Chemoselective C(sp)-H Borylation of Terminal Alkynes Catalyzed by a Bis(N-heterocyclicsilylene) Manganese Complex

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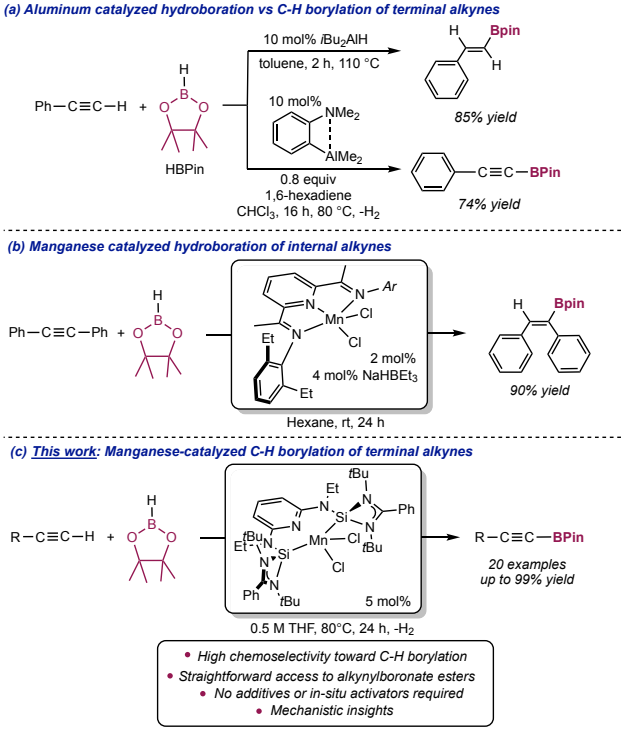
ABSTRACT: The manganese(II) complex [Mn(SiNSi)Cl_2] (SiNSi = 2,6-[EtNSi($NtBu$)$_2$CPh]$_2$$C_5H_3N$) was an efficient catalyst for the chemoselective C(sp)-H borylation of terminal alkynes. Aliphatic as well as aromatic alkynes containing electron-withdrawing and -donating substituents in different positions have been efficiently borylated. In all cases, the catalyst showed an excellent chemoselectivity towards C-H borylation and the reactions proceeded without additives or *in-situ* activators. Paramagnetic Mn complexes are involved in catalytic turnover which is proposed to occur by a redox-neutral Mn(II) cycle. Stoichiometric reactions support that the [Mn(SiNSi)Cl_2] precatalyst enters the catalytic cycle by reaction with HBPin. KIE experiments point toward C-H activation of the alkyne as not being involved in the rate-determining step.

