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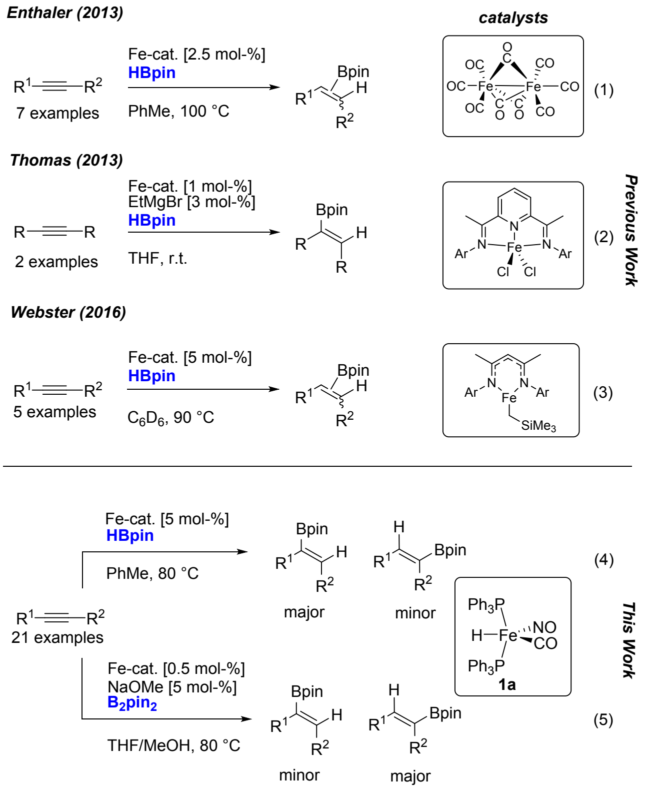
Hydroboration of Internal Alkynes Catalyzed by $FeH(CO)(NO)(PPh_3)_2$: a Case of Boron-Source controlled Regioselectivity

Fabian Rami,[a] Franziska Bächtle,[a] and Bernd Plietker[a]

The structurally defined Fe-H complex $FeH(CO)(NO)(Ph_3P)_2$ catalyzes the efficient stereoselective hydroboration of a variety of internal alkynes using either pinacolborane (HBpin) or *bis*(pinacolato)diboron (B_2pin_2) as boron source. Upon hydroboration of internal unsymmetric alkynes, a boron-source dependent regioselectivity was observed. Whereas the use of HBpin provides access to products that can be rationalized through a borylferration mechanism, the complementary regioselectivity was observed using B_2pin_2, which is indicative for a hydroferration mechanism.

Introduction

Vinylboronates are accessible through hydroboration of alkynes.[1] This process is commonly catalyzed by means of precious transition metal complexes.[2] In recent years, Fe-catalyzed hydroboration processes have gained significant attention.[3-12] In 2013, Enthaler disclosed the first breakthrough study on hydroboration of mainly terminal alkynes catalyzed by the readily available Fe-complex $Fe_2(CO)_9$ using pinacolborane (HBpin) as boron source (eq. (1), Scheme 1).[5] Upon using internal alkynes, the corresponding vinylboronates were isolated in good to excellent yield, albeit as mixtures of regio- and stereoisomers. In the same year, the group of Thomas presented an interesting hydroboration using a *bis*iminopyridyl-Fe-complex that is converted into the reactive catalyst species upon reduction using alkyl Grignard reagents.[6] Remarkably, hydroboration of olefins but also of two internal alkynes at room temperature were performed (eq. (2), Scheme 1). Despite the development of alternative catalytic systems by the groups of Szymczak,[7] Sreedhar,[8] Webster (eq. (3), Scheme 1),[9] or most recently Nishibayashi,[10] Kirchner[11] and Findlater,[12] a broadly applicable, yet efficient Fe-catalyzed hydroboration of internal alkynes is still scarce; in most cases only a very limited number of internal alkynes have been tested. Based on previous work on Fe-nitrosyl-complexes in catalysis,[13] we report here a selective hydroboration of internal alkynes using a Fe-H-nitrosyl complex as catalyst. Both HBpin as well as B_2pin_2 can be employed as boron sources, the corresponding vinylboronates are accessible in good to quantitative yields. Further, we observed a boron-source dependent preferential formation of different regioisomers (eq. (4) and (5), Scheme 1). To the best of our knowledge, control of regioselectivity by choice of boron source was not reported for iron catalysts so far, only for Cu-based systems.[14]



Scheme 1. Fe-catalyzed hydroboration of internal alkynes – state of research and content of this work.

