Tandem Manganese Catalysis for the Chemo-, Regio-, and Stereoselective Hydroboration of Terminal Alkynes: In Situ Precatalyst Activation as a Key to Enhanced Chemoselectivity

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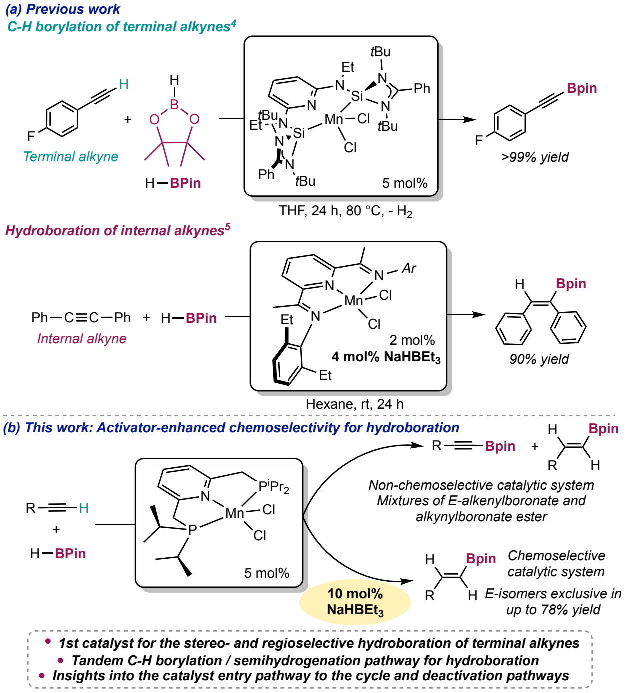
ABSTRACT: The manganese(II) complex [Mn(^{iPr}PNP)Cl$_2$] (^{iPr}PNP = bis(diisopropylphosphine)pyridyl)) was found to catalyze the stereo- and regioselective hydroboration of terminal alkynes employing HBPin (pinacolborane). In the absence of in situ activators, mixtures of alkynylboronate and *E*-alkenylboronate esters were formed, whereas when NaHBEt$_3$ was employed as in situ activator, *E*-alkenylboronate esters were exclusively accessed. Mechanistic studies revealed a tandem C-H borylation / semihydrogenation as the pathway accounting for the formation of the products. Stoichiometric reactions hint toward reaction of a Mn-H active species with the terminal alkyne as the catalyst entry pathway to the cycle, whereas reaction with HBPin led to catalyst deactivation.

Introduction

The discovery of chemoselective catalysts for the functionalization of small molecules is key to access versatile synthons with applications in fine chemistry. The functionalization of alkynes with boronate esters (HB(OR)$_2$) is one of the most relevant transformations, rendering access to synthetically valuable alkynyl-, alkenyl- or alkyl-boronate esters.[1] The functionalization of terminal alkynes represents a challenge for chemoselectivity control in catalysis, due to the competition of the functionalization of the triple and of the C(sp)-H bond. In transition metal-catalyzed reactions of terminal alkynes with boronate esters, the preferred reactivity, either hydroboration[2] or C-H borylation,[3] is determined by the identity of the metal complex, which dictates whether C-H activation or alkyne insertion steps are preferred. To avoid this competition, some catalysts have been reported efficient only for internal alkynes,[4] and there are few insights into the keys leading to chemoselective hydroboration of terminal alkynes,[2c,d] including how the other components of the catalytic system (such as in situ activators, solvent identity or temperature) impact the chemoselectivity.[2d]



Scheme 1. (a) Manganese-catalyzed dehydrogenative borylation of terminal alkynes (top) and hydroboration (bottom) of internal alkynes with two different Mn complexes; (b) This work: stereo- and regioselective hydroboration of terminal alkynes.

Manganese-catalysis is a rising field, with Mn(I) catalysts containing CO ligands being well-established, in particular for reduction processes.[5] In contrast, low-oxidation state (0, +I or +II) Mn complexes lacking CO ligands have been comparatively less explored for small molecule functionalization.[6] We have recently reported that when the manganese complex [Mn(SiNSi)Cl$_2$][6a] (**Mn1**) was employed as precatalyst for the functionalization of terminal alkynes with HBPin, alkynylboronate esters were exclusively formed by C-H borylation (Scheme 1a, top).[7] However, this precatalyst was found inefficient for the functionalization of either internal or terminal alkynes when it was *in situ* activated with NaHBEt$_3$. In contrast, Rueping and coworkers reported that *in situ* activation with NaHBEt$_3$ triggered the catalytic activity of the [Mn(^{Et}PDI)Cl$_2$] complex for the hydroboration of symmetrical *internal* alkynes to yield alkenylboronate esters from the *syn* addition of HBPin (Scheme 1a, bottom).[8] However, the substrate scope was limited to symmetric *internal* alkynes, where competition of the C(sp)-H activation was not a concern. Whereas Earth-abundant transition metal catalysts, mainly of Fe and Co,[2b-d, 2f-o] for the hydroboration of terminal alkynes are well-known, most of them being *Z*-stereoselective, a manganese catalyst for this transformation has not been described. The main challenge stands on controlling the chemo-, stereo- and regioselectivity of the reaction for this type of substrates. Due to manganese being the third most abundant transition-metal in the Earth crust, a manganese catalyst for this process would contribute to the development of sustainable processes in synthetic chemistry.