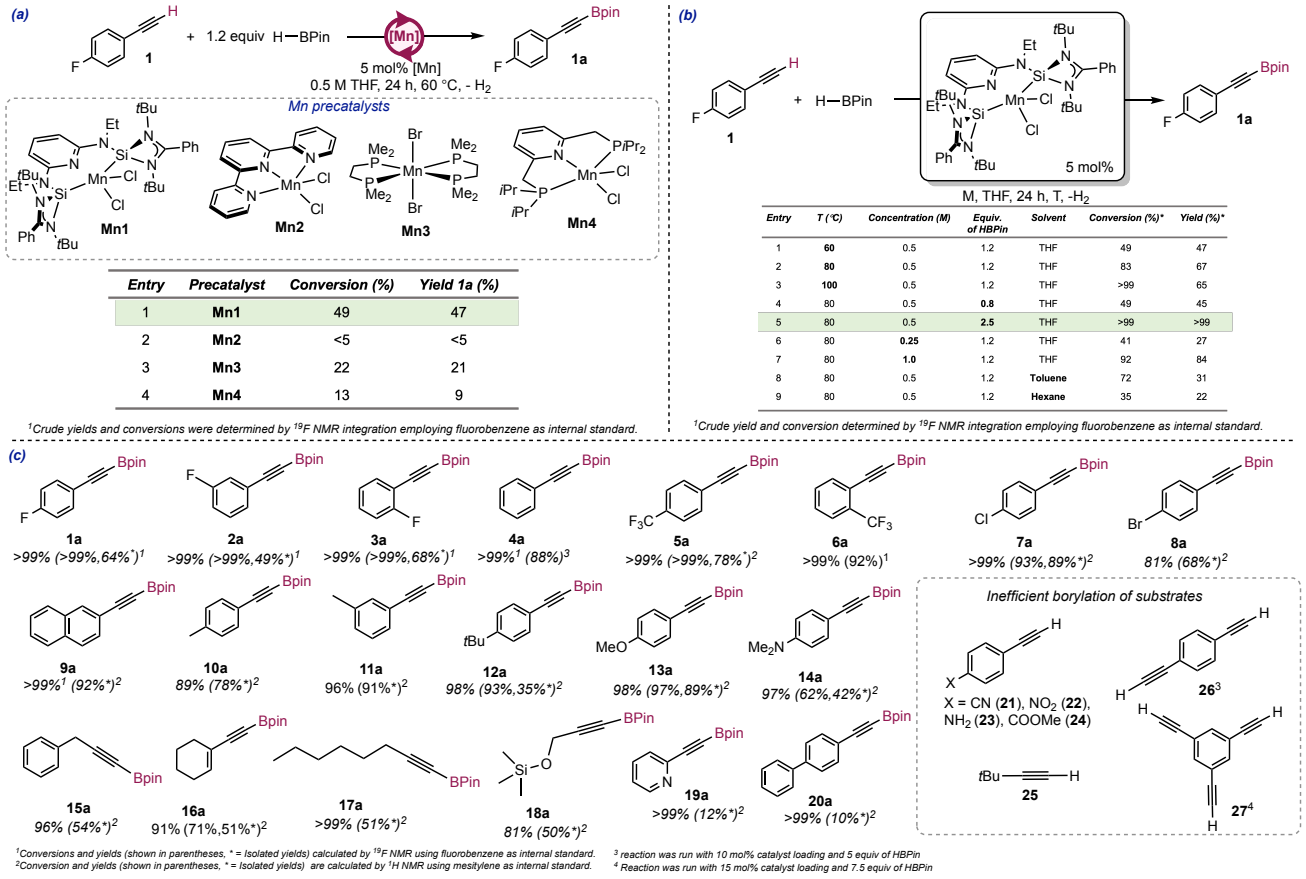
Earth-abundant transition-metal complexes have emerged as sustainable catalysts for small molecule functionalization processes traditionally carried out by precious metals.[1] Cobalt, iron and nickel catalysts are well-established for C-H functionalization, in particular, for C-H borylation,[2] whereas manganese has received scarce attention, despite its sustainable supply and environmentally benign nature. Although the borylation of C(sp^2)-H bonds catalyzed by manganese complexes has been reported,[3] manganese catalysts for the borylation of C(sp)-H bonds remain unknown. Transition-metal catalyzed C(sp)-H borylation of *terminal* alkynes renders access to synthetically valuable alkynylboronate esters[4] in one step, generating H_2 as the only byproduct. However, fundamental steps involving the insertion of the triple bond into M-X (X = H, B(OR)$_2$) bonds compete with the activation of the C(sp)-H bond. As a result, only a few transition-metal catalysts have been reported for the C(sp)-H borylation of terminal alkynes,[5] the vast majority being chemoselective for hydroboration[6] or tandem C-H borylation / hydroboration[7] or diboration,[8] resulting in the functionalization of the triple bond in the alkynylboronate ester. The main challenge strives on unraveling the catalyst designing principles to promote the C(sp)-H activation over alkyne insertion fundamental steps. A strategy relying on Frustrated Lewis Pairs has been reported to favor C-H alumination (Scheme 1a, bottom)[9] over hydroalumination (Scheme 1a, top)[10] resulting on an efficient Al hydride catalyst for the C-H borylation of terminal alkynes. The efficiency of this strategy is attributed to a decrease in the Lewis acidity at Al with a concomitant increase in the basicity of the hydrides. However, in order to achieve synthetically useful chemoselectivity for the C-H borylation, the reaction requires additives to prevent hydroboration from trace BH_3. Analogous strategies to promote C-H borylation over hydroboration are lacking in the realm of transition-metal catalysts. A promising approach would involve the use of strong-field

Scheme 1. (a) Strategy to promote C-H borylation over hydroboration employing aluminum catalysts;[9,10] (b) redox-active PDI ligands enable manganese-catalyzed hydroboration of internal alkynes[14] and (c) this work: a chemoselective manganese catalyst containing a redox non-active strong-electron donor bis(silylene) ligand for C(sp)-H borylation of terminal alkynes.



and electron-donating ligands to access highly electron-rich metal centers capable of C-H activation. The use of strong-field ligands to promote C-H activation in small

Scheme 2. (a) Catalyst screening for the C-H borylation of 4-fluorophenylacetylene with HBPin; (b) selected optimization of the reaction conditions employing Mn1 as precatalyst (see Table S1 in the SI for full optimization details); (c) substrate scope for the C-H borylation of terminal alkynes employing the optimized conditions.



