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Iron-Catalyzed Dehydrogenative Borylation of Terminal Alkynes

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Abstract. The catalytic system based on $Fe(OTf)_2$ (2.5 mol%) and DABCO (1 mol%) selectively promotes the dehydrogenative borylation of both aromatic and aliphatic terminal alkynes to afford alkynylboronate derivatives in the presence of 1 equiv. of pinacolborane at 100 °C in toluene. This methodology is applicable to a variety of terminal alkynes (16 examples, yield: 62-93%).

Keywords: Iron; alkyne; dehydrogenative borylation; pinacolborane; alkynylboronates

Thanks to the impressive progress made in Suzuki-Miyaura coupling reactions,[1] the selective preparation of organoboron compounds has attracted broad interest over the last two decades.[2] More particularly, efficient accesses to these versatile intermediates by C-H dehydrogenative borylation have been described.[3] In the area of metal-catalyzed hydroboration of alkenes and alkynes, a competing side reaction, namely the dehydrogenative borylation, can operate. However, an accurate design of the catalytic system can be performed to favor such pathway, then yielding alkenyl- or alkynyl-boronates from terminal alkenes or alkynes, respectively.[4] Alkynylboronates are useful building blocks and are classically prepared by deprotonation of the corresponding alkynes by *n*-BuLi, then reaction with a boric ester and finally quench with anhydrous acid.[5] Transition metal catalyzed dehydrogenative borylation of terminal alkynes was only scarcely reported: the known catalytic systems are SiNN and PNP pincer iridium complexes,[6] silver[7] or NHC-copper[8] well defined complexes.

On the other hand, even if its catalytic ability has been demonstrated for a long time in the Haber process for ammonia production,[9] iron catalysis has made a real breakthrough during the two last decades and is now able to compete favorably with noble metals.[10]

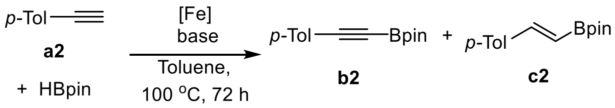
More particularly, there has recently been intense interest in developing first row transition metal complexes for catalytic hydroboration of alkenes,[11] alkynes,[12] and enynes.[13] By contrast, the dehydrogenative hydroboration of alkenes was more scarcely reported.[14]

Here we describe the use of iron salt as catalyst for the selective dehydrogenative borylation of terminal alkynes leading to the corresponding alkynylboronates.

Our initial studies showed that the dehydrogenative borylation of *p*-tolylacetylene **a2** could be achieved in toluene solution at 100 °C for 72 h with 1 equiv. of HBpin (pin = pinacolate) in the presence of 10 mol% of $Fe(OTf)_2$[15-16] as precatalyst, and 10 mol% of pyridine in 67% conversion. The borylated *p*-tolylacetylene **b2** was obtained as the major product (87%) along with trace amounts of the hydroborated derivative **c2** (7%) and of 4-methylstyrene (5%) (Table 1, entry 1). The chemoselectivity decreased significantly when 2,6-lutidine, 2,2'-bipyridine or Et_3N (10 mol%) was used as the base (entries 2-4). Upon screening various bases, DABCO was found to lead to both high conversion (84%) and selectivity towards the formation of the borylated *p*-tolylacetylene **b2** (87%) besides trace amounts of the alkenyl derivative **c2** (10%) and of 4-methylstyrene (3%) (Entry 5).

$Fe(OTf)_2$ and DABCO loadings can be efficiently decreased to 2.5 mol% as full conversion was obtained after 72 h at 100 °C, **b2** being produced selectively in 84% NMR yield (entry 6). Decreasing the reaction time to 48 h led to lower conversion (90%, entry 7). However, with only 1 mol% of $Fe(OTf)_2$ and DABCO, even with 90% conversion, the selectivity dropped (**b2**/**c2** = 45:47, entry 9). Noticeably, the addition of hydrogen scavengers such as norbornadiene or cyclooctene has a deleterious effect on the chemoselectivity of the reaction (entries 10-11).