Interested in elucidating the role that the ligand plays on the chemoselectivity of the manganese-catalyzed reaction between a terminal alkyne and HBPin, we hypothesized that a Mn complex containing a less electron-donating and sterically hindered pincer ligand than the SiNSi[9] in **Mn1**, may render access to a catalyst capable of insertion steps affording alkenylboronate esters. In this work we report that the Mn(II) complex, [Mn(^{iPr}PNP)Cl_2], is the first catalyst for the hydroboration of unactivated *terminal* alkynes showing an excellent stereo- and regio-selectivity for the *E*-alkene upon *in situ* activation with $NaHBEt_3$ (Scheme 1b). The role of $NaHBEt_3$ as activator is key to enhance the chemoselectivity of the catalyst for hydroboration. Insights into the reaction pathway as well as on the precatalyst entry to the cycle and deactivation pathways are provided.

Results and discussion

1. Catalytic competency of [Mn(^{iPr}PNP)Cl_2] for the functionalization of terminal alkynes with HBPin

Our research commenced with the synthesis of the manganese precatalyst [Mn(^{iPr}PNP)Cl_2][10] (**Mn2**, ^{iPr}PNP = 2,6-bis(diisopropylphosphino)pyridine) and the assessment of its efficiency for the functionalization of phenylacetylene (**1**) with HBPin (Pin = pinacolate) in the absence of strong hydride or alkyl sources as *in situ* activators. The initial conditions employed for the reaction were those identified as optimal in our lab for the C-H borylation of terminal alkynes catalyzed by [Mn(SiNSi)Cl_2] (**Mn1**)[7] (5 mol% catalyst loading, 2.5 equiv HBPin, 80 °C, 24 h, 0.5 M solution in THF). Under these conditions, **Mn2** led to a low conversion of the starting material (23%) affording the *E*-alkenylboronate ester **1b** as the major product in a 14% yield, with the alkynylboronate ester **1a** formed in <5% yield (crude yields and conversion determined by GC, see entry 2 in table in Scheme 2a). This result points toward **Mn2** as less efficient than **Mn1** for the functionalization of terminal alkynes with HBPin, with a preference for hydroboration instead of C-H borylation. A mixture of the alkynyl (15% yield) and the *E*-alkenylboronate ester (7% yield) was obtained for 4-fluorophenylacetylene with the reaction also proceeding to low conversion (24%, see page S6 in the SI). However, when 2-fluoro- or 3-fluorophenylacetylene were employed as substrates, the reactions proceeded to 51% and 52% conversions respectively affording the corresponding alkynylboronate esters exclusively (45% and 19% yields respectively, see page S6 in the SI). These results suggest that **Mn2** does not have a strong preference for either C-H borylation of hydroboration, with the identity of the substrate being capable of determining the preferred pathway. Employing the Mn(II) dihalide complexes containing a ^{tBu}PNP (2,6-bis(ditertbutylphosphino)pyridine, **Mn3**) or a ^{Et}PDI ligand (^{Et}PDI = (2,6-diethylphenyl)pyridyldiimine, **Mn4**,[8] see entries 3 and 4 in table in Scheme 2a) as precatalysts, resulted in low conversion of the starting material with formation of the *E*-alkenylboronate ester as the major product, although in moderate yields (22% for **Mn3** and 55% for **Mn4**). It is worth noting that all the precatalysts employed (**Mn2**-**Mn4**) were chemoselective for hydroboration, suggesting that the stronger-electron donating and sterically demanding SiNSi ligand in **Mn1** is key to favor C-H borylation over hydroboration.

Aiming to understand the factors that resulted in a switch of the chemoselectivity, the functionalization of 4-fluorophenylacetylene (**2**) with HBPin catalyzed by **Mn2** was monitored for 4 hours by ^{1}H, ^{19}F, ^{11}B and ^{31}P NMR spectroscopy in THF-d_8 at 80 °C in a J. Young NMR tube where the headspace was evacuated (see pages S13-S16 in the SI). The results support that both products, the alkynyl- (**2a**, at -108.4 ppm) and the *E*-alkenylboronate (**2b**, at -111.9 ppm) esters were formed in a 0.8:1 **2a**:**2b** ratio after 1h. In contrast, when **Mn1** was employed as precatalyst, product **2b** was only formed at high substrate conversion,[7] again highlighting the key role of the SiNSi ligand in the chemoselectivity for C-H borylation. The **2a**:**2b** ratio changes over the course of 4 hours (1.4:1 after 2 h, 2.3:1 after 3 h and 3.4:1 after 4 h) hinting a faster increase in the amount of alkynylboronate ester than that of *E*-alkenylboronate ester, suggesting two independent catalytic cycles operative in solution, one for C-H borylation and one for hydroboration. Further supporting this hypothesis, the ^{31}P NMR spectra showed two signals at 38.0 and 38.5 ppm, consistent with the presence of two diamagnetic catalyst-resting states, one for each of the cycles operative (see Figure S5 in the SI).