Entry	Precatalyst	Conversion (%)	Yield 1a (%)
1	Mn1	49	47
2	Mn2	<5	<5
3	Mn3	22	21
4	Mn4	13	9

[1]Crude yields and conversions were determined by ^{19}F NMR integration employing fluorobenzene as internal standard.

Entry	T (°C)	Concentration (M)	Equiv. of HBPin	Solvent	Conversion (%)*	Yield (%)*
1	**60**	0.5	1.2	THF	49	47
2	**80**	0.5	1.2	THF	83	67
3	**100**	0.5	1.2	THF	>99	65
4	80	0.5	**0.8**	THF	49	45
5	80	0.5	**2.5**	THF	>99	>99
6	80	**0.25**	1.2	THF	41	27
7	80	**1.0**	1.2	THF	92	84
8	80	0.5	1.2	**Toluene**	72	31
9	80	0.5	1.2	**Hexane**	35	22

[1]Crude yield and conversion determined by ^{19}F NMR integration employing fluorobenzene as internal standard.

[1]Conversions and yields (shown in parentheses, * = Isolated yields) calculated by ^{19}F NMR using fluorobenzene as internal standard.
[2]Conversion and yields (shown in parentheses, * = Isolated yields) are calculated by ^{1}H NMR using mesitylene as internal standard.
[3] reaction was run with 10 mol% catalyst loading and 5 equiv of HBPin
[4] Reaction was run with 15 mol% catalyst loading and 7.5 equiv of HBPin

molecules by 1st-row transition metal complexes has proved successful for Co and Fe complexes,[11] and has been leveraged to the discovery of catalysts for the C(sp^2)-H borylation of arenes.[2a-e] However, this approach has barely been exploited in earlier transition metals like manganese, resulting on scarce precedents of C-H functionalization manganese catalysts,[3,12] which contrasts with their rising popularity in reduction and hydrofunctionalization processes.[13] Accordingly, whereas a Mn(II) complex containing a redox-active pyridyldiimine (PDI) ligand has been reported an efficient catalyst for the hydroboration of symmetric *internal* alkynes (Scheme 1b),[14] manganese catalysts for C(sp)-H borylation remain unknown. Our hypothesis is that redox non-active stronger-electron donating ligands than PDI may play a key role in promoting C-H activation over alkyne insertion, opening new avenues for the discovery of manganese catalysts for C-H functionalization processes. Silylenes are among the strongest electron-donating ligands and emerge as promising for efficient transition-metal catalysts,[2d,e,15] although their applications in catalysis still remain underexplored.

In this work we report the first *chemoselective* manganese catalyst containing a strong-field silylene ligand for the C(sp)-H borylation of *unactivated terminal* alkynes (Scheme 1c).

Our research commenced with the synthesis of the Mn(II) dihalide complexes **Mn1**-**Mn4**[3a,13a,16] and the evaluation of their catalytic activity for the C-H borylation of 4-fluorophenylacetylene (**1**) with HBPin (Pin = pinacolate). The results in Scheme 2a show that [Mn(SiNSi)Cl_2] (**Mn1**) (SiNSi = 2,6-[EtNSi($NtBu)_2$CPh]$_2C_5H_3N$) was the most efficient and chemoselective catalyst for C-H borylation, yielding the alkynylboronate ester **1a** in a 47% yield and the corresponding alkenylboronate ester in <5% yield. Remarkably, **Mn1** does not require *in-situ* activation with hydride or alkyl sources neither of the presence of additives as BH_3 scavengers to suppress competing hydroboration.[9] Interestingly, when 10 mol% of $NaHBEt_3$ was employed as an *in-situ* activator with 5 mol% of catalyst loading, product **1a** was not detected in the reaction crude and a mixture of other unidentified products was observed by GC, suggesting that the presence of the hydride source precludes selective catalysis. Control experiments for the reaction of **1** and HBPin in THF at 60 °C for 24 h were run (a) without **Mn1**, (b) in the presence of 5 mol% of $MnCl_2$ and (c) in the presence of 5 mol% of SiNSi. Only in case (b) product **1a** was observed by GC, however, it was formed in a significantly lower yield than under the catalytic conditions (23%). To find out whether heterogenous catalysis was operative under the reaction conditions, a Hg drop was added to the catalytic borylation of **1** with HBPin in the presence of 5 mol% of **Mn1**. The catalytic activity was not inhibited and product **1a** formed in a 50% yield, comparable to that of the reaction in the absence of Hg (47%), supporting homogenous catalysis.

