Chemoselective Hydroboration of Propargylic Alcohols and Amines Using a Manganese(II) Catalyst

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ABSTRACT: The first manganese-catalyzed hydroboration of propargylic alcohols and amines as well as internal alkynes is reported. High regio- and stereoselectivity is achieved by applying 2 mol % of a manganese pre-catalyst based on the readily accessible bis(imino)pyridine ligand and MnCl₂ as metal source. Propargylic alcohols and amines, as well as symmetric internal alkynes, were efficiently converted into the corresponding functionalized alkenes, which can serve as important and valuable intermediates for further synthetic applications such as cross-coupling reactions.

The main goals of sustainable chemistry are associated with the application of relatively cheap and environmental benign catalysts, which allow transformations to be performed under mild reaction conditions with minimum waste production.¹ In order to fulfill these requirements new catalytic systems are under continuous investigation. In this context, metal-catalyzed hydrometallation reactions gained interest due to their high atom-economic nature. Among the developed processes, the hydroboration is one of the most powerful transformations as the resulting boronic acid derivatives can undergo further useful derivatization in organic synthesis, for example in C-C bond formation *via* Suzuki-Miyaura cross-coupling reactions.² Conventional methodologies providing synthetically useful alkenylboranes consist of metal exchange reaction occurring between organometallics (organolithium, Grignard reagents) and boron electrophiles,³ non-catalytic hydroboration reaction,⁴ and haloboration.⁵ However, selective hydrofunctionalization of alkynes still remains a challenging task due to the regioselectivity issues and formation of undesired byproducts.⁶ The catalytic hydroboration of internal alkynes is straightforward and an atom economic method for the synthesis of multi-substituted vinylboronates, which can serve as building blocks and intermediates in various reactions applied in both, academia and industry.⁷

The increasing interest in the application of first row transition metal catalysts in modern chemistry is strongly correlated with their more environmentally friendly nature, earth-abundance of metal precursors and often lower cost in comparison with commonly applied noble metals. Since 2016 manganese pincer complexes have been gaining a lot of attention as potential catalysts and proved to be a powerful tool, mainly in (de)hydrogenation and transfer hydrogenation reactions.^{8,9} The

pincer ligands provide exceptional stabilities for the corresponding complexes and allow for the facile modification of their electronic and steric properties by modifying the so-called pincer-arms.¹⁰ Nonetheless, manganese-pincer-catalyzed hydrofunctionalization still remains underexplored and known reports usually address the hydrosilylation of carbonyl groups.¹¹ In this context, in 2014 Trovitch et al. reported the first application of manganese pincer complexes in the hydrosilylation of ketones.^{11b} More recently, the group of Huang described an asymmetric approach.^{11d} The hydroboration of multiple bonds by manganese-pincer complexes is even less developed, with only few reports regarding the conversion of carbonyl groups and alkenes.^{11a,12} Based on our interest in the development of base metal catalyzed transformations we decided to investigate the hydroboration of internal alkynes, in particular propargylic alcohols and amines (Scheme 1).

Scheme 1. Manganese-catalyzed hydroboration of internal alkynes

Our preliminary studies were performed applying TBDMS-protected 3-phenylprop-2-yn-1-ol **1a** as model substrate and HBpin as borylating agent. The investigated catalyst precursors were activated *in situ* using NaBHET₃, allowing for application of easily accessible and bench stable manganese(II) complexes.

Figure 1. Manganese complexes used in this study.

The initial reaction performed with 2 mol % of **Mn1**^{9c} (Figure 1) which was effective in the reduction of alkynes, did not show any conversion of the starting material (Table 1, entry 1). Likewise, use of the terpyridine complex **Mn2**^{12b} also did not show any activity towards the formation of the desired product (entry 2). Bis(imino)pyridine(PDI)-based manganese complexes were our next choice.^{13,14} To our delight, the reaction of **1a** with HBpin catalyzed by 2 mol % of **Mn3**¹⁵ upon addition of NaBHET₃ (4 mol %) at room temperature in hexane for 24h resulted in the formation of trisubstituted alkene **2a-β** in 76% yield (entry 3). Moreover, no formation of the **2a-α** isomer was detected, showing the high regioselectivity of the applied manganese system. The more sterically hindered **Mn4**¹⁶ pre-catalyst proved to be the most effective, yielding the product in 88% yield (entry 4). A subsequent experiment has shown that no product is formed in the absence of the manganese catalyst (entry 5).