Aiming to determine the impact that the presence of a strong hydride or alkyl source as *in situ* activator had on the chemoselectivity of the catalytic system, the efficiency of **Mn2** for the functionalization of **1** with HBPin was assessed in the presence of strong hydride and alkyl sources. Employing 10 mol% of RLi (R = Me, Ph) or KO*t*Bu as *in situ* activators of 5 mol% of **Mn2** resulted in poor conversions and yields of borylated products (see Table S1 in the SI). In contrast, when 10 mol% of $NaHBEt_3$ were employed as the activator, full conversion of the starting material was observed, with the *E*-alkenylboronate ester (**1b**) being formed as the major product in a 78% yield. The *E*-isomer was exclusively obtained, and neither the *Z* isomer, α-alkenylboronate esters nor product **1a** were detected by GC in the reaction crude, supporting **Mn2** / $NaHBEt_3$ as a stereo-, regio- and chemoselective catalytic system for the hydroboration of **1**. Styrene was detected in <5% yield in the crude reaction mixture by GC, as well as trace amounts of 1,2,4 and 1,3,5-triphenylbenzene from alkyne cyclotrimerization.[11] The presence of trace amounts of styrene in the reaction medium can be attributed to the semihydrogenation of **1** catalyzed by **Mn2** / $NaHBEt_3$ and is consistent with the report of **Mn2** as an efficient catalyst for the *Z*-selective semihydrogenation of internal and terminal alkynes employing NH_3BH_3 as the H_2 source.[10]

Whereas the use of $NaHBEt_3$ as in situ activator in the reaction of **1** with HBPin catalyzed by **Mn1** led to a mixture of unidentified products (see scheme 2b, entry 1 in table), the results presented above support that **Mn2** is capable of generating an active species by reaction of $NaHBEt_3$ that catalyzed the hydroboration of **1**. Moreover, the presence of

(a) Without NaHBEt$_3$

Entry	*Precatalyst*	*Conversion (%)*	*1a (%)*	*1b (%)*
1*	**Mn1**	>99	88**	<5
2	**Mn2**	23	<5	14
3	**Mn3**	42	<5	22
4	**Mn4**	56	N. D.	55

Non-chemoselective Mn catalysts

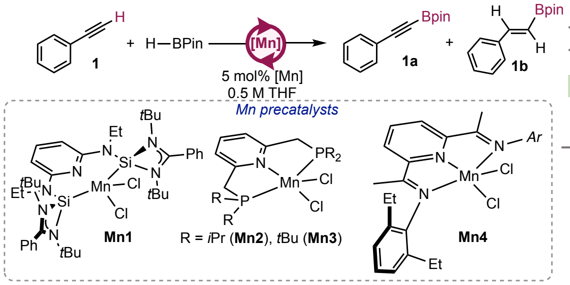
** Result reported in reference 9. ** Isolated yield is reported.*

*% yields of **1a** and **1b** are reported*

Conditions: 2.5 equiv HBPin, 24 h, 80 ℃

*^{1}Crude yields of **1a** and **1b** and conversions were determined by ^{19}F NMR integration employing fluorobenzene as internal standard.*

Conditions: 2.5 equiv HBPin, 24 h, 80 ℃



(b) With 10 mol% of NaHBEt$_3$

Entry	*Precatalyst*	*Conversion (%)*	*1a (%)*	*1b (%)*
1	**Mn1**	64	<5	<5
2	**Mn2**	91	N. D.	78
3	**Mn3**	58	<5	7
4	**Mn4**	50	N. D.	<5

Chemoselective Mn2 catalyst

*Products from hydrogenation of the triple bond in **1** were observed*

Conditions: 10 mol% of NaHBEt$_3$, 1.75 equiv HBPin, 16 h, 30 ℃

N. D. = Not Detected

*^{1}Crude yields of **1a** and **1b** and conversions were determined by ^{19}F NMR integration employing fluorobenzene as internal standard.*

Conditions: 10 mol% of NaHBEt$_3$, 1.75 equiv HBPin, 16 h, 30 ℃

Scheme 2. Catalyst screening for the functionalization of phenylacetylene with HBPin (a) without and (b) with NaHBEt$_3$ as in situ activator .