Aiming to increase the yield of the alkynylboronate ester, an optimization of the reaction components was carried out. When HBCat (Cat = catecholate), HBDan (Dan = 1,8-diaminonaphthalene) or B_2Pin_2 were employed as borylating agents instead of HBPin, the reaction proceeded to low conversion and the corresponding alkynylboronate esters were formed in low yields (<5%), supporting HBPin as the most efficient borylating agent (see Table S1). Interestingly, when OAc, Br or OTf (CF_3SO_3) ligands were present in the precatalyst instead of Cl, the reaction also proceeded to low conversion and product **1a** was formed in low yields (see Table S1), suggesting that the identity of the halide ligand played a relevant role in catalysis, presumably on the generation of the catalytically active species. Optimization of the reaction conditions (see Scheme 2b and Table S2 for the full optimization) revealed 80 °C, a 0.5 M solution of THF and 2.5 equiv of HBPin as the optimum conditions, affording **1a** in >99% crude yield with a >99% conversion of the starting material. Lowering down the equiv of HBPin (Scheme 2b, entry 4), the catalyst loading (table S2, entries 22 and 23) or the reaction time (table S2, entry 17) resulted in a decrease of the yield of the product. The concentration of the solution also played a relevant role, as either a decrease (Scheme 2b, entry 6) or an increase (Scheme 2b, entry 7) led to diminished yields of product **1a**. The identity of the solvent was also found to play a key role in the efficiency of the catalyst, as other solvents such as toluene (Scheme 2b, entry 8), hexane (Scheme 2b, entry 9), fluorobenzene (table S2, entry 13) or 2-methylTHF (table S2, entry 16) led to decreased product yields and/or poorer chemoselectivity. Conducting the reaction under blue light irradiation (400 nm) at room temperature led to formation of trace amount of the product (table S2, entry 9), suggesting that thermal conditions are required for **Mn1** to be efficient. Therefore, the conditions described above were selected for the evaluation of the substrate scope.

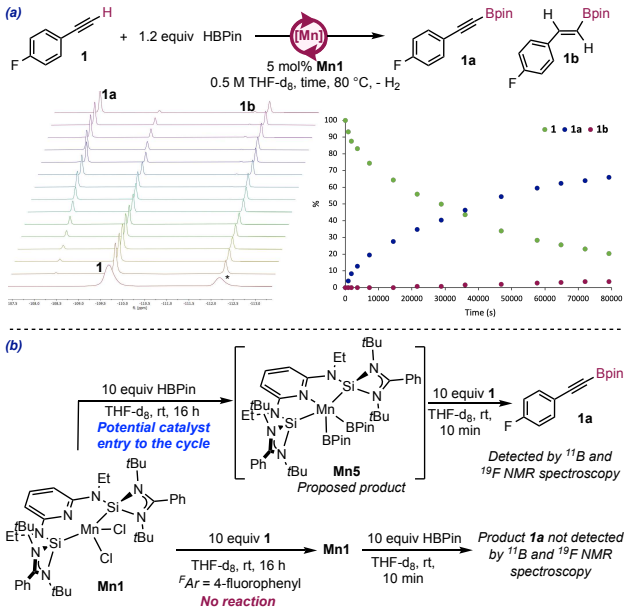
The substrate scope for the transformation showed that **Mn1** is an efficient catalyst for the C-H borylation of aromatic alkynes containing electron-withdrawing and -donating substituents at different positions of the phenyl ring (Scheme 2c). For fluoro-substituted phenyl acetylenes, **Mn1** was able to yield the borylated product in comparable yields regardless of the position of the F atom (products **1a**, **2a** and **3a**). Interestingly, products **2a** and **3a** have not previously been reported. **Mn1** tolerated well other halides like Cl (**7a**) and Br (**8a**). Remarkably, no transition-metal catalysts have been described for the C-H borylation of the later. CF_3 groups at the *para* (**5a**) and *ortho* (**6a**) positions were well-tolerated and the alkynylboronate esters were formed in comparable yields (>99% and 92% respectively), suggesting little impact of the steric hindrance imposed by the CF_3 group in the *ortho* position on the catalytic reaction. The catalyst also tolerated the presence of electron-donating groups at the *para* position of phenyl ring, mainly OMe (**13a**) and NMe_2 (**14a**), although the yield of **14a** was slightly lower than when electron-withdrawing groups were present. Remarkably, **Mn1** was chemoselective toward C(sp)-H borylation even in the presence of an internal alkene (**16a**) suggesting a higher barrier for an insertion step of the alkene than for the C(sp)-H activation step. Aliphatic alkynes **15**, **17** and **18** were also borylated, although the corresponding alkynylboronates were obtained in lower yields than those of aromatic alkynes. Remarkably, the borylation of 2-pyridylacetylene (**19**) yielded the borylated product **19a**, although in a low yield (12%). Interestingly, **Mn1** has been reported inefficient for the semihydrogenation of **19**,[13a] and no catalysts are known to borylate this substrate with no alternative synthetic routes described in the literature for its synthesis. Remarkably, the C-H borylation of 4-ethynylbiphenyl also yielded the corresponding alkynylboronate ester **20a** in low yield (10%), this substrate being particularly challenging and not reported for other transition-metal catalysts capable of C(sp)-H borylation.[5] **Mn1** was not efficient for the borylation of aryl acetylenes containing CN (**21**), NO_2 (**22**), NH_2 (**23**) or COOMe (**24**) substituents at the *para* position, neither for *tert*-butylacetylene (**25**) or for phenyl polyacetylenes **26** and **27**.

