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Communication

Z-Selective Alkyne Functionalization Catalyzed by a *trans*-Dihydride N-Heterocyclic Carbene (NHC) Iron Complex

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ABSTRACT: The *Z*-selective functionalization of terminal alkynes is a useful transformation in organic chemistry and mainly catalyzed by noble metals. Here, we present the *Z*-selective hydroboration of terminal alkynes catalyzed by a stable *trans*-dihydride iron complex [$(PC_{NHC}P)Fe(H)_2N_2$)] (**2**). Overall, the reaction occurs at room temperature and provides near quantitative yields of the *Z*-vinylboronate ester. Interestingly, the same catalyst could also provide the *E*-vinylboronate by heating the reaction mixture at slightly elevated temperatures (50 °C). If, however, the reaction is performed in the absence of HBpin, rapid *Z*-selective alkyne dimerization is observed, which is further discussed in this report.

The transition metal catalyzed hydroboration of unsaturated C−C and C−X bonds (X = N or O) is a powerful synthetic method in organic chemistry.[1] To illustrate, the hydroboration of terminal alkynes offers an atom economical route toward vinylboronate esters that are important starting materials in a diverse set of organic transformations.[2] Because the addition of the borane is typically *syn* with respect to the C≡C bond, product selectivity commonly favors the more stable (*E*)-vinylboronate.[3] Accessing the (*Z*)-vinylboronate is challenging and has mainly been reported with noble metal catalysts like ruthenium,[4] rhodium, or iridium.[5] Recent studies, however, have shown that earth-abundant metals can also facilitate the *Z*-selective hydroboration of terminal alkynes.[6] For instance, Chirik and co-workers reported the first example of an earth-abundant cobalt catalyst capable of *Z*-selective hydrobration.[6b] Kirchner and co-workers reported a nonclassical iron polyhydride catalyst [$Fe(PNP)(H)_2(\eta^2\text{-}H_2)$] that also showed excellent selectivity for the corresponding (*Z*)-vinylboronate.[6a] Interestingly, a few years earlier, Leitner and co-workers reported a similar ruthenium complex [$Ru(PNP)(H)_2(\eta^2\text{-}H_2)$] that also showed comparable *Z* selectivity.[4c]

A common feature of these catalysts is that they all contain a rigid pincer ligand with a central pyridine donor (Figure 1). Intriguingly, pincer ligands with an XNX (X = NR, $P(OR)_2$, PR_2) type geometry and a central amino or pyridine donor have been fundamental to the development of earth-abundant metal catalysis.[7] Expanding on the versatility of the pincer ligand design, we recently reported the first example of a $PC_{NHC}P$ functionalized iron complex [$(PC_{NHC}P)FeCl_2$] (**1**), which facilitated catalytic hydrogen isotope exchange (HIE) at aromatic hydrocarbons upon formation of the stable *trans*-dihydride iron complex [$(PC_{NHC}P)Fe(H)_2N_2$)] (**2**).[8] Given the importance of transition-metal hydrides in alkyne functionalization strategies,[4c,6a] we were intrigued if complex **2** could facilitate the *Z*-selective hydroboration of alkynes, which still remains uncommon with earth-abundant metals.[6]

Here, we demonstrate that iron complex **2** facilitates the hydroboration of alkynes with excellent selectivity. The reaction occurs at room temperature and provides near quantitative yields of the corresponding (*Z*)-vinylboronate within 4 h. Interestingly, the corresponding (*E*)-vinylboronate could also be exclusively accessed via isomerization of the formed (*Z*)-vinylboronate at 50 °C. In addition, we found that when the reaction is performed in the absence of borane, the *Z*-selective homodimerization of alkynes was observed. Overall, complex **2** presents a dual alkyne functionalization strategy that, in particular for alkyne hydroboration, exhibits a good

