzed hydroboration of alkynes with pinacolborane, where the corresponding *E*-isomers are obtained selectively.



D evelopment of synthetic approaches to prepare organoboron compounds is quite important because these compounds can be directly used for various transformations including a carbon–carbon (C-C) bond formation.¹ In particular, boronic acids are quite useful reagents because of their stability and ease of handling. To obtain boronic acids, transition-metal-catalyzed hydroboration across C–C multiple bonds is a straightforward and efficient method.² Although precious metals have played a central role in achieving the transformation, the use of cheap and earth-abundant metals has attracted considerable attention in recent years.

Iron is the most earth-abundant transition metal and seems to be nontoxic. Therefore, the use of iron complexes as catalysts for organic transformations is quite attractive.³ In the past few years, several groups have reported iron-catalyzed hydroboration of alkynes.^{4,5a} In 2013, Enthaler and co-workers reported the first iron-catalyzed hydroboration of alkynes by using Fe₂(CO)₉ as a catalyst.^{4a} Since this first report, several groups have reported iron-catalyzed reactions by using various iron complexes as catalysts. However, these catalytic reactions usually require heating conditions^{4a,G,e} or the use of activators such as highly reactive reductants and basic reagents for iron complexes.^{4b-d} As a result, development of a novel reaction system to promote the catalytic reaction under mild conditions with broad scope of substrates is of significant importance.

To control the reactivity of iron complexes, the design of ligands around the iron center occupies a critical role. Recently, a pyrrolide-based PNP pincer ligand (2,5-bis-(phosphinomethyl)pyrrolide) has emerged as a variant of the anionic pincer ligand.^{6–9} Although various transition metal complexes bearing a pyrrolide-based PNP pincer ligand have been synthesized, the application of the complexes to catalytic reactions has been limited to only a few cases.⁷ Our group has succeeded in the synthesis of a series of iron complexes bearing a pyrrolide-based PNP pincer ligand (1-4), as shown in Figure 1.⁸ We also found some of these iron complexes work as effective catalysts to convert dinitrogen into ammonia under mild reaction conditions.⁸ The success in the catalytic nitrogen



Figure 1. Iron complexes bearing a pyrrolide-based PNP pincer ligand.

fixation motivated us to apply these iron complexes to organic transformations. In the course of this attempt, we have found these iron complexes effectively catalyze hydroboration of alkynes with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinacolborane: HBpin) at room temperature to give the corresponding (E)-alknenyl boranes as exclusive products. Herein, we report our investigation on the iron-catalyzed hydroboration of alkynes with pinacolborane under ambient reaction conditions.

At first, the optimization of reaction conditions was carried out by using phenylacetylene (5a) as a model substrate. Typical results are shown in Table 1. In the presence of 1 mol % of iron complexes (1-4), reactions of 5a with 1.1 equiv of HBpin in hexane as a solvent were carried out at room temperature for 16 h (Table 1, entries 1-4). The use of iron-chloro complex (1) and iron-methyl complex (2) gave the corresponding (E)alkenyl borane (6a) in low to moderate yields (Table 1, entries 1 and 2, respectively). The use of iron-hydride complex (3)promoted the hydroboration effectively to give 6a in 88% yield (Table 1, entry 3). Iron-dinitrogen complex 4 also worked as an effective catalyst under the same reaction conditions (Table 1, entry 4). Other solvents such as toluene and THF were also applicable, although the yields of 6a were slightly lower than that in hexane as a solvent (Table 1, entries 5 and 6). Separately, we confirmed no reaction occurred at all when the reaction was performed in the absence of the iron complex (Table 1, entry 7).

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Table 1. Optimization of Reaction Conditions^a

Ph-	—────────────────────────────── 5a (1.1 equiv)	catalyst (1 mol %) solvent rt, 16 h	Ph Bpin 6a
entry	catalyst	solvent	yield of 6a (%) ^b
1	1	hexane	21
2	2	hexane	43
3	3	hexane	$88 (88)^c$
4	4	hexane	81
5	3	toluene	79
6	3	THF	78
7	none	hexane	0

 a Sa (0.30 mmol) was reacted with HBpin (0.33 mmol) in the presence of catalyst complex (0.0030 mmol) in solvent at room temperature for 16 h. b NMR yield. ^cIsolated yield.