Due to the scarce precedents of manganese catalysts for C-H functionalization processes,[3,12] as well as of mechanistic insights for complexes lacking CO ligands, we sought to investigate the mechanism for the C-H borylation of alkynes. Addition of 1 equiv of TEMPO to the borylation of **1** did not inhibit the catalytic reaction, supporting that a mechanism involving radicals is not operative for this transformation.

To gain insights into the reaction pathway as well as into the identity of the Mn active species, the catalytic C-H borylation of **1** with HBPin in the presence of 10 mol% of **Mn1** at 80 °C was monitored by ^1H, ^{11}B and ^{19}F NMR spectroscopy in THF-d_8 employing fluorobenzene as internal standard. The ^{19}F and ^{11}B NMR spectra showed the formation of **1a** (-108 ppm in the ^{19}F NMR spectrum) at the expense of **1** (-110 ppm in the ^{19}F NMR spectrum, see Scheme 3a, left for the ^{19}F NMR spectra). A reaction profile accounting for the species present in solution is shown in Scheme 3a, right. An induction period was not observed and product **1a** was formed as soon as the reaction mixture was heated up to 80 °C. The ^1H NMR spectra showed a singlet at 4.5 ppm hinting the presence of H_2 in the reaction mixture. This signal gradually increased its intensity as the reaction proceeded, consistent with the accumulation of the H_2 formed as a byproduct from C-H borylation (see Figure S4). Interestingly, the *E*-alkenyl boronate ester (**1b**, -112 ppm in the ^{19}F NMR spectrum) was detected in trace amounts only after 8 hours, presumably formed by the semihydrogenation of **1a** with H_2 catalyzed by **Mn1**, suggesting that **Mn1** has low efficiency for this process. Neither the ^{19}F nor the ^{11}B spectra showed signals attributable to -BPin or -C≡C^{F}Ar ligands in diamagnetic Mn complexes, whereas signals attributable to a SiNSi ligand were not identified in the ^1H NMR spectra. The signals attributable to the starting materials **1** and HBPin were broaden when **Mn1** was added to the mixture at room temperature and during the catalytic reaction, suggesting that paramagnetic Mn complexes were responsible for catalysis. Attempts to isolate or crystallize any catalytically relevant Mn species from the catalytic reaction mixture after 10 minutes by slow diffusion of hexane into the THF reaction mixture at -35 °C failed, and only crystals of the precatalyst **Mn1** could be grown. The fact that only **Mn1**

could be isolated from the catalytic reaction suggests that either the activation of the **Mn1** precatalyst was incomplete, or that the Mn active species was in equilibrium with **Mn1** during catalysis. Although catalytically active Mn species were present in the reaction medium after 10 minutes, **Mn1** may be the complex with the lowest solubility under the conditions employed for crystallization.

Scheme 3. (a) Left: ^{19}F NMR monitoring of the borylation of 1 with 1.2 equiv of HBPin in the presence of 5 mol% Mn1. The first spectrum from the bottom corresponds to a mixture of 1, HBPin and Mn1 at room temperature after 15 minutes. The following spectra were collected after reaction at 80 °C for: 15 min, 30 min, 1 h, 2 h, 4 h, 6 h, 8 h, 10 h, 13 h, 16 h, 18 h, 20 h, 22 h and 38 h. * denotes fluorobenzene employed as internal standard. Right: Quantitative reaction profile. (b) Reactions of Mn1 with HBPin (top) or 1 (bottom) followed by addition of 1 or HBPin respectively.