Table 1. Optimization of the reaction parameters for *p*-tolylacetylene.[a]



Entry	[Fe] (mol%)	Base (mol%)	Conv. (%)	**b2**/**c2**	Yield (%) **b2**
1	$Fe(OTf)_2$ (10)	Pyridine (10)	76	87/7	66
2	$Fe(OTf)_2$ (10)	2,6-lutidine (10)	93	43/36	40
3	$Fe(OTf)_2$ (10)	2,2'-bipyr (10)	85	44/43	37
4	$Fe(OTf)_2$ (10)	Et_3N (10)	57	54/20	31
5	$Fe(OTf)_2$ (10)	DABCO (10)	84	87/10	73
6	$Fe(OTf)_2$ (2.5)	DABCO (2.5)	99	84/8	83
7	$Fe(OTf)_2$ (2.5)	DABCO (2.5)	90	85/9	77[b]
8	$Fe(OTf)_2$ (2.5)	DABCO (1.0)	99	81/11	80
9	$Fe(OTf)_2$ (1.0)	DABCO (1.0)	90	45/47	41
10	$Fe(OTf)_2$ (2.5)	DABCO (1.0)	88	59/12	52[c]
11	$Fe(OTf)_2$ (2.5)	DABCO (1.0)	91	76/17	69[d]
12	None	DABCO (5.0)	<1	-	<1
13	$Fe(OTf)_2$ (5.0)	None	80	34/29	27
14	FeF_2 (2.5)	DABCO (2.5)	99	24/58	24
15	$FeCl_2$ (2.5)	DABCO (2.5)	59	11/9	6
16	$FeBr_2$ (2.5)	DABCO (2.5)	99	42/24	42
17	$Fe(OAc)_2$ (2.5)	DABCO (2.5)	98	33/44	33

[a] Reaction conditions: $Fe(OTf)_2$ (2.5-10 mol%), toluene (0.5 mL), alkyne (0.5 mmol), HBpin (0.5 mmol) and base (1-10 mol%) at 100 °C for 72 h. Conversion and yield were measured by ^{1}H NMR analysis of the crude product, based on **a2**, and the identity of the products **b2** and **c2** was confirmed by GC–MS. [b] 48 h. [c] with 2 equiv. of norbornadiene. [d] with 2 equiv. of cyclooctene. Bipyr: bipyridine; DABCO: 1,4-diazabicyclo[2.2.2]octane

Notably, using DABCO, without iron precursor, resulted in no activity (entry 12). By contrast, a low yield and selectivity was obtained using $Fe(OTf)_2$ (2.5 mol%) without base, even if the conversion can reach 80%, thus showing the crucial role of the DABCO catalytic additive on the efficiency and chemoselectivity of this transformation (entry 13 and SI).

The influence of the nature of the iron precursors was also investigated. FeF_2, $FeBr_2$ and $Fe(OAc)_2$ (2.5 mol%) in association with DABCO (2.5 mol%) led to full conversion under standard conditions but with a lower selectivity towards **b2** (24-42%, entries 14-17), whereas $FeCl_2$ was less active (entry 15). No improvement was observed when 2-methyl-THF, Bu_2O and dimethylcarbonate were used as solvent (see Table S2). Hence, the optimal conditions selected to probe the substrate scope of the reaction are 2.5 mol% of $Fe(OTf)_2$, 1.0 mol% of DABCO, in toluene (1M) at 100 °C for 72 h (Table 2).

Phenylacetylene and arylacetylene derivatives bearing *para*-electron-donating substituents, e.g. *p*-methyl, *p*-*tert*-butyl or *p*-methoxy, led selectively to the corresponding borylated arylacetylene compounds **b1-b4** with isolated yields up to 85% (Table 2, entries 1-4).

It is worth noting that electron-withdrawing substituted arylacetylene derivatives such as *p*-trifluoromethylphenylacetylene, required shorter reaction times (24 h instead of 72 h at 100 °C, entry 5) to lead to the corresponding borylated acetylenic derivative **b5** specifically obtained with 87% isolated yield. Interestingly, the extension of the reaction time to 72 h permitted to only obtain specifically pinacol (*E*)-styrylborane **c5** in 92 % yield (entry 6). This result suggests that the production of the hydroborylated compounds **c5** could occur through the hydrogenation of the borylated acetylenic derivative **b5.** Noteworthy, the bis(ethynyl)benzene afforded selectively the bis(pinacolborylethynyl) benzene **b6** in 93% yield (entry 7).