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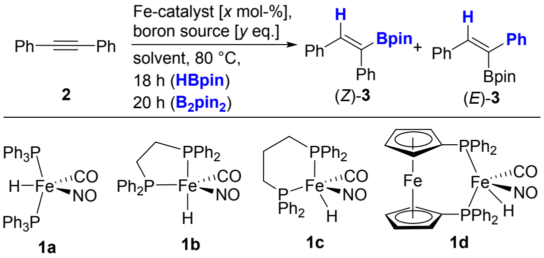
Results and discussion

The readily accessible, acidic Fe-H-complex $FeH(CO)(NO)(Ph_3P)_2$ **1a** that showed excellent catalytic performances in hydrosilylation reactions of internal alkynes,[13a] ketones,[13c] phosphine oxides[13c] and dehydrogenative silylations,[13b] was chosen for the initial experiments using similar experimental conditions to those that proved successful for the Fe-catalyzed hydrosilylation of internal alkynes (Table 1).

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



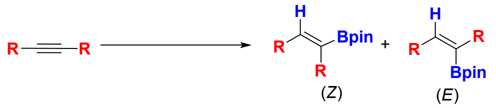
Entry	Cat. [x mol-%]	Solv.	B-source [y eq.]	Yield [%][b,c]
1	**1a** (5)	PhMe	HBpin (2.2)	85
2	**1b** (5)	PhMe	HBpin (2.2)	9
3	**1c** (5)	PhMe	HBpin (2.2)	26
4	**1d** (5)	PhMe	HBpin (2.2)	67
5	**1a** (10)	PhMe	B_2pin_2 (1.2) NaOMe (1.2)	88
6[d]	**1a** (0.5)	THF	B_2pin_2 (1.5) NaOMe (0.05)	96

[a] Reactions were run on 0.3 mmol scale. [b] (*Z*)/(*E*) ratio was determined by ^1H NMR or GC integration and was always >95/5. [c] Determined by ^1H NMR integration with 1,3,5-trimethylbenzene as internal standard. [d] Yield after 9 hours.

Indeed, those experimental conditions already resulted in good yields for the hydroboration of diphenylacetylene (entry 1, Table 1).[15] Among the solvents tested, toluene gave the highest isolated yield of vinylboronate ***(Z)*-3**. Moreover, a strong ligand effect was observed. The use of alternative Fe-H-complexes **1b-d** with bidentate phosphine ligands did not improve the overall catalytic activity (entries 2 – 4, Table 1).[16] Subsequently, we tested B_2pin_2 as an alternative boron source. Already initial experiments indicated this protocol to be very powerful. Excellent conversion and (*Z*)/(*E*)-selectivity were observed with only 0.5 mol-% of catalyst **1a** in the presence of 5 mol-% NaOMe (entry 6, Table 1).

Having these two alternative protocols for Fe-catalyzed alkyne hydroborations in hand, we evaluated their scope and limitations for symmetrical internal alkynes (Table 2). Various internal alkynes were successfully reacted into the corresponding vinylboronates in good to excellent yields and stereoselectivities. In the majority of investigated substrates the B_2pin_2-protocol gave higher yields and better selectivities, especially in the case of the *bis*(*meta*-ester)alkyne (entry 5, Table 2) and the two *ortho*-substituted starting materials (entries 6 and 7, Table 2).

Table 2. Fe-catalyzed hydroboration – scope and limitations of the HBpin versus B_2pin_2-protocol using symmetrical internal alkynes.[a]



conditions:

(**I**) Fe-catalyst **1a** [5 mol-%]
HBpin [2.2 eq.]
PhMe, 80 °C, 18 h

(**II**) Fe-catalyst **1a** [0.5 mol-%]
$\mathbf{B_2pin_2}$ [1.5 eq.]
NaOMe [5 mol-%]
THF/MeOH (3/1), 80 °C, 9 h