Aiming to elucidate how the precatalyst generates the catalytically active species and its identity, the reaction of **Mn1** with 10 equivalents of HBPin was monitored by ^{1}H and ^{11}B NMR spectroscopy in THF-d$_8$ in a J. Young NMR tube at room temperature for 16 h. A color change from yellow to orange was observed upon 16 h of reaction, however, the ^{1}H spectra did not show any signal attributable to a diamagnetic Mn complex, and the ^{11}B NMR spectra only showed the presence of HBPin with no signals attributable to BPin ligands. These observations point toward a paramagnetic Mn complex formed by reaction of **Mn1** and HBPin. Addition of 10 equiv of **1** to the reaction mixture at room temperature resulted in the immediate formation of **1a**, as evidenced by the ^{11}B (signal at 26.15 ppm) and the ^{19}F NMR spectrum (signal at -108.24 ppm) (Scheme 3b, top), supporting the formation of a catalytically active species, **Mn5**, upon reaction of **Mn1** with HBPin. Because the formation of product **1a** has not been detected by ^{19}F NMR spectroscopy when **Mn1**, **1** and HBPin were mixed at room temperature for 15 minutes in THF-d$_8$, the formation of **1a** upon addition of **1** at room temperature to the previous reaction mixture must occur upon reaction of complex **Mn5** with **1** and not from a mixture of **Mn1**, **1** and HBPin. Longer reaction times at room temperature resulted in a slow increase of the peak attributed to **1a** in the ^{19}F NMR spectrum, consistent with catalytic turnover taking place at slow rates. Interestingly, upon heating the reaction mixture up to 80 °C, the intensity of the peak attributed to **1a** increased faster over time with a concomitant disappearance of the starting material, supporting catalytic turnover taking place at a faster rate.

Aiming to elucidate the identity of **Mn5**, its independent synthesis was carried out by reaction of **Mn1** with 10 equiv of HBPin in THF at room temperature for 16 hours. The IR spectrum of the product did not match the spectrum for **Mn1** (see Figure S12), hinting that **Mn1** reacted with HBPin. The IR spectrum of the product did not show any stretching band attributable to a Mn-H stretch, typically in the range of 1900-2000 cm^{-1}.[13a] Aiming to gain more insights on the identity of the product, its reaction with CCl_4 was conducted. The ^{1}H NMR spectrum of the resulting solution did not show a signal attributable to $CHCl_3$, well-established reactivity for hydridic transition metal hydrides and borohydride complexes in the presence of hydrocarbons containing weak C-X bonds (X = Cl, Br).[17] Furthermore, when the reaction of **Mn1** with 2 equiv of HBPin in THF-d$_8$ was conducted and monitored by ^{13}C and ^{11}B NMR spectroscopy, signals attributable to ClBPin[18] formed as a byproduct were not detected. Addition of alkyne **1** to the product (the absence of unreacted HBPin was confirmed by ^{11}B NMR spectroscopy) resulted in the formation of product **1a** (detected by ^{19}F NMR spectroscopy) after heating up at 80 °C for 2 h.

Based on (a) the absence of a signal in the ^{11}B NMR spectrum attributable to ClBPin upon reaction of **Mn1** with HBPin, (b) the absence of a Mn-H stretching band in the IR spectrum of the product and (c) the absence of $HCCl_3$ upon reaction of the product with CCl_4, Mn mono- or dihydride complexes can be tentatively ruled out as the product of the reaction of **Mn1** with HBPin. Based on the evidence presented above, and the fact that upon addition of **1** to the product **1a** was formed (Scheme 3b, top), we propose the formation of a Mn(II) bis(boryl) complex (**Mn5**), although Mn(I) boryl or Mn borohydride complexes cannot be ruled out. A proposed structure for **Mn5** is shown in Scheme 3b top. The formation of **Mn5** presumably takes place by a metathesis reaction involving the H-B and the Mn-Cl bonds in **Mn1**. Due to its electronic unsaturation, **Mn5** may exist as a THF adduct in solution to increase its electron count from 15 to 17 electrons. Transition-metal boryl complexes are well-known intermediates in catalytic C-H borylation,[2,19] with monoboryl, bisboryl and trisboryl complexes being known and responsible for the C-H activation step. Further efforts are ongoing in our laboratory to isolate and fully characterize **Mn5**.