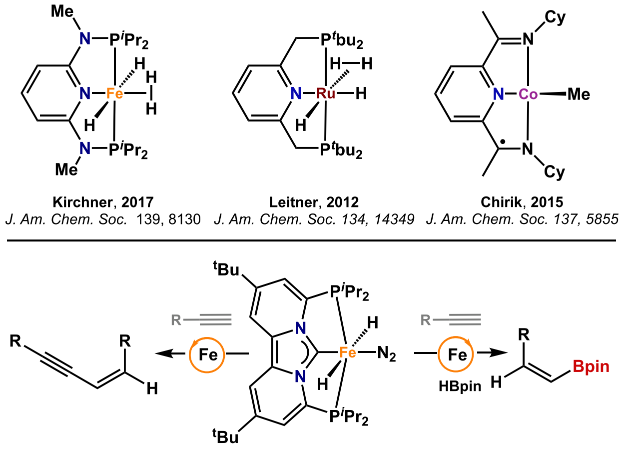

Figure 1. (Top) reported transition metal pincer complexes for *Z*-selective alkyne hydroboration. (Bottom) Herein reported *Z*-selective alkyne functionalization with iron $PC_{NHC}P$ pincer complex [$(PC_{NHC}P)Fe(H)_2(N_2)$] (**2**).

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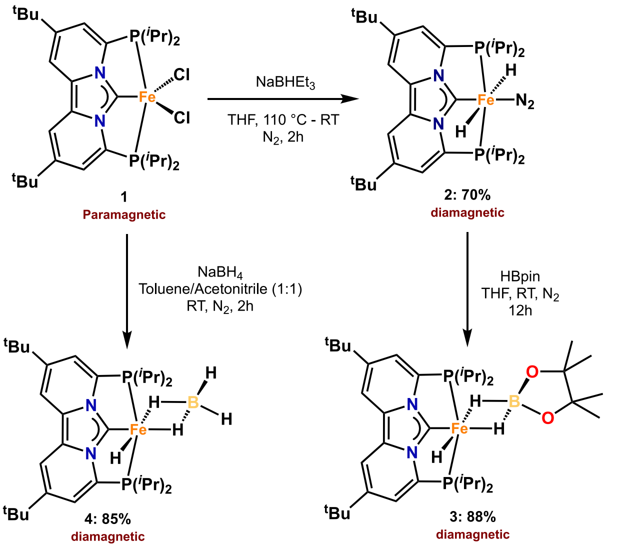
substrate scope and functional group tolerance (e.g., esters, ethers, halides).

Previously, we reported an efficient method for synthesizing $\mathrm{PC_{NHC}P}$ functionalized iron complexes.[8] The catalyst of interest, the *trans*-dihydride iron complex $[(\mathrm{PC_{NHC}P})\mathrm{Fe(H)_2N_2})]$, was readily obtained upon treating **1** with 2 equiv of $\mathrm{NaBHEt_3}$ (Scheme 1). Having facile access to such a stable iron(II) *trans*-dihydride prompted us to investigate its reactivity toward terminal alkynes in the presence of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin). Gratifyingly, addition of **2** to a solution of phenylacetylene and HBpin in THF resulted in the quantitative formation of (*Z*)-phenylvinylboronate ester (**5a**) with excellent stereoselectivity (*E*/*Z*; 2:98). Given that complex **2** is active for the hydroboration of phenylacetylene, other terminal alkynes were explored as well (Table 1). For example, *p*-tolylacetylene yielded the corresponding (*Z*)-tolylvinylboronate ester with excellent stereoselectivity and in excellent yields. Changing the substitution pattern to either *meta* or *ortho* did not considerably change the yield or stereoselectivity (Table 1; **5b**−**5d**).