Entry	R	Prod.	(*Z*): (*E*)[b]	Yield [%]
1	Ph	**3**	95:5 (**I**) 98:2 (**II**)	85 (**I**) 92 (**II**)
2	*p*-MeC_6H_4	**4**	97:3 (**I**) 98:2 (**II**)	87 (**I**) 94 (**II**)
3	*p*-ClC_6H_4	**5**	77:23 (**I**) 98:2 (**II**)	80 (**I**) 44 (**II**)
4	*p*-$MeOC_6H_4$	**6**	98:2 (**I**) 97:3 (**II**)	86 (**I**) 94 (**II**)
5	*m*-$MeO_2CC_6H_4$	**7**	77:23 (**I**) 97:3 (**II**)	25 (**I**) 87 (**II**)
6	*o*-MeC_6H_4	**8**	99:1 (**I**) 99:1 (**II**)	54 (**I**) 68 (**II**)
7	*o*-BrC_6H_4	**9**	99:1 (**I**) 98:2 (**II**)	39 (**I**) 71 (**II**)
8	Et	**10**	98:2 (**I**) 99:1 (**II**)	54 (**I**) 64 (**II**)
9	*n*-Pr	**11**	99:1 (**I**) 99:1 (**II**)	69 (**I**) 86 (**II**)
10	*n*-Bu	**12**	99:1 (**I**) 99:1 (**II**)	68 (**I**) 87 (**II**)

[a] Isolated yields for reactions on 0.5 mmol scale. [b] (*Z*)/(*E*) ratio was determined by GC.

This finding caught our attention since it points into the direction of different modes of action using the same catalyst. We therefore investigated the hydroboration of non-symmetrical internal alkynes (Table 3). Indeed, both protocols allow for the preparation of vinylboronates in good yields, and we were pleased to find that the regioselective course is mainly directed through the boron source employed in the reaction. A general tendency can clearly be delineated from these results. The use of HBpin (protocol **I**, Table 3) leads to the expected Markovnikov-type products in moderate to good regioselectivities. The use of B_2pin_2/MeOH on the other hand provides access to the complementary *anti*-Markovnikov products in comparable regioselectivities (protocol **II**, Table 3). Even for structurally and electronically similar substituents as in vinylboronate **22A** and **22B** a moderate, but orthogonal regioselectivity was observed. Further, **22** allows for exclusion of a radical pathway for both of our methods, as ring opening of the cyclopropyl substituent was not detected. While attempts to isolate reactive intermediate Fe-complexes were unsuccessful,[17] the results point into the direction of a boron-

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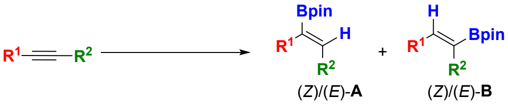
source dependent mechanistic dichotomy. If it is assumed that the regioselectivities are the results of either a borylferration (Markovnikov-selectivity) or a hydroferration mechanism (*anti*-Markovnikov-selectivity), an alteration of the steric demand on one of the two alkyne substituents should have a remarkable influence on the regioselective course of one of two protocols. To test this hypothesis, arylalkylalkynes with alkyl groups of different steric demand were subjected to the reaction conditions. Indeed, while for *n*-hexylphenylethine a clear boron-source dependent regioselectivity inversion in the product **17** from 82 : 18 (HBpin) to 24 : 76 (B_2pin_2) was observed, an increase in the steric demand of the alkyl group results in decreased regioselectivities for the B_2pin_2-protocol. Whereas the use of HBpin led to an increase of the regioselectivity from 82 : 18 (product **17**) to 96 : 4 (product **19**), a severe decrease of both yield and regioselectivity using B_2pin_2 from 24 : 76 (product **17**) down to 59 : 41 (product **19**) was observed. These results are indicative for a strong interaction of the alkyl-substituent with the incoming Fe-complex.