Next, we examined reactions of various alkynes with pinacolborane under the optimized reaction conditions. Typical results are shown in Scheme 1. The use of *p*-tolylacetylene and



^{*a*}**5** (0.30 mmol) was reacted with HBpin (0.33 mmol) in the presence of **3** (0.0030 mmol) in hexane at ambient temperature for 16 h. ^{*b*}Isolated yield. ^{*c*}3 mol % of **3** was used. ^{*d*}5 mol % of **3** was used. ^{*e*}2 equiv of HBpin was used. ^{*f*}NMR yield.

m-tolylacetylene gave the corresponding alkenyl boranes (**6b** and **6c**) in good yields, whereas the use of *o*-tolylacetylene did not give the desired product (**6d**) in reasonable yield, probably due to the steric hindrance. Reactions of alkynes bearing fluoro, chloro, and trifluoromethyl groups at the benzene ring were successful to give **6e**-**h**, although slightly higher catalyst loading was required to obtain **6g** and **6h** in good yields. Alkynes bearing coordinating functional groups such as ester and ether at the benzene ring were compatible with this reaction system, and the desired products (**6i** and **6j**) were obtained in good yields. As well as alkynes with a benzene ring,

an alkyne with a 3-thiophene ring was available to gain the corresponding product (6k) in 73% yield. Not only aromatic alkynes but also aliphatic alkynes can be applied to this reaction system to give the corresponding products (6l and 6m) in good yields. Unfortunately, internal alkyne cannot be applied to this reaction system. The reaction of diphenylacetylene afforded the desired product (6n) in 21% yield, despite the use of 5 mol % of catalyst and 2.0 equiv of HBpin.

To obtain insight on chemoselectivity of alkynes and alkenes, reactions with enynes were examined as shown in Scheme 2.





When a conjugated envne (50) was applied in this reaction system, the hydroboration of the alkyne moiety proceeded selectively (Scheme 2a). Furthermore, we tested the 4ethynylstyrene (5p) as a substrate bearing both terminal alkyne and alkene moieties (Scheme 2b). Interestingly, the selective transformation of the alkyne moiety afforded 6p in 73% yield. An analogous intermolecular reaction with a 1:1 mixture of ptolylacetylene (5b) and styrene was also examined, where dominant transformation of 5b was observed with almost quantitative recovery of styrene (Scheme 2c). In these reactions, products via hydroboration of the alkene moiety were not observed in the crude mixture. These results indicate that the present reaction system provides the completely selective hydroboration of alkynes even in the presence of the alkenes. In several previous examples of iron catalysts, hydroboration of both alkenes and alkynes was performed under the same reaction conditions,^{4b,d,e} whereas selective hydroboration of alkynes over terminal alkenes was rare.^{5b}

Additionally, we found the higher turnover number (TON) of 3 can be achieved at a higher reaction temperature. The reaction of 5a with 1.1 equiv of HBpin in the presence of 0.1 mol % of 3 at 60 °C for 16 h afforded the corresponding product 6a in 73% yield (Scheme 3). Separately, we confirmed that the reaction in the absence of 3 even under the heating conditions proceeded sluggishly. Accordingly, the TON is

Scheme 3. Reaction at High Temperature

estimated to be 710, and this is the highest TON ever reported for the iron-catalyzed hydroboration reactions of alkynes with hydroboranes.^{4,5}

To obtain mechanistic insight, treatment of 3 with an excess amount of HBpin was carried out (Scheme 4a). After the

Scheme 4. Generation and Reactivity of Iron–Boryl Complex 7



reaction, formation of iron-boryl complex 7 was observed as a new species. We succeeded in the isolation of 7 in a separate manner, and an ORTEP drawing is shown in Figure 2. We also



Figure 2. ORTEP drawing of iron-boryl complex 7.

examined the use of 7 as a catalyst for the present hydroboration, where the hydroboration product was obtained in a yield comparable to that in the case of 3 (Scheme 4b).

Previously, Webster and co-workers proposed a reaction pathway via reaction of iron-hydride with alkynes and subsequent σ -bond metathesis.^{4e} At present, we cannot exclude the possibility of the reaction pathway via iron-hydride. However, we consider that the reactivity of 7 indicates an alternative possibility of participation of iron-boryl species as a key intermediate in the iron-catalyzed hydroboration. More detailed mechanistic study will be reported in due course.

In summary, we have disclosed that the iron complexes bearing a pyrrolide-based pincer ligand worked as efficient catalysts toward hydroboration of alkynes with pinacolborane under ambient reaction conditions. The present reaction system has achieved the complete regioselectivity (exclusive formation of *E*-isomer) and chemoselectivity (transformation of alkynes over alkenes). The highest TON of 710 has been achieved when the reaction was carried out at 60 °C. Further utilization of pyrrolide-based PNP complexes is now in progress.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.7b01995.

Experimental details, additional discussion, spectroscopic data (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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