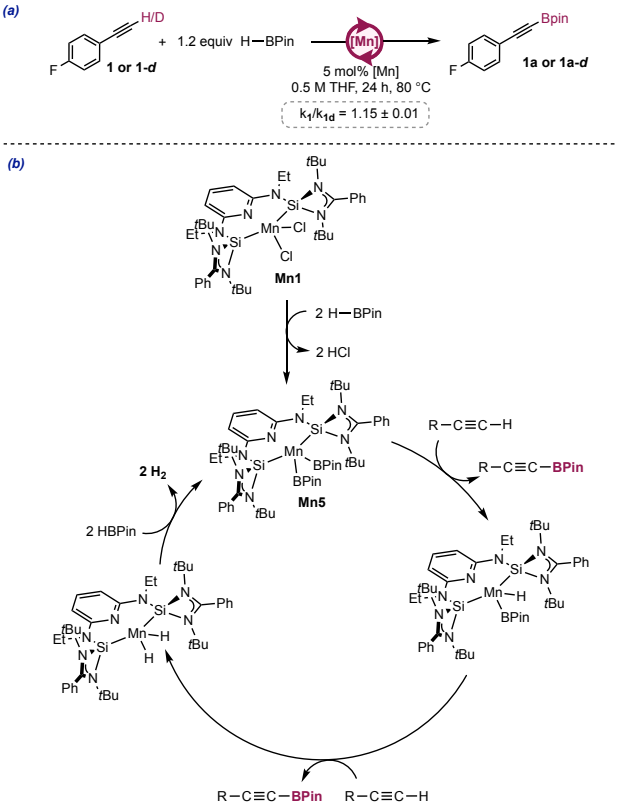
The identity of the active species plays a crucial role in the chemoselectivity shown by **Mn1** for the functionalization of *terminal* alkynes. The preference for C-H activation versus alkyne insertion is remarkable considering that **Mn1** *in-situ* activated with NH_3BH_3 has been previously reported as an efficient catalyst for the semihydrogenation of *internal* alkynes and is, therefore, capable of alkyne in-

sertion.[13a] However, upon activation of **Mn1** with HBPin, a mechanism involving a C-H activation step is preferred over one involving alkyne insertion, which would lead to the hydroboration of the triple bond. These observations support the generation of different active species when **Mn1** is activated with either NH_3BH_3 or HBPin. A Mn hydride is proposed as the active species formed upon reaction of **Mn1** with NH_3BH_3,[13a] although isolation and characterization of such species is lacking, and its oxidation state is unknown. The formation of boryl complexes as catalytic intermediates in the C-H borylation of terminal alkynes could account for the different reactivity observed when HBPin is present as the activator. Furthermore, as evidenced by the trace amount of the alkenylboronate ester formed in the reaction, **Mn1** has low efficiency for the semihydrogenation of **1a** with H_2 and no efficiency for the hydroboration of **1a** with HBPin, as no diboration products have been identified in the reaction mixtures. In fact, when the alkynylboronate ester **1a** was treated with 2.5 equivalents of HBPin in THF and heated up to 80 °C for 24 h in the presence of 5 mol% of **Mn1**, only signals attributed to the starting material **1a** were identified in the ^{1}H NMR spectrum of the crude reaction mixture. Additionally, **Mn1** was also found inefficient for the hydrosilylation of the alkynylboronate ester **1a** with $HSi(OEt_3)$. The presence of a BPin substituent in **1a** is likely not the origin of this inefficiency toward hydrofunctionalization, because when the hydroboration of the internal alkyne methylphenylacetylene was attempted, only starting material was recovered and no signals for alkenylboronate esters were detected in the ^{1}H NMR spectrum of the crude reaction. These results suggest that the barriers for alkyne insertion into the Mn-B bonds of the proposed manganese bis(boryl) complex **Mn5** are higher than those for C-H activation, and, therefore, the later fundamental steps are preferred.

Aiming to identify other Mn species involved in the catalytic reaction, the reaction of **Mn1** with 10 equiv of **1** at room temperature was monitored by ^{1}H, ^{11}B and ^{19}F NMR spectroscopy in THF-d_8 in a J. Young NMR tube for 16 h. During this time, no significant changes in color of the solution nor in the ^{1}H or ^{19}F NMR spectra were observed and no signals attributable to a diamagnetic Mn complex were identified. Addition of 10 equiv of HBpin to the reaction mixture at room temperature did not yield signals attributable to product **1a**, however, heating up the reaction mixture to 80 °C for 1 h and 30 min resulted in the formation of product **1a**, supporting catalytic turnover. These results support that **Mn1** is not able to activate the C-H bond in **1** at room temperature and only after addition of HBPin and heating up the reaction mixture catalytic turnover takes place generating product **1a**. A yellow solid was isolated from the reaction of **Mn1** with 10 equiv of **1** in THF at room temperature for 16 hours (the absence of **1** was corroborated by ^{19}F NMR spectroscopy prior to the addition of HBPin), which did not yield product **1a** upon addition of excess HBPin and heating up to 80 °C for 16 h as evidenced by ^{11}B and ^{19}F NMR spectroscopy. The IR spectrum of the isolated solid matched that of **Mn1** (see Figure S17), unequivocally confirming the identity of the solid as **Mn1** and ruling out the formation of a catalyst deactivation product.