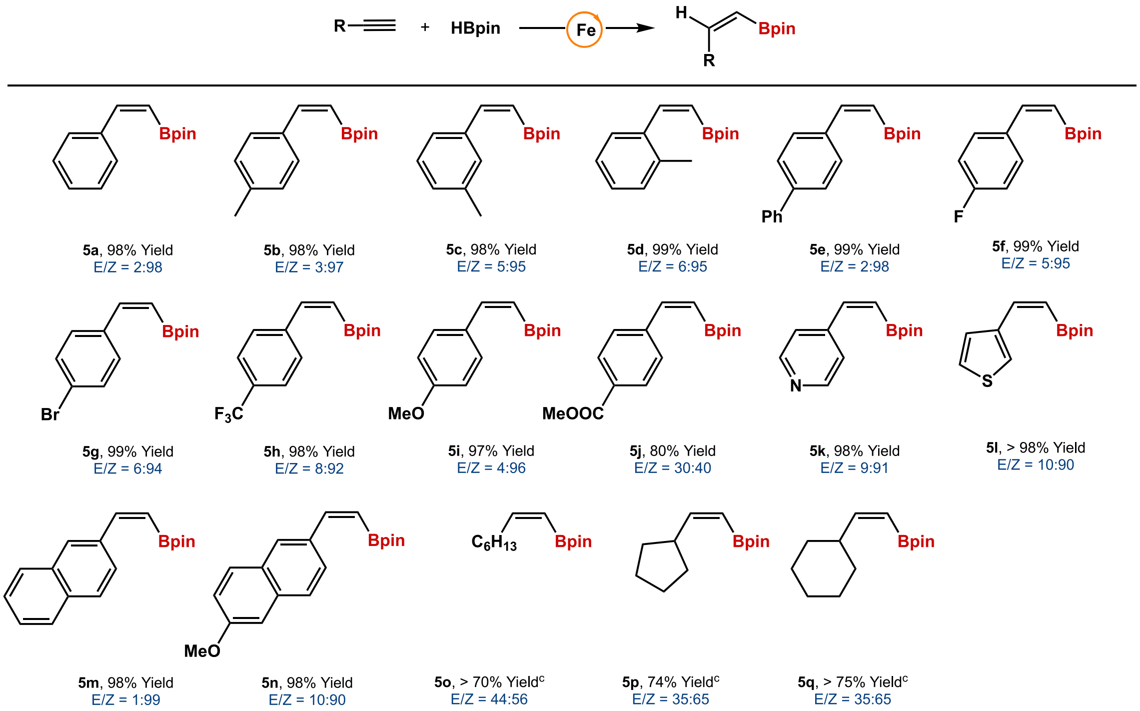
Scheme 1. Synthesis of Iron $\mathrm{PC_{NHC}P}$ Pincer Complexes 1−4



Electronically differentiated phenylacetylenes were also hydroborated efficiently. For example, *para* substituted phenylacetylenes that bear both electron withdrawing (**5f**, −F; **5g**, −Br; **5h**, $-\mathrm{CF_3}$) and electron donating (e.g., **5i**, −OMe) substituents are hydroborated in excellent yields (>95%) with similar *Z* selectivities (Table 1). Other functional groups such as esters (**5j**) or heteroaromatics (**5k** and **5l**) are also tolerated, although for the ester (**5j**) a diminished yield and erosion of the *Z* selectivity was observed.

In contrast, for aliphatic acetylenes, higher catalyst loadings and longer reaction times were necessary to obtain reasonable conversion of the starting materials. Yet, under these conditions, diminished *Z* selectivity was observed when compared to their aromatic counterparts. For example, for 1-octyne, only moderate stereo selectivity was obtained (Table 2; *E*/*Z* ∼ 45:55). Using sterically more demanding alkynes did not result in a significant improvement of the observed *Z* selectivity (Table 1). The diminished selective could be the result of a competing alkene isomerization side reaction that might occur at prolonged reaction times and catalyst loadings (*vide infra*). No hydroboration is observed for internal alkynes. These results demonstrate that the herein reported iron

Table 1. Scope and Limitations of the Iron Catalyzed (2) Hydroboration of Alkynes[a–c]