NaHBEt$_3$ as the activator increases the catalyst efficiency but, more importantly, is key to drive the chemoselectivity of the reaction toward hydroboration. Employing [Mn(^{tBu}PNP)Cl$_2$] (**Mn3**) as the precatalyst, containing *t*Bu groups at the P-donors, resulted in a lower conversion of the starting material (58%) and the formation of **1b** in low yield (7%) (Scheme 2b, entry 3 in table). Furthermore, the alkynylboronate ester **1a** was detected in the reaction crude, whereas when **Mn2** was employed as precatalyst, product **1a** was not detected (see below for a mechanistic rationale). Even though **Mn4** has been previously reported as an efficient catalyst for the hydroboration of *internal* alkynes,[8] it showed no catalytic activity for the hydroboration of *terminal* alkynes under the conditions in Scheme 2b (see entry 4 in table). Therefore, **Mn2** constitutes the first stereo- and regioselective Mn catalyst for the hydroboration of *terminal* alkynes.

Control experiments for the reaction of **1** and HBPin in THF at 30 °C for 24 h were run (a) in the presence of 10 mol% of NaHBEt$_3$, (b) in the presence of 5 mol% of MnCl$_2$ and 10 mol% of NaHBEt$_3$, (c) in the presence of 5 mol% of ^{iPr}PNP and 10 mol% of NaHBEt$_3$ and (d) without any added species (see page S11 in the SI). In all cases, the reactions proceeded to <35% conversion of the starting material yielding a mixture of products that did not include **1b** except in (c) and (d) where **1b** was formed in <5% yield (determined by GC). These results support the need of all the reagents to access **1b** in a synthetically useful yield and rule out trace borane as the catalytic species responsible for the catalytic activity (experiment (a)).[12]

Encouraged by the chemoselectivity shown by the **Mn2** / NaHBEt$_3$ system for the reaction of **1** with HBPin, we set out to investigate the factors that impacted the yield of the product. The efficiency of other borylating agents, mainly HBDan and B$_2$Pin$_2$ for the hydroboration of **1** was assessed (see Table S2 in the SI), in both cases, affording yields for **1b** of <5%. Employing 5 mol% of MnCl$_2$, 5 mol% of ^{iPr}PNP and 10 mol% of NaHBEt$_3$ as the precatalyst instead of in situ activated **Mn2**, led to a catalytic activity comparable to that of **Mn2** (74% yield for **1b**), suggesting that the active species can be *in situ* generated from the previous mixture. In contrast, when MnBr$_2$, Mn(OAc)$_2$ or Mn(OTf)$_2$ were employed as the Mn source, the yield of **1b** decreased significantly (18% yield of **1b** for MnBr$_2$ and <5% yield for Mn(OAc)$_2$ and Mn(OTf)$_2$, see table S3 in the SI), highlighting the relevance of the Mn source in the formation of the active species. The order of addition of the components in the catalytic reaction also impacted the yield of **1b** (see table S4 in the SI). When (a) NaHBEt$_3$ was added to a mixture of **Mn2** and **1** followed by the addition of HBPin, the yield of **1b** decreased to 44%, whereas when (b) NaHBEt$_3$ was added to a mixture of **Mn2** and HBPin followed by addition of **1**, product **1b** was formed only in trace amount. These observations suggest that the *in situ* activator should be added last, presumably to minimize decomposition of the catalytically active species as well as the semihydrogenation of **1** in the absence of HBPin in case (a) (see below).

Aiming to increase the yield of **1b**, the reaction conditions were optimized (see Table S5 in the SI). The results showed that conducting the reaction with 10 mol% of catalyst loading, 20 mol% of NaHBEt$_3$ at 30 °C, in a 0.5 M solution of THF and with 1.75 equiv of HBPin for 24 h afforded **1b** in an 86% yield with the reaction proceeding to >99% conversion. Increasing the temperature of the reaction above 30 °C resulted in lower yields for **1b**, presumably due to competition of the semihydrogenation of **1**, as evidenced by the increased amounts of styrene formed as byproduct. Employing other solvents in the reaction such as toluene, acetonitrile or methanol led to decreased yields of **1b** (acetonitrile) or to complete loss of the catalytic activity (toluene, methanol). Preactivation of **Mn2** with 2 equiv NaHBEt$_3$ also led to a diminished yield for product **1b** (34%), suggesting that the catalytically active species generated upon reaction of **Mn2** with NaHBEt$_3$ might decompose in the absence of the substrates.

The evaluation of the substrate scope for the **Mn2** / NaHBEt$_3$ system under the optimized conditions is currently undergoing in our laboratory.