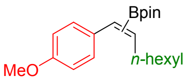
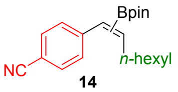
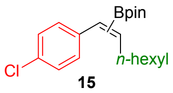
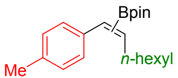
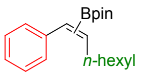
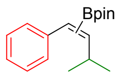
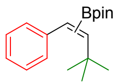
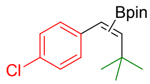
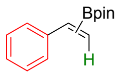
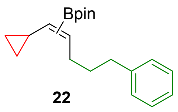
Table 3. Regioselectivity of Fe-catalyzed hydroboration.[a,b]



conditions:

(**I**) Fe-catalyst **1a** [5 mol-%]
HBpin [2.2 eq.]
PhMe, 80 °C, 18 h

(**II**) Fe-catalyst **1a** [0.5 mol-%]
B_2pin_2 [1.5 eq.]
NaOMe [5 mol-%]
THF/MeOH (3/1), 80 °C, 9 h

	I	II
 **13**	83%, **A** : **B** = $\boxed{74}$: 26	82%, **A** : **B** = 18 : $\boxed{82}$
 **14**	25%, **A** : **B** = $\boxed{87}$: 13	64%, **A** : **B** = 4 : $\boxed{96}$
 **15**	75%, **A** : **B** = $\boxed{84}$: 16	85%, **A** : **B** = 19 : $\boxed{81}$
 **16**	82%, **A** : **B** = $\boxed{75}$: 25	80%, **A** : **B** = 24 : $\boxed{76}$
 **17**	85%, **A** : **B** = $\boxed{82}$: 18	50%, **A** : **B** = 24 : $\boxed{76}$
 **18**	55%, **A** : **B** = $\boxed{90}$: 10	45%, **A** : **B** = 31 : $\boxed{69}$
 **19**	84%, **A** : **B** = $\boxed{96}$: 4	55%, **A** : **B** = $\boxed{59 : 41}$
 **20**	87%, **A** : **B** = $\boxed{94}$: 6	51%, **A** : **B** = $\boxed{58 : 42}$
 **21**	13%, **A** : **B** = 0 : 100	35%, **A** : **B** = 0 : 100
 **22**	85%, **A** : **B** = $\boxed{61}$: 39	90%, **A** : **B** = 32 : $\boxed{68}$

[a] Isolated yields for reactions on 0.5 mmol scale. [b] Ratio of regioisomers was determined by GC integration.

At the current state of research, we consider the following working model to provide suitable first explanations for the observed experimental results (Figure 1).

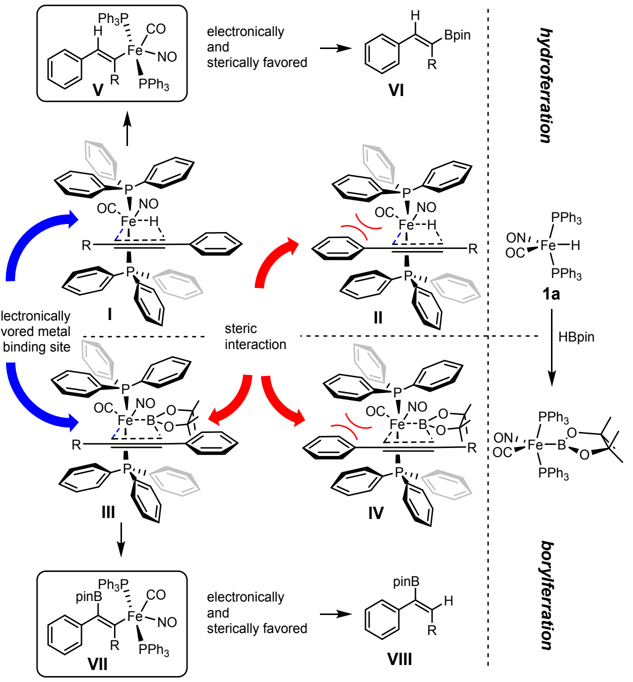


Figure 1. Fe-catalyzed hydroboration of internal alkynes - working model.