5a, 98% Yield E/Z = 2:98	**5b**, 98% Yield E/Z = 3:97	**5c**, 98% Yield E/Z = 5:95	**5d**, 99% Yield E/Z = 6:95	**5e**, 99% Yield E/Z = 2:98	**5f**, 99% Yield E/Z = 5:95
5g, 99% Yield E/Z = 6:94	**5h**, 98% Yield E/Z = 8:92	**5i**, 97% Yield E/Z = 4:96	**5j**, 80% Yield E/Z = 30:40	**5k**, 98% Yield E/Z = 9:91	**5l**, > 98% Yield E/Z = 10:90
5m, 98% Yield E/Z = 1:99	**5n**, 98% Yield E/Z = 10:90	**5o**, > 70% Yield[c] E/Z = 44:56	**5p**, 74% Yield[c] E/Z = 35:65	**5q**, > 75% Yield[c] E/Z = 35:65	

[a] Reactions were performed with alkyne (0.5 mmol), HBpin (0.55 mmol, 1.1 equiv), and catalyst **2** (2 mol %) in THF (0.5 mL) at room temperature (RT) for 4 h. [b] Yields and selectivity were determined by ^{1}H NMR spectroscopy with trimethoxybenzene as an internal standard. [c] For aliphatic alkynes **5o**−**5q**, reactions were performed with 5 mol % catalyst for 12 h at RT.

$PC_{NHC}P$ pincer complex **2** is a good catalyst for the *Z*-selective hydroboration of terminal alkynes and one of the few earth-abundant metal alternatives.[6] However, for aliphatic alkynes the observed stereoselectivity is lower than the *state-of-the-art* as reported by Chirik and Kirchner and a limitation of the catalyst.

A clear advantage of the herein reported method is, however, that by controlling the temperature, catalyst selectivity could be selectively switched from the (*Z*)-vinylboronate to the (*E*)-vinylboronate (Figure 2). To illustrate, products **5a**, **5b**, **5f**, **5i**, **5n**, and **5l** are selectively converted to the (*E*)-vinylboronate esters (**6**) after stirring the reaction mixture for an additional 4 h at slightly elevated temperatures (50 °C). The corresponding (*E*)-vinylboronate esters were isolated with excellent stereoselectivity (*E*/*Z* ≥ 99:1) and in near quantitative yields. (Figure 2). In the absence of a catalyst, the isolated *Z*-vinylboronate esters did not convert to their corresponding (*E*)-isomers.

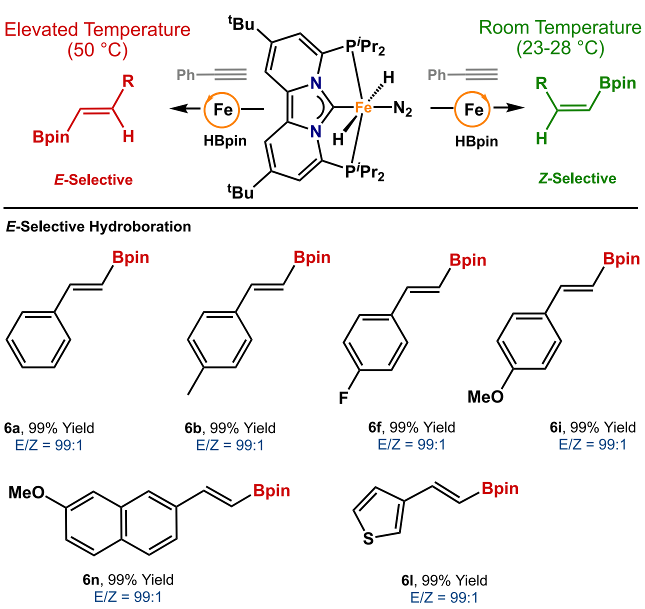


Figure 2. (Top) Temperature dependent stereoselective synthesis of *E*- and *Z*-vinylboronate esters. (Bottom) Selective formation of **6a**, **6b**, **6f**, **6i**, **6n**, and **6l** with catalyst **2** under elevated temperatures (50 °C).