To gain preliminary insights into the kinetics of the reaction and the identity of the rate-determining step, the KIE for the C-H borylation of **1** was determined employing initial rates in 2 separate vessels.[2b,c] The k_H/k_D is 1.15 (see Scheme 4a and Table S3) which is consistent with C-H activation of the alkyne *not* being involved in the rate-determining step. This value is lower than that obtained for the C-H borylation of terminal alkynes catalyzed by an Al complex (1.4),[9] where an asynchronous deprotonation during the rate-determining step was proposed to operate, suggesting that an alternative mechanism for C-H activation could be operative for **Mn1**.

Scheme 4. (a) KIE determination employing initial rates in two separate vessels; (b) Proposed mechanism for the C-H borylation of a terminal alkyne employing Mn1 as a precatalyst and HBPin as the borylating agent.



Taking together the mechanistic evidence presented above, a plausible catalytic cycle that accounts for the formation of an alkynylboronate ester by C-H borylation of a terminal alkyne is shown in Scheme 4b. Because Mn(II) complexes are not known to undergo metal-centered oxidative addition, a redox-neutral Mn(II) cycle is proposed, involving bond-activation and -formation events taking place by redox-neutral pathways. The precatalyst **Mn1** is proposed to enter the cycle by reaction with HBPin to generate a Mn(II) bis(boryl) active species, **Mn5**, capable of activating the C-H bond in a terminal alkyne and forming a new C-B bond to yield the alkynylboronate ester and a Mn(II) hydride boryl complex. Reaction of this complex with another equivalent of alkyne would result in the formation of a second equivalent of alkynylboronate ester and

a Mn(II) dihydride that upon reaction with 2 equiv of HBPin would regenerate the Mn(II) bis(boryl) **Mn5**. Alternatively, the hydride boryl complex could also react with HBPin to regenerate **Mn5**. Further mechanistic studies, including isolation and characterization of catalytically active species, and kinetic and computational studies are currently undergoing in our laboratory aiming to provide further support for the proposed mechanism.

In summary, we have discovered the first manganese catalyst chemoselective for the C(sp)-H borylation of terminal alkynes. The catalyst does not require the presence of additives or *in-situ* activators and has been found efficient for the borylation of aliphatic terminal alkynes and aromatic terminal alkynes with different substitution patterns and electron-donating and -withdrawing groups at the phenyl ring. Stoichiometric reactions support that reaction with HBPin leads to a catalytically active species that is proposed to be a Mn(II) bis(boryl) complex. No deactivation pathways have been identified. The KIE for the reaction points toward C-H activation of the alkyne as not being involved in the rate-determining step. The high chemoselectivity of **Mn1** toward C-H borylation suggests that C-H activation is the preferred pathway over alkyne insertion into a Mn-B bond. Further mechanistic studies are currently undergoing in our laboratory to understand the role of ligand identity and metal oxidation state on the chemoselectivity of the reaction.

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

RA conceived the project, designed the experiments, supervised the experimental work and drafted the manuscript. HA designed the experiments, optimized the catalytic reaction conditions, evaluated the substrate scope and conducted mechanistic reactions. HK designed the experiments and carried out mechanistic experiments, including the NMR monitoring of the reactions and the KIE determination.
The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript. / ‡These authors contributed equally.

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Notes

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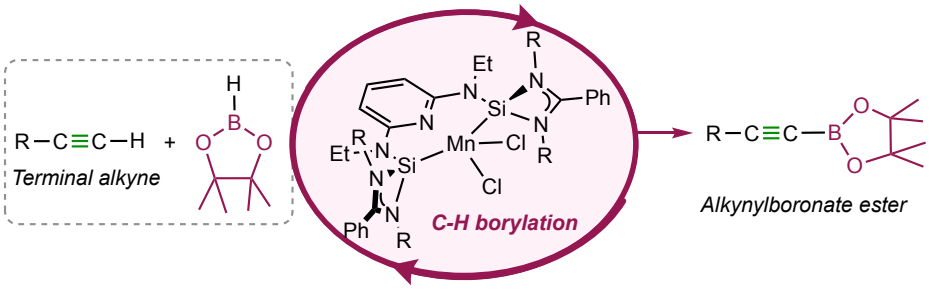
Controlling Chemoselectivity in Manganese-Catalyzed Alkyne Functionalization



- *Earth-abundant manganese catalyst for the C-H borylation of terminal alkynes*
- *Strong-electron-donating silylene ligand promotes C-H activation over alkyne hydrofunctionalization*
- *High efficiency and broad substrate scope*
- *No additives or in-situ activators required*
- *Mechanistic insights*