Table 1. Optimization of the reaction conditions^a

entry	cat. (mol %)	activator (mol %)	solvent	yield (%) ^b
1	Mn1 (2)	NaBHET ₃ (4)	hexane	n.r.
2	Mn2 (2)	NaBHET ₃ (4)	hexane	n.r.
3	Mn3 (2)	NaBHET ₃ (4)	hexane	76
4	Mn4 (2)	NaBHET ₃ (4)	hexane	88
5	-	NaBHET ₃ (4)	hexane	n.r.
6	Mn4 (2)	-	hexane	n.r.
7	Mn4 (2)	NaOtBu (4)	hexane	n.r.
8	Mn4 (2)	KOtBu (4)	hexane	11
9	Mn4 (2)	NaBHET ₃ (4)	toluene	83
10	Mn4 (2)	NaBHET ₃ (4)	Et ₂ O	19
11	Mn4 (2)	NaBHET ₃ (4)	THF	n.r.
12	Mn4 (2)	NaBHET ₃ (4)	MeCN	n.r.
13	MnCl₂ (10)	NaBHET ₃ (4)	hexane	n.r.
14 ^c	Mn4 (2)	NaBHET ₃ (4)	hexane	86

^aReactions were performed on 0.25 mmol scale with 2 mL of hexane and 2.5 equiv. of HBpin at r.t. in a culture tube under an inert atmosphere for 24h. ^bYields were determined by the ¹H NMR analysis of the crude reaction mixture using mesitylene as an internal standard. ^cThe reaction was performed with a drop of mercury.

Further investigation of the reaction conditions proved the need for the addition of NaBHET₃ in order to form the catalytically active Mn-species (entry 6). Hence, we decided to check the catalyst performance upon activation with milder additives such as NaOtBu and KOtBu, however both attempts were unsuccessful (entries 7 and 8). Next, we investigated the effect of the solvent on the reaction outcome. Only aprotic and non-polar reaction media were suitable for our transformation. The reaction performed in toluene led to 83% of product (entry 9), whereas in sharp contrast only 19% of product could be observed when Et₂O was applied (entry 10). Reactions performed in THF and MeCN led to no conversion, probably due to the coordinative nature of these solvents and poisoning effect on the catalyst (entries 11 and 12). The presence of the bis(imino)pyridine ligand was essential for the manganese-catalyzed hydroboration of alkynes, as the sole MnCl₂ did not show activity even when applying higher catalyst loading (entry 13). Addition of a drop of mercury did not affect the catalytic performance of [(^EPDI)MnCl₂], suggesting a homogenous nature of the applied catalyst (entry 14).

With the optimized reaction conditions in hand we explored the scope of the reaction with **Mn4** complex as pre-catalyst and the results are summarized in Scheme 2. Under the developed reaction conditions various substrates were successfully converted into the corresponding products preserving the high stereo- and regioselectivity towards formation of β-substituted (Z)-alkenes. Most alkynes reacted smoothly in the presence of 2 mol % catalyst. Alkynes containing electron withdrawing as well as electron donating groups could be effectively converted into trisubstituted alkenes. Propargylic functionalized alcohols bearing a methyl substituent in different positions of the aromatic ring underwent hydroboration leading to the corresponding products **2b-d** in high yields. Phenyl substituted alkyne **1e** also reacted smoothly giving the corresponding alkene in 91% yield. Additionally, alkynes containing a halogen-substituted aromatic ring proved to be suitable for our protocol (products **2f-h**). Substrate **1i** containing a stronger electron-withdrawing CF₃ substituent yielded the corresponding product in high yield (88%). In general, alkynes with *ortho*- and *meta*-substituents on the aromatic ring required application of higher catalyst loading, nevertheless high yields were obtained. Moreover, our method worked efficiently for thiophene-derived alkyne **1j**, which was successfully reduced giving the corresponding product in 95% yield. Alkynes with enhanced steric hindrance on the carbon atom in the vicinity of the alcohol moiety were easily converted into the corresponding products **2k-m** in high yields. We also demonstrated that aliphatic alkynes can be successfully applied in our protocol (**2n**).

In order to show the synthetic utility of our method we performed the Mn-catalyzed hydroboration on larger scale. Under the given conditions, 1 mmol of *tert*-butyldimethyl((3-phenylprop-2-yn-1-yl)oxy)silane **1a** was successfully transformed into 85% of isolated functionalized alkene **2a**, proving that our protocol can be scaled-up without any loss of efficiency.