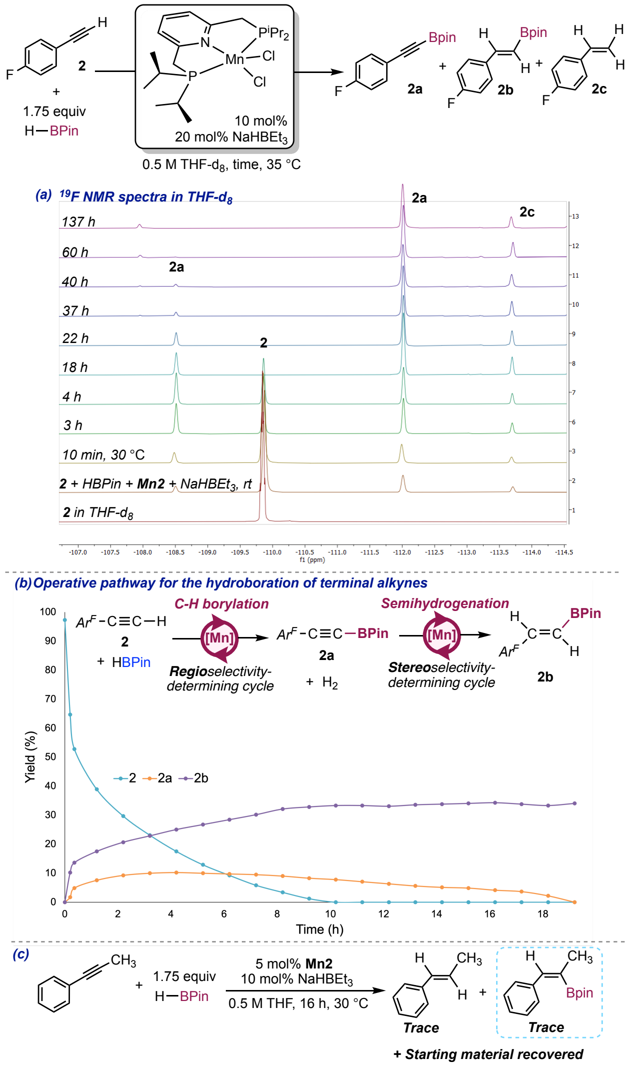
2. Mechanistic insights into the hydroboration of terminal alkynes with HBPin catalyzed by Mn(^{iPr}PNP)Cl$_2$ / NaHBEt$_3$

Insights into the reaction pathway

Intrigued by the role of NaHBEt$_3$ in the ability of **Mn2** to increase the chemoselectivity of the reaction, we set out to study the mechanism of this transformation. To interrogate whether there was heterogeneous catalysis involved in the transformation, a Hg drop was added to the catalytic borylation of **1** with HBPin in the presence of 5 mol% of **Mn2** and 10 mol% of NaHBEt$_3$. The catalytic activity was not inhibited and product **1b** formed in a 73% yield, comparable to that when the reaction was run in the absence of Hg (78% yield) and supporting homogenous catalysis operative in the reaction.

To gain insights into the reaction pathway as well as into the identity of the Mn active species, the catalytic hydroboration of 4-fluorophenylacetylene (**2**) with HBPin in the presence of 10 mol% of **Mn2** and 20 mol% of NaHBEt$_3$ employing 1,4-difluorobenzene as internal standard was monitored by ^{1}H, ^{11}B, ^{31}P and ^{19}F NMR spectroscopy in THF-d$_8$ at