In addition, the reaction can be also efficiently performed with 1-dodecyne or terminal akynes bearing a benzyloxy group, leading to the corresponding borylated alkynes **b7-b9** in 78-93% isolated yields (entries 8-10). Trimethylsilylacetylene is also a suitable starting material as the corresponding borylated compound **b10** was isolated in 89% yield (entry 11).

Using alkadiynes such as 1,7-octadiyne or 1,6-heptadiyne, the monofunctionalization was only observed in the presence of 2 equiv. of HBpin and the corresponding monoborylated derivatives **b11** and **b12** were obtained selectively in 70-72% isolated yields (entries 12 and 13). Noticeably, no trace of diborylated compounds was detected, the only by-products observed in the crude mixture being the corresponding alkenyl borylated compounds resulting from the hydroborylation of one terminal triple bond.

With more steric demanding terminal alkynes such as *tert*-butylacetylene and cyclopropylacetylene, both dehydroborylation and borylated products were selectively obtained depending upon the reaction time. Pinacol *tert*-butylethynylborane **b13** and pinacol cyclopropylethynylborane **b14** were isolated in 62 and 63% yields, respectively, after 60 h and 36 h (entries 14 and 16).

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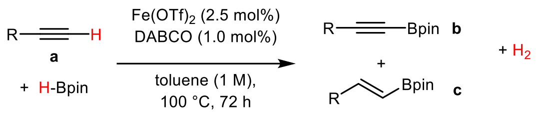
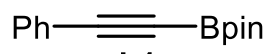
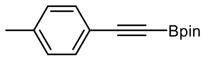
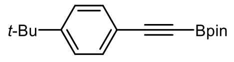
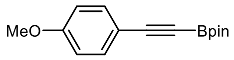
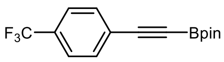
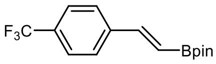
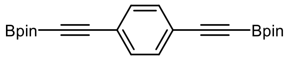
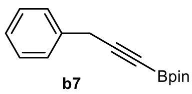
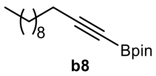
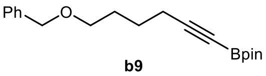
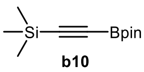
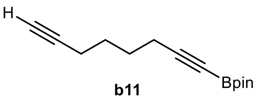
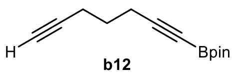
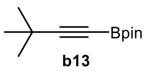
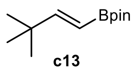
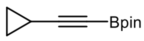
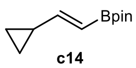
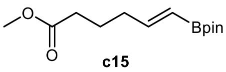
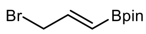
Table 2. Scope of the reaction.[a]



Entry	borylated product	Time [h]	Conv. [%][b]	b/c[b]	Yield [%][c]
1	 b1	72	> 98	89:11	80(65)
2	 b2	72	> 98	88:12	85
3	 b3	72	> 98	90:10	85
4	 b4	72	86	90:10	75
5[d]	 b5	24	> 98	99:1	87
6	 c5	72	> 98	1:99	92
7	 b6	72	> 98	97:3	93
8	 b7	72	>98	95:5	81
9	 b8	72	>98	85:15	78
10	 b9	72	>98	99:1	93
11	 b10	72	>98	93:7	89(55)
12[e]	 b11	72	>98	87:13	70
13[e]	 b12	72	>98	83:17	72
14[d]	 b13	60	75	91:9	62(66)
15	 c13	72	>98	1:99	90
16[d]	 b14	36	78	84:16	63
17	 c14	72	>98	1:99	85
18	 c15	9	>98	1:99	
19		72	>98	1:99	95
20	 c16	9	>98	1:99	
21		72	>98	1:99	92

[a] General conditions: alkyne (0.5 mmol), HBpin (0.5 mmol), $Fe(OTf)_2$ (2.5 mol%), DABCO (1.0 mol%), toluene (0.5 mL), 100 °C; [b] Measured by ^{1}H NMR of the crude mixture. [c] Isolated yields. In parentheses, isolated yield on gram scale reaction. [d] Reaction in a Young NMR tube in C_6D_6. [e] 2 equiv. of HBpin.