Accordingly, we postulate that dependent on the nature of the boron source, the initial step of the reaction involves either a hydroferration or a borylferration of the alkyne. In both cases two different regioisomers **I** – **IV** are accessible. In case of the hydroferration (protocol **II**) the strong backbinding CO- and NO-ligands lead to a decrease of electron density at the metal center favoring transition state **I**, in which the metal center is coordinating to the more electron-rich carbon atom of the C-C-double bond. In addition, unfavorable steric interactions between the aryl group, in particular when substituted at the *ortho*-position, and the bulky metal complex disfavor transition state **II**. As a result, formation of the *anti*-Markovnikov products **VI** *via* vinyl-Fe-complex **V** is favored. Increasing the size of the alkyl groups affects the regioselectivity due to the increasing steric interactions between the R-group and the metal center in **I**. As a result, a decrease in the regioselectivity is observed (protocol **II**, products **18**, **19**, and **20**, Table 3). On the contrary, addition of HBpin (protocol **I**) leads to the formation of an Fe-B-complex that undergoes a borylferration *via* transition states **III** or **IV**. Although electronically favored, transition state **III** faces stronger steric interactions between the boryl ligand and the aryl substituent on the alkyne moiety. Increasing these steric interactions through *ortho*-substitution, a significant decrease in yields might be expected and was experimentally observed (entries 6 and 7, protocol **I**, Table 2). Moreover, increasing the size of the R-group also increases the unfavorable interactions to the boryl ligand in transition state **IV**, which ultimately leads

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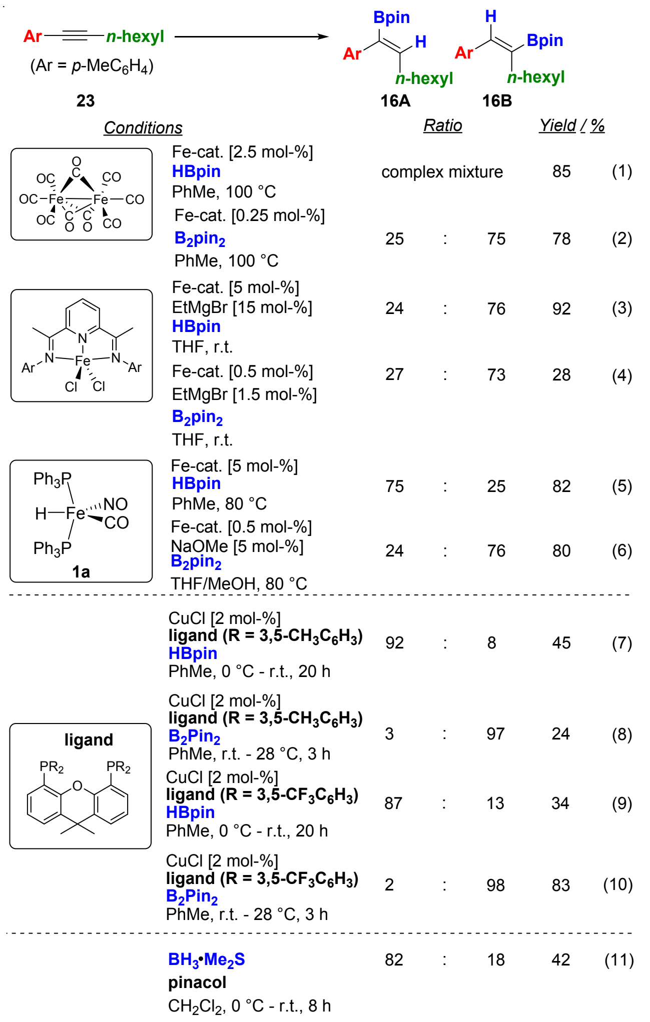
to significantly higher regioselectivities (protocol **I**, products **18**, **19**, and **20**, Table 3).

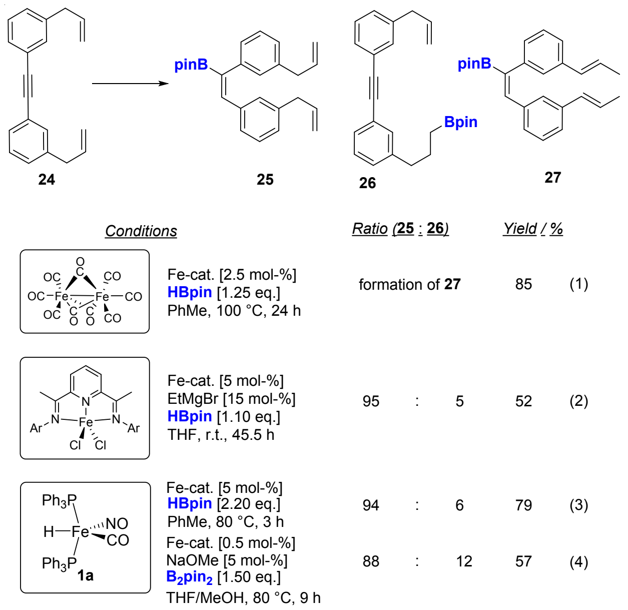
To benchmark the abovementioned results, different reported Fe-catalysts were prepared and subjected to the reaction conditions using either HBpin or B_2pin_2 as boron source (eq. (1) - (6), Scheme 2).[18]



Scheme 2. Fe-catalyzed hydroboration of internal alkynes – a comparative study.