30 °C for 160 h. An induction period was not observed, and the ^{1}H and ^{19}F NMR spectra showed the immediate formation of several species at the expense of the starting material (Scheme 3a). The major species was identified as the *E*-alkenylboronate ester **2b** whereas the minor species present were (a) the alkynylboronate ester **2a**, (b) 4-fluorophenylethylene (**2c**) and (c) 4-fluorophenylethane (**2d**). Minor upfield-shifted unidentified signals were also present in the ^{19}F NMR spectra which can be tentatively attributed to the presence of products from alkyne cyclotrimerization (detected in the crude GC for the hydroboration of **1**) and/or Mn-alkenyl or Mn-alkynyl complexes. The fact that **2a** is present in the reaction medium hints that **Mn2** is efficient for the C(sp)-H borylation of **2**. Consistent with this hypothesis, H_2 was observed (singlet at 4.55 ppm) in the ^{1}H NMR spectra. The presence of **2c** in the reaction medium supports that **Mn2** is also efficient for the semihydrogenation of **2**, which is consistent with previous reports describing **Mn2** as an efficient catalyst for the *Z*-stereoselective transfer semihydrogenation of *internal* alkynes.[10] The starting material was consumed in 10 hours, however, the amounts of **2a** and **2b** kept on changing after full conversion (Scheme 3b). The changes in the yields of **2a** and **2b** over time supported that **2b** formed at the expense of **2a.** The ^{1}H NMR spectra showed the formation of H_2 followed by its gradual consumption as **2b** was forming at the expense of **2a** (see Figure S8 in the SI). These observations point toward a reaction pathway involving tandem C-H borylation / semihydrogenation to access **2b** with the C-H borylation cycle being the regioselectivity-determining and the semihydrogenation the stereoselectivity-determining (Scheme 3b). Because both, **2a** and **2b**, are present at the initial stages of the reaction, exclusive formation of **2b** by stereo- and regioselective hydroboration of **2** may also be operative. Interestingly, **Mn2** / $NaHBEt_3$ is *E*-stereoselective for the semihydrogenation of **2a**, which stands in contrast to the reported *Z* stereoselectivity for the semihydrogenation of internal alkynes with NH_3BH_3 catalyzed by **Mn2**,[10] suggesting that the identity of the substrate (internal alkyl or aryl alkyne *vs.* alkynylboronate ester) and/or the identity of the activator (NH_3BH_3 vs. $NaHBEt_3$) play a relevant role in the stereoselectivity of the semihydrogenation reaction. Because 4-fluorophenylstyrene (**2c**) is also formed as a byproduct, at least three catalytic cycles are operative in the reaction medium: (a) one for the semihydrogenation of **2**, (b) one for the C-H borylation of **2**, and (c) one for the semihydrogenation of **2a**, with cycles (b) and (c) being responsible for the formation of **2b**. The ^{31}P NMR spectra showed signals for 3 P-containing species (at 0.60 (major), -0.50 (minor) and -2.18 ppm (minor), see bottom spectrum in Scheme 4e) which did not correspond to free ^{iPr}PNP ligand, neither to putative products from the reaction of the free ^{iPr}PNP ligand with HBPin and can be tentatively assigned to catalyst resting-states. The signal at -0.50 ppm disappeared after 2 h of reaction, whereas the those at 0.60 and -2.18 ppm remained intact during catalytic turnover, pointing toward these species as the catalyst resting-states for the C-H borylation and semihydrogenation cycles responsible for the formation of **2b**. Furthermore, both signals appeared at different chemical shifts than those for the catalyst resting-states when **Mn2** was employed in the absence of $NaHBEt_3$ (38.0 and 38.5 ppm, see Figure S5 in the SI), supporting different catalyst resting-states when the reaction is conducted in the presence of $NaHBEt_3$. Signals attributable to diamagnetic Mn species were not identified in the ^{1}H NMR spectra of the reaction, presumably obscured by the signals of **2**, **2a**, **2b** and **2c**.



Scheme 3. Mechanistic experiments to gain insights into the reaction pathway, (a) ^{19}F NMR monitoring of the catalytic reaction, (b) proposed reaction pathway and quantitative monitoring of the species during the catalytic reaction and (c) attempted hydroboration of an internal alkyne.

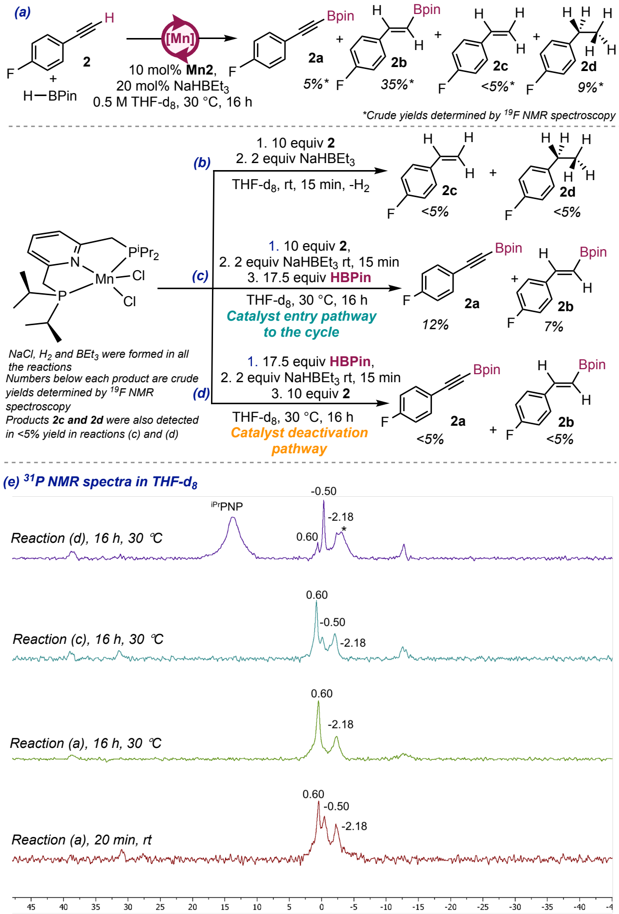
Further supporting a tandem C-H borylation / semihydrogenation pathway operative in catalysis, the hydroboration of the internal alkyne 1-phenyl-1-propyne catalyzed by **Mn2** / $NaHBEt_3$ proceeded to low conversion with the corresponding *E*-alkenylboronate ester and alkene detected in trace amounts in the reaction crude (by ^{1}H NMR spectroscopy and GC, see Scheme 3c). Because **14** lacks C(sp)-H groups, a C-H borylation / semihydrogenation pathway is not accesible, and only a hydroboration cycle involving alkyne insertion and C(sp^2)-B formation steps can be operative to yield the alkenylboronate ester, however, this cycle may be inaccessible due to high energy barriers resulting in no catalytic activity for this process.