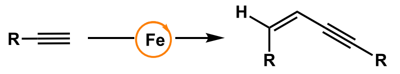
The mechanism for *Z*-selective hydroboration has been explored for both earth-abundant and precious metal catalysts. For earth-abundant metals, Chirik and Kirchner proposed a mechanism centered on the *syn*-hydrometalation of an alkynylboronate intermediate.[6b,9] In contrast, for precious metal catalysts such as rhodium, iridium, and ruthenium, Miyaura and Leitner proposed a metal vinylidene pathway.[4c,5] Both mechanisms feature an overall 1,1-*trans* addition of the borane to the alkyne. Recently, a more rare 1,2-*trans* addition was also described.[4a,10] To distinguish between the 1,1-*trans* or 1,2-*trans* hydroboration mechanism, we performed a series of isotope labeling studies. Under the optimized reaction conditions, deuterium labeling experiments with DBpin and phenylacetylene resulted in almost exclusive incorporation of the deuterium label at the β-carbon (Figures S1−S3). Incorporation of the deuterium label at the β-carbon rules out a 1,2-*trans*-hydroboration mechanistic pathway that has been recently reported for copper[10] and ruthenium.[4a] Additional isotope labeling experiments with phenylacetylene-d_1 did not provide additional information in order to discern between the different types of 1,1-*trans* hydroboration pathways; e.g., a metal vinylidene or *syn*-hydrometalation based pathway.[11]

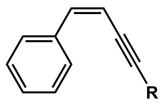
To gain further mechanistic insight into the herein reported hydroboration, we performed a series of stoichiometric experiments. The addition of 1 equiv of HBpin to complex **2** led to the exclusive formation of $[(PC_{NHC}P)Fe(H)(\mu\text{-}H)_2Bpin)]$ (Scheme 1; **3**), which might be an important catalytic intermediate. Such a proposal would certainly be consistent with the results reported by Kirchner and Leitner who have shown that their analogous iron and ruthenium complexes ($[(PNP)Fe(H)(\mu\text{-}H)_2Bpin)]$) and ($[(PNP)Ru(H)(\mu\text{-}H)_2Bpin)]$) are competent precatalyst for the Z-selective hydroboration of alkynes.[4c,6a] However, under the herein reported reaction conditions, complex **3** gave 15% yield of the (*Z*)-vinylboronate after 24 h, suggesting that **3** is an off-cycle species rather than an active (pre)catalyst. It is possible that the poor activity might be related to the reactivity of the Fe−H bond. Recent studies have shown that for a related iron species $[(PNP)Fe(H)(\mu\text{-}H)_2BH_2]$, the Fe−H bond is quite stable and unreactive toward alkynes.[6a] To verify for our system, we have synthesized the corresponding complex $[(PC_{NHC}P)Fe(H)(\mu\text{-}H)_2BH_2]$ (**4**) and found out that **4** is also catalytically inactive. These data imply that the Fe−H bonds in **3** and **4** are not reactive enough to initiate the hydroboration of terminal alkynes.

Because neither the isotope labeling experiments nor the stoichiometric experiments provided clear evidence for a metal vinylidene or *syn*-hydrometalation pathway, we attempted to isolate an iron(II) bis(acetylide) species that might be formed upon the addition of the alkyne to iron complex **2**. Metal-acetylides have been shown by both Chirik and Kirchner to be relevant intermediates in the *syn*-hydrometalation pathway.[6b,9] Unfortunately, adding 2 equiv of alkyne to complex **2** resulted in rapid alkyne dimerization, even when trimethylsilylacetylene was used. Not dismayed by the additional reactivity of **2** (*vide infra*), we realized that such intermediates might also be generated by the addition of phenylacetylene to complex **1** in the presence of base. Although the bis(acetylide)iron(II) species could still not be isolated, the addition of phenylacetylene to complex **1** in the presence of HBpin and base (NaHMDS) resulted in the formation of the corresponding (*Z*)-vinylboronate ester, which is consistent with the observations by Kirchner and co-workers (Figure S80).[9] Because the reactivities of complexes **1** and **2** in these experiments are identical to that observed by Kirchner and co-workers, and other mechanistic studies have proven to be inconclusive (*vide supra*), we believe that it is plausible that a similar mechanism might be operating akin to that proposed by Chirik and Kirchner (Figure S81).[6b,9]