Moreover, Tsuji's Cu-based catalyst system[14] was prepared. In order to cross-check the influence of the ligand, both HBpin and B_2pin_2 were employed using two structurally related Xantphos-ligands (eq. (7) - (10), Scheme 2). We also referenced these results to the metal-free hydroboration using Knochel's *in-situ* protocol of $BH_3{\cdot}Me_2S$/pinacol (eq. (11), Scheme 2).[19] Depending on the reaction conditions, different regioselectivities in the hydroboration of *n*-hexyarylethyne **23** were observed. Both Enthaler's and Thomas' catalytic systems led to hydroboration, however, depending on the boron source, either varying yields ranging from 28 to 92 % or complex product mixtures were observed (eq. (1) - (4), Scheme 2). In all cases, the *anti*-Markovnikov product **16B** was formed in a maximum selectivity of 24 : 76 (eq. (3), Scheme 2). In contrast, the Fe-NO complex **1a** showed boron-source dependent regioselectivity, yielding either **16A** or **16B** with a regioisomeric ratio of 75 : 25 or 24 : 76 (eq. (5) versus (6), Scheme 2). Tsuji's Cu-based system shows superior regioselectivities, however, yields were significantly lower (eq. (7) - (10), Scheme 2). Finally, employing Knochel's catalyst-free hydroboration using a mixture of pinacol and $BH_3{\cdot}Me_2S$ led to the formation of vinylboronates **16**, but in moderate yields and a regioselectivity of 82 : 18 in favor of the Markovnikov product **16A** (eq. (11), Scheme 2).

Finally, we tested the chemoselectivities of the different Fe-based catalytic systems using the symmetrical *m,m´-bis*allylarylethyne **24** as a test substrate (Scheme 3).



Scheme 3. Chemoselectivities in Fe-catalyzed hydroboration of alkynes.

The use of $Fe_2(CO)_9$ as a catalyst led to the hydroboration of the alkyne but, very much to our surprise, also to a π-bond isomerization of the terminal olefins to give vinylboronate **27** in good yield (eq. (1), Scheme 3). On the contrary, Thomas' Fe-*bis*iminopyridyl complex catalyzes the chemoselective hydroboration of the alkyne moiety to **25**. Only minor amounts of the alkylboronate **26** were isolated, isomerization of the π-bond to **27** was not observed (eq. (2), Scheme 3). Employing the Fe-NO-complex **1a** as a catalyst led to the formation of vinylboronate **25** in moderate to good yields and good to high chemoselectivites (eq. (3) and (4), Scheme 3).

Based on these results, we propose the following mechanistic rationale (Figure 2): in presence of HBpin (protocol **I**), iron complex **1a** reacts under H_2-evolution to form the catalytically active Fe-boryl complex ***AI***. This complex adds to the alkyne in a borylferration reaction under the constraints outlined in Figure 1 to give the intermediate vinyliron species ***AII*** (please note: ***AII*** corresponds to **VII** in Figure 1). After oxidative addition of another equivalent of HBpin, ***AIII*** is formed which undergoes subsequent reductive elimination to furnish the product in Markovnikov selectivity while ***AI*** is regenerated. For

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B_2pin_2 as boron source (protocol **II**), **1a** directly adds to the alkyne in a hydroferration pathway to intermediate ***BI*** (which corresponds to **V** in Figure 1). With B_2pin_2, NaOMe and MeOH, complex ***BII*** is formed. Under reductive elimination, the product is released in *anti*-Markovnikov selectivity, and species ***BIII*** is formed. ***BIII*** acts as the catalytically active species in the following cycles.