Although catalysts capable of performing tandem C-H borylation / hydroboration are known,[13] the potential of manganese catalysts in tandem processes, which is still the realm of precious metals,[14] is underexploited. Therefore, the results reported here constitute a first step toward the design of manganese complexes efficient as catalysts for tandem transformations.

Insights into the precatalyst entry to the cycle for the hydroboration of alkynes catalyzed by Mn2 / NaHBEt$_3$

To gain insights into the precatalyst entry pathway to the cycle, 2 equivalents of NaHBEt$_3$ were added to a THF solution of **Mn2** at -78 °C. The ^{1}H and ^{31}P of the reaction crude in C$_6$D$_6$ showed signals attributable to free ^{iPr}PNP ligand and no signals attributable to other diamagnetic Mn complexes, hinting decomposition of the product. Previous work has supported the formation of a catalytically active Mn(I)-H for the semihydrogenation of internal alkynes catalyzed by **Mn2** in the presence of NH$_3$BH$_3$ as *in situ* activator.[10] If the same catalytically active species was formed upon activation with NaHBEt$_3$, its electronic unsaturation (14 electrons) could lead to decomposition in the absence of substrates. This is consistent with the observation that preactivation of **Mn2** with NaHBEt$_3$ lead to a lower yield of the *E*-alkenylboronate ester **1b** in the catalytic hydroboration of **1** (see above). Aiming to stabilize the putative Mn-H complex, the addition of 2 equiv of NaHBEt$_3$ to **Mn2** was conducted in the presence of 2 equivalents of 2-electron donor ligands such as PMe$_3$, *t*BuCN or 2,6-Me$_2$C$_5$H$_4$CN. In all cases the efforts to isolate and characterize a manganese complex failed and only when *t*BuCN was employed, a signal consistent with the presence of a hydride ligand (at -4.53 ppm, t, $^2J_{HP}$ = 49.2 Hz) in a diamagnetic {Mn(^{iPr}PNP)} complex[15] could be detected in the reaction crude by ^{1}H NMR spectroscopy (see Figure S14 in the SI). Further work is ongoing in our laboratory to isolate and fully characterize this complex.

To identify whether the putative Mn-H enters the cycle by reaction with the alkyne, the reaction of **Mn2** with 2 equiv of NaHBEt$_3$ in the presence of 10 equivalents of **2** was conducted in THF-d$_8$ in a J. Young NMR tube at room temperature in the presence of 1,4-difluorobenzene as internal standard and the ^{1}H, ^{11}B, ^{19}F and ^{31}P NMR spectra were registered (see pages S26-S32 in the SI and Scheme 4b and c). Immediately after the addition of NaHBEt$_3$ to the mixture of **Mn2** and **2**, the ^{19}F NMR spectra showed signals consistent with the presence of **2c** (-113.4 ppm) and 4-fluorophenylethane (**2d**, -117.0 ppm) (see Figure S17 in the SI and Scheme 2b), formed by hydrogenation of **2** (-109.4 ppm). Accordingly, the ^{1}H NMR spectra hinted the presence of H$_2$ (4.50 ppm). As in the monitoring of the catalytic reaction, minor upfield shifted signals in the ^{19}F NMR spectra may hint the presence of Mn-alkenyl or Mn-alkynyl complexes and of products from alkyne cyclotrimerization. The ^{31}P NMR spectra did not show any signal attributable to diamagnetic Mn complexes neither to free ^{iPr}PNP. These results suggest that, in the absence of HBPin, **Mn2** can catalyze the semihydrogenation of **2** to **2c** and the full hydrogenation to **2d** with the H$_2$ generated from precatalyst activation and allow to rationalize the presence of **2c** and **2d** as byproducts in the hydroboration of **2**.



Scheme 4. (a) Product yields in the catalytic reaction after 16 h. Mechanistic experiments to gain insights into precatalyst entry pathway to the cycle, (b) addition of NaHBEt$_3$ to a mixture of Mn2 and excess 2; (c) addition of NaHBEt$_3$ to a mixture of Mn2 and excess 2 followed by addition of excess HBPin and (d) addition of NaHBEt$_3$ to a mixture of Mn2 and excess HBPin followed by addition of excess 2. (e) Stacked ^{31}P NMR spectra in THF-d$_8$ for the catalytic reaction (a) and reactions (c) and (d). Chemical shifts are reported in ppm close to each signal. * denotes an unidentified signal at -3.13 ppm.