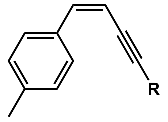
Because in the above-mentioned experiments alkyne dimerization was observed, we explored this reaction in more detail.[12] The addition of phenylacetylene to a solution complex **2** (0.5 mol %) in THF gave the corresponding enyne in quantitative yield and with exclusive *Z* selectivity. At present, the substrate scope is limited to aromatic acetylenes such as, tolyl-, biaryl-, arylhalide-, anisole-, and thiophene-substituted acetylenes (Table 2). All of these substrates give quantitative conversion within 2 h to the corresponding (*Z*)-enynes. Aliphatic alkynes, such as 1-octyne, only produced an intractable mixture of products. Compared to the *state-of-the-art* for earth-abundant metals,[12a] the obtained *Z* selectivity in

Table 2. Dimerization of Variously Substituted Alkynes by Iron Complex 2[a,b]

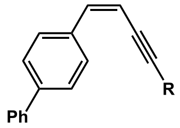




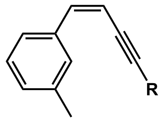
7a, > 99% Yield
E/Z = 1:99



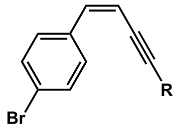
7b, > 99% Yield
E/Z = 1:99



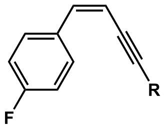
7c, > 99% Yield
E/Z = 1:99



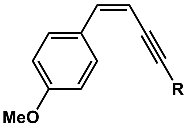
7d, > 99% Yield
E/Z = 1:99



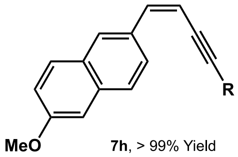
7e, > 99% Yield
E/Z = 1:99



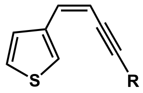
7f, > 99% Yield
E/Z = 1:99



7g, > 99% Yield
E/Z = 1:99



7h, > 99% Yield
E/Z = 1:99



6i, > 99% Yield
E/Z = 1:99

[a] Reactions were performed with alkyne (0.5 mmol) and catalyst **2** (0.5 mol %) in THF (0.5 mL) at room temperature for 2 h (Table 1). [b] Yields and selectivity were determined by ^1H NMR spectroscopy with trimethoxybenzene as an internal standard.

our studies are comparable to those reported by Milstein and Kirchner,[6a13] although the herein reported reaction times are generally shorter. However, the scope of Milstein's catalyst is much larger and also features cross-dimerization. It is interesting to note that Mashima and co-workers observed the opposite *E* selectivity for cross-dimerization with a cobalt bipyridine catalyst,[14] while Song and co-workers have shown geminal specific dimerization with an FeCp* catalyst containing a bidentate NHC ligand.[15] None of these dimerization patterns have been observed in the herein reported method under the herein used standard catalytic conditions (RT, N_2).

In summary, we have shown that the stable *trans*-dihydride iron complex $[(PC_{NHC}P)Fe(H)_2N_2)]$ (**2**) is highly active for the *Z*-selective hydroboration of terminal alkynes. The reaction occurs at room temperature and exhibits a reasonable functional group tolerance that includes halides, ethers, esters, and heteroaromatics. The corresponding (*E*)-vinylboronates could also be accessed by the same catalyst, by increasing the reaction temperature to 50 °C. Isotope labeling experiments suggest a mechanism most-likely based on a formal *syn*-hydrometalation of an alkynylboronate intermediate. Additional experiments established that complex **2** was not only active for alkyne hydroboration but also for Z-selective alkyne dimerization. Although the substrate scope was not as extensive as for the hydroboration, these experiments do demonstrate that earth-abundant metal complexes based on our newly reported $PC_{NHC}P$ pincer platform can exhibit diverse reactivity. Current efforts are directed toward synthesizing the corresponding manganese, cobalt, and nickel complexes and exploring their reactivity in a variety of organic transformations

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02057.

Synthetic procedures, characterization data, and catalytic procedures (PDF)

Accession Codes

CCDC 1994925−1994926 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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