Scheme 2. Manganese-catalyzed hydroboration of TBDMS-protected hydroxyalkynes^a

^aReaction conditions: **1** (0.25 mmol), HBpin (0.375 mmol), catalyst **Mn4** (2 mol %) and NaBHET₃ (4 mol %) in hexane (2 mL) were stirred at r.t. for 24h in a culture tube under an inert atmosphere. Yields were determined by ¹H NMR analysis of the crude reaction mixture using mesitylene as an internal standard. Yields after column chromatography given in parentheses. ^bYield for the reaction on 1 mmol scale. ^c**Mn4** (8 mol %), NaBHET₃ (16 mol %). ^d**Mn4** (3 mol %), NaBHET₃ (6 mol %). ^e**Mn4** (10 mol %), NaBHET₃ (20 mol %). ^f**Mn4** (4 mol %), NaBHET₃ (8 mol %).

After the successful hydroboration of propargylic functionalized alcohols, we focused our attention to the hydroboration of related propargylic amines. The expected products, trisubstituted enamines, can be applied as valuable synthons and building blocks in the synthesis of heterocycles and bioactive amines.¹⁷ To our delight, dibenzyl-protected amines bearing both electron-donating and electron-withdrawing substituents in different positions of the aryl ring proved to be suitable substrates (Scheme 3, **4a-4f**). Moreover, thiophene-derived propargylic amine reacted smoothly, yielding the corresponding functionalized alkene **4g** in 85% yield.

Scheme 3. Manganese-catalyzed hydroboration of Bn-protected propargylic amines^a

^aReaction conditions: **3** (0.25 mmol), HBpin (0.375 mmol), **Mn4** (4 mol %) and NaBHET₃ (8 mol %) in hexane (2 mL) were stirred at 60 °C for 24h in a culture tube under an inert atmosphere. Yields were determined by ¹H NMR analysis of the crude reaction mixture using hexamethyldisiloxane as an internal standard. Yields after column chromatography given in parentheses. ^b**Mn4** (6 mol %), NaBHET₃ (12 mol %).

Furthermore, we decided to demonstrate that the obtained borylated products can serve as substrates for the stereochemically controlled synthesis of trisubstituted olefins. For this purpose, the obtained vinylboronate **2a** was applied in Suzuki-Miyaura cross-coupling with bromobenzene in the presence of 5 mol % of Pd(OAc)₂, which resulted in 70% of isolated product **2aa** (Scheme 4).

Scheme 4. Synthetic application of the obtained vinylboronates

Finally, our catalytic system was active also in the hydrofunctionalization reaction of symmetrically substituted aromatic and aliphatic internal alkynes (Scheme 5). Interestingly, complex **Mn3** showed higher activity than **Mn4** and led to the formation of *syn*-addition products exclusively in high yields. Alkynes with methyl substituents in different positions of the aromatic ring reacted smoothly yielding the corresponding products **6b-c** in high yields. Alkynes **5d-f** enriched with electron-withdrawing substituents were also successfully applied in hydroboration. Reactions with

thiophene-derived substrates **5g-h** proceeded almost quantitatively, giving 92% and 96% of the corresponding product **6g** and **6h**. We were glad to observe, that aliphatic alkyne **5i** reacted to give 98% of the borylated product.

Scheme 5. Manganese-catalyzed hydroboration of symmetric alkynes^a

^aReaction conditions: **5** (0.25 mmol), HBpin (0.375 mmol), catalyst **Mn3** (2 mol %) and NaBHET₃ (4 mol %) in hexane (1 mL) were stirred at r.t. for 24h in a culture tube under an inert atmosphere. Isolated yields are given. ^b**Mn3** (4 mol %), NaBHET₃ (8 mol %). ^c**Mn3** (6 mol %), NaBHET₃ (12 mol %).

In conclusion, the first example of a manganese-catalyzed hydroboration of alkynes, which is characterized by high regio- and stereoselectivity, is presented. The hydrofunctionalization of various functionalized internal alkynes as well as propargylic alcohols and amines proceeds under homogenous reaction conditions and leads to the formation of valuable alkenylboranes in good yields. The corresponding products can serve as valuable intermediates as demonstrated by their application in cross-coupling reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and characterization of compounds (file type, i.e., PDF)

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Notes

The authors declare no competing financial interest.

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