Addition of excess HBPin to the reaction mixture resulted in the immediate formation of **2a** (-108.0 ppm) and **2b** (-111.5 ppm) (see Figure S17 in the SI). This result supports reaction of the putative Mn-H active species with the alkyne **2** as the catalyst entry pathway to the cycle. Therefore, the active Mn-H would activate the C-H bond of **2** to yield **2a** in a first C-H borylation cycle followed by insertion of the triple bond of **2a** in a second semihydrogenation cycle that would yield **2b**. The ^{31}P NMR spectra showed the presence of 3 species at 0.60 (major), -0.50 (minor) and -2.18 ppm (minor), consistent with diamagnetic Mn complexes present in the reaction medium. More importantly, these species were also present in the ^{31}P NMR spectra of the catalytic reaction (see see Scheme 4e and Figure S21 in the SI), further supporting these two species as the catalyst resting-states for the C-H borylation and semihydrogenation cycles responsible for the formation of **2b** and reaction of the Mn-H with the alkyne as the catalyst entry pathway to the C-H borylation cycle. Attempts to isolate or characterize a Mn complex from the reaction of **Mn2** with 2 equiv of NaHBEt$_3$ in the presence of 3 equivalents of **2** failed and the crude ^{1}H and ^{19}F NMR spectra showed peaks consistent with the presence of **2c** and **2d**, suggesting that the in situ generated Mn-H catalyzed the hydrogenation of **2**.

The results presented above support that, when only H$_2$ is present in the reaction medium after precatalyst activation, the C-H bond activation pathway is unproductive and the insertion pathways yielding **2c** and **2d** are preferred. However, in the presence of HBPin, the tandem C-H borylation/semihydrogenation catalytic cycles are preferred, accounting for the formation of the major product **2b**. Because the amount of **2c** increases over time even in the presence of HBPin but to a lower extent than the amounts of **2b** and **2a**, the semihydrogenation of **2** is still operative in the presence of HBPin, however, it is slower than the tandem C-H borylation / semihydrogenation that yields **2b**.

Aiming to identify other catalytically active species, the reaction of **Mn2** with 2 equiv of $NaHBEt_3$ in the presence of 10 equivalents of HBPin was conducted in THF-d_8 in a J. Young NMR tube and the ^1H, ^{11}B and the ^{31}P NMR spectra were registered at room temperature (see pages S32-S37 in the SI and Scheme 4e). The ^1H and ^{11}B NMR spectra only showed signals attributable to HBPin, however, the ^{31}P showed two signals, at 13.4 ppm (major), attributable to free ^{iPr}PNP ligand, and at -0.50 ppm (minor) (see Figure S26 in the SI and Scheme 4e), which also appeared as a minor species at early stages of the catalytic reaction and when HBPin was added to a mixture of **Mn2**, **2** and $NaHBEt_3$. The presence of free ^{iPr}PNP ligand in the reaction crude points toward partial decomposition of the manganese complex formed upon reaction of **Mn2** with HBPin and $NaHBEt_3$.

Addition of excess **2** to the reaction mixture resulted in the formation of products **2a**, **2b** and **2c** (see ^{19}F NMR monitoring in Figure S22 of the SI), suggesting catalytic turnover taking place after addition of **2**. However, the reaction only proceeded to 18% conversion after 16 hours, significantly lower than the conversion for the catalytic reaction (98% after 16 hours) and than when HBPin was added to a mixture of **Mn2**, $NaHBEt_3$ and **2** (64% after 16 hours). This result points to the reaction of the putative Mn-H with HBPin as a catalyst deactivation pathway, consistent with the presence of free ^{iPr}PNP ligand in the ^{31}P NMR spectra (see top ^{31}P NMR spectrum in Scheme 4e). Additionally, the ^{31}P NMR spectra showed the presence of the signals at 0.60, -0.50 and -2.18 ppm, consistent with the presence of catalytically active species that would be responsible for the formation of products **2a**, **2b** and **2c**. However, because the species formed after reaction of **Mn2** / $NaHBEt_3$ with HBPin decomposed to a large extent as evidenced by the presence of free ^{iPr}PNP ligand as the major product, the concentration of the catalytically active species was low, leading to low conversion of the starting material and low yields of the products.

Further mechanistic studies are currently undergoing in our laboratory aiming to elucidate the identity of the catalytically active species.

3. Conclusions

In summary, we have discovered the first manganese catalyst for the hydroboration of terminal alkynes. The presence of $NaHBEt_3$ as precatalyst activator was found to enhance the chemoselectivity of the process and the efficiency of the precatalyst. The reaction was found to proceed by a tandem C-H borylation / *E*-stereoselective semihydrogenation pathway, with the C-H borylation step resulting on β-regioselectivity and the semihydrogenation step affording exclusively the *E*-alkenylboronate ester. Stoichiometric reactions support that the precatalyst entered the cycles by reaction with $NaHBEt_3$ followed by reaction with the alkyne, whereas reaction with HBPin led to decomposition of the Mn complex and constituted a catalyst deactivation pathway. Evaluation of the substrate scope and further mechanistic studies are currently being carried out in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge.
Complete experimental details, characterization data, NMR spectroscopic data (PDF)

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Author Contributions

R. A. designed the experiments, supervised the experimental work and drafted the manuscript. V. D. A. designed the experiments, conducted the experimental work and drafted the SI.
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Notes

The authors declare no competing financial interest.

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