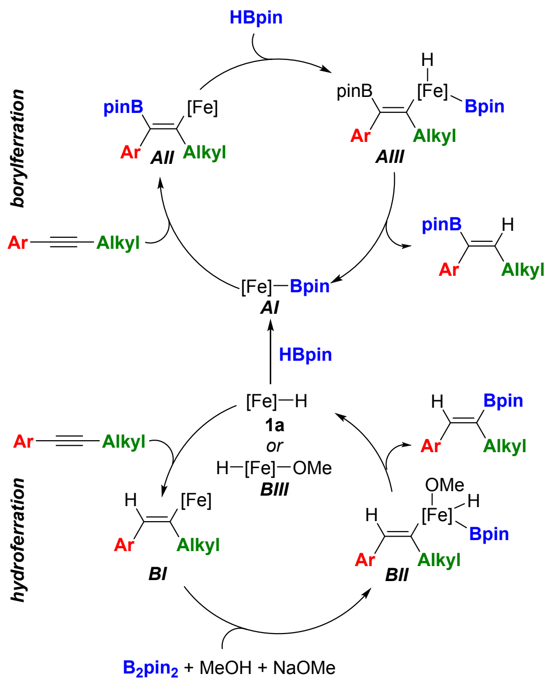

Figure 2. Proposed reaction mechanism for the Fe-H-catalyzed hydroboration of alkynes.

Experimental Section

Method A (HBpin as boron source): A 10 mL-screw cap Schlenk tube was briefly dried with a heat gun and charged with **1a** (16.0 mg, 0.025 mmol). Dry toluene (0.67 mL), the respective alkyne (0.5 mmol) and pinacolborane (160 μL, 1.1 mmol) were added and the reaction mixture was stirred at 80 °C for 18 hours. After cooling to room temperature, the mixture was filtered over a pad of silica gel (eluent: diethyl ether). The solvent was evaporated and the crude mixture was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate mixture) to yield the corresponding vinylboronate.

Method B (B_2pin_2 as boron source): A 10 mL-screw cap Schlenk tube was dried with a heat gun and charged with **1a** (0.75 mL of a catalyst stock solution in dry THF, 2.5 μmol). The respective alkyne (0.5 mmol) was added, followed by NaOMe (0.25 mL of a stock solution in dry methanol, 0.025 mmol) and B_2pin_2 (190.5 mg, 0.75 mmol). The reaction mixture was stirred at 80 °C for 9 hours. After cooling to room temperature, the mixture was filtered over a pad of silica gel (eluent: diethyl ether). The solvent was evaporated and the crude product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate mixture) to yield the corresponding vinylboronate.

Conclusions

Herein we report the use of the structurally well-defined Fe-NO-hydride complex **1a** as a catalyst for the chemoselective hydroboration of internal alkynes. A variety of aliphatic or aromatic alkynes were successfully reacted into the corresponding vinylboronates with very high *(Z)*/*(E)*-ratios in moderate to high yields using both HBpin and B_2pin_2 as boron sources. Interestingly, employing the latter boron source allowed to reduce the catalyst loading to only 0.5 mol-% without affecting the *(Z)*/*(E)*-selectivities or the yields. For unsymmetrical internal alkynes, different regioisomers were formed preferentially in dependence of the boron source: while the use of HBpin led to a preferred formation of the Markovnikov-products, the selectivities were inverted upon employing B_2pin_2 as boron source. This finding is indicative for the formation of different catalytic species depending on the boron source. Comparative studies with literature-reported Fe-based catalytic systems showed that this inversion of selectivity is only found for the Fe-NO-hydride complex **1a**. Tsuji's Cu-based system[14] shows a similar boron-source dependent formation of different regioisomers, however, a change of the ligand is required in order to obtain synthetically useful yields. The experimental results presented in this manuscript are indicative for a boron-source dependent mechanistic dichotomy. Investigations into the mechanism are currently ongoing and will be reported separately.

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The structurally defined Fe-H complex $FeH(CO)(NO)(Ph_3P)_2$ catalyzes the efficient stereoselective hydroboration of a variety of internal alkynes using either pinacolborane (HBpin) or *bis*(pinacolato)diboron (B_2pin_2) as boron source. Upon hydroboration of internal unsymmetric alkynes, a boron-source dependent regioselectivity was observed. Whereas the use of HBpin provides access to products that can be rationalized through a borylferration mechanism, the complementary regioselectivity was observed using B_2pin_2, which is indicative for a hydroferration mechanism.