A prolonged 72 h of reaction permitted to switch the chemoselectivity as pinacol (*E*)-2-*tert*-butylvinylboranate **c13** and pinacol (*E*)-2-cyclopropylvinylboranate **c14** were selectively isolated in 85 and 90% yields, respectively (entries 15 and 17). Notably, cyclopropylacetylene furnished **b14** and **c14** in quantitative yield, which seem to indicate that the reaction did not proceed via stable radical intermediates.

Starting from methyl hex-6-ynoate or 3-bromo-1-propyne, only the hydroborated derivative **c15** and **c16** were obtained in high yields, 95 and 92%, respectively, whatever the reaction time, 9 or 72 h (entries 18 and 19). Additionally, under the optimized reaction conditions, no reaction was observed with terminal alkynes bearing primary amine, alcohol or carboxylic acid substituents (see Table S4).

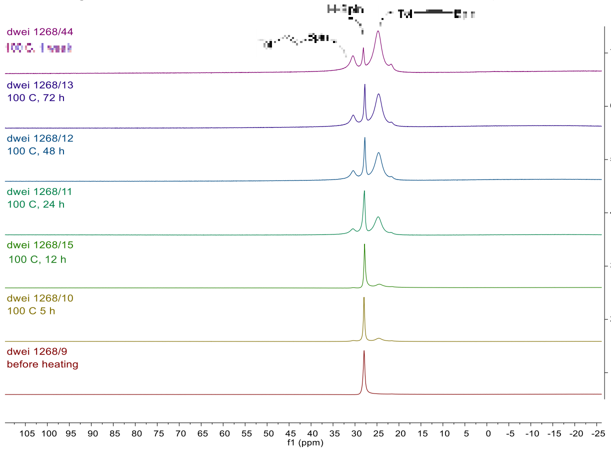


Figure 1: ^{11}B NMR spectra recorded at 96 MHz of the reaction of *p*-tolylacetylene **a2** with HBpin in C_6D_6 at 100 °C leading to the compounds **b2** and **c2**.

Preliminary experiments aimed at gaining an insight into the reaction course were then performed. The reaction outlined in Table 2, entry 2, was achieved in a Young NMR tube, charged under argon atmosphere with 2.5 mol% of $Fe(OTf)_2$ in C_6D_6 (1.0 mol/L), 0.5 mmol of **a2**, 0.5 mmol of HBpin and DABCO (1 mol%) at 100 ºC for indicated time. Analysis of ^{11}B NMR spectra showed that the dehydroborylated and the borylated compound **b2** and **c2** were formed simultaneously, **b2** being always the major product (Figure 1). Additionally, the results described in Table 2, entries 6, 15 and 17 indicated that the formation of the alkenyl boronates results from the reduction of the corresponding alkynylboronates. On the other hand, the evolution of the H_2 gas was also identified in ^{1}H NMR at 4.47 ppm (see Figure S2).

From a mechanistic point of view, as a Lewis acid, $Fe(OTf)_2$ should be able to activate the B-H bond, thus enhancing the electrophilic capacity of the boron center to react with acetylenic derivative. This process would be accelerated by the presence of DABCO which increases the nucleophilicity of the terminal acetylenic carbon.[17,18]

In summary, we have reported the first example of a highly selective catalytic dehydrogenative borylation of terminal alkynes with pinacolborane, using iron as an inexpensive earth abundant metal and DABCO as a co-catalyst. Further studies on the mechanism and synthetic applications are in progress in our laboratory.

Experimental Section

General procedure for $Fe(OTf)_2$ catalyzed dehydrogenative borylation of terminal alkynes: in an argon filled glove box, a 20 mL Schlenk tube was charged with $Fe(OTf)_2$ (2.5 mol%), toluene (1.0 mol/L), alkyne (0.5 mmol), HBpin (0.5 mmol) and DABCO (1 mol%, stock solution in toluene) in this order. Then the reaction mixture was stirred at 100 ºC for 72 h. After cooling the mixture to room temperature, the solution was diluted with pentane (2 mL) and filtered through a small pad of celite (2 cm in a Pasteur pipette). The celite was washed with pentane (2 mL×2). The filtrate was evaporated and the crude residue was then purified by recrystallization (slow evaporation form pentane) or bulb to bulb distillation.

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