Hydroboration of Terminal Alkynes Catalyzed by a Mn(I) Alkyl PCP Pincer Complex following Two Diverging Pathways

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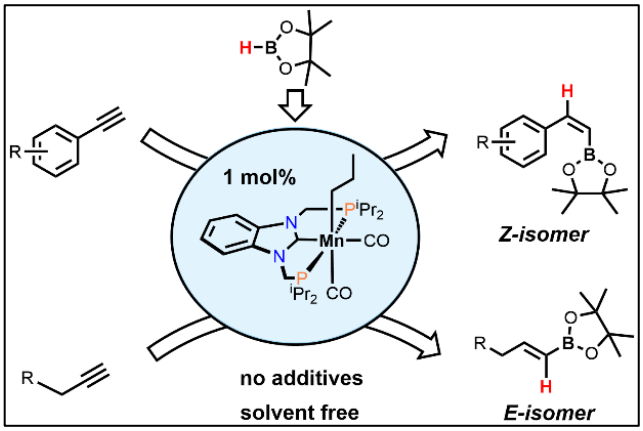
ABSTRACT: A stereo- and regioselective Mn(I)-catalyzed hydroboration of terminal alkynes with pinacolborane (HBPin) is described. The hydroboration reaction is highly *Z*-selective in the case of aryl alkynes and *E*-selective in the case of aliphatic alkynes. The reaction requires no additives and proceeds with a catalyst loading of 1 mol % at 50 - 70°C. The most active pre-catalyst is the bench-stable alkyl Mn(I) complex *cis*-[Mn(PCP-*i*Pr)(CO)$_2$($CH_2CH_2CH_3$)]. The catalytic process is initiated by migratory insertion of a CO ligand into the Mn-alkyl bond to yield an acyl intermediate. This species undergoes C-H and B-H bond cleavage of the alkyne (aromatic alkynes) and HBPin (in the case of aliphatic alkynes) forming the active Mn(I) acetylide and boryl catalysts [Mn(PCP-*i*Pr)(CO)(C≡CR)] and [Mn(PCP-*i*Pr)(CO)(BPin)], respectively. A broad variety of aromatic and aliphatic alkynes were efficiently and selectively borylated. Mechanistic insights are provided based on experimental data and DFT calculations. The functionalized alkenes can be used for further applications in cross-coupling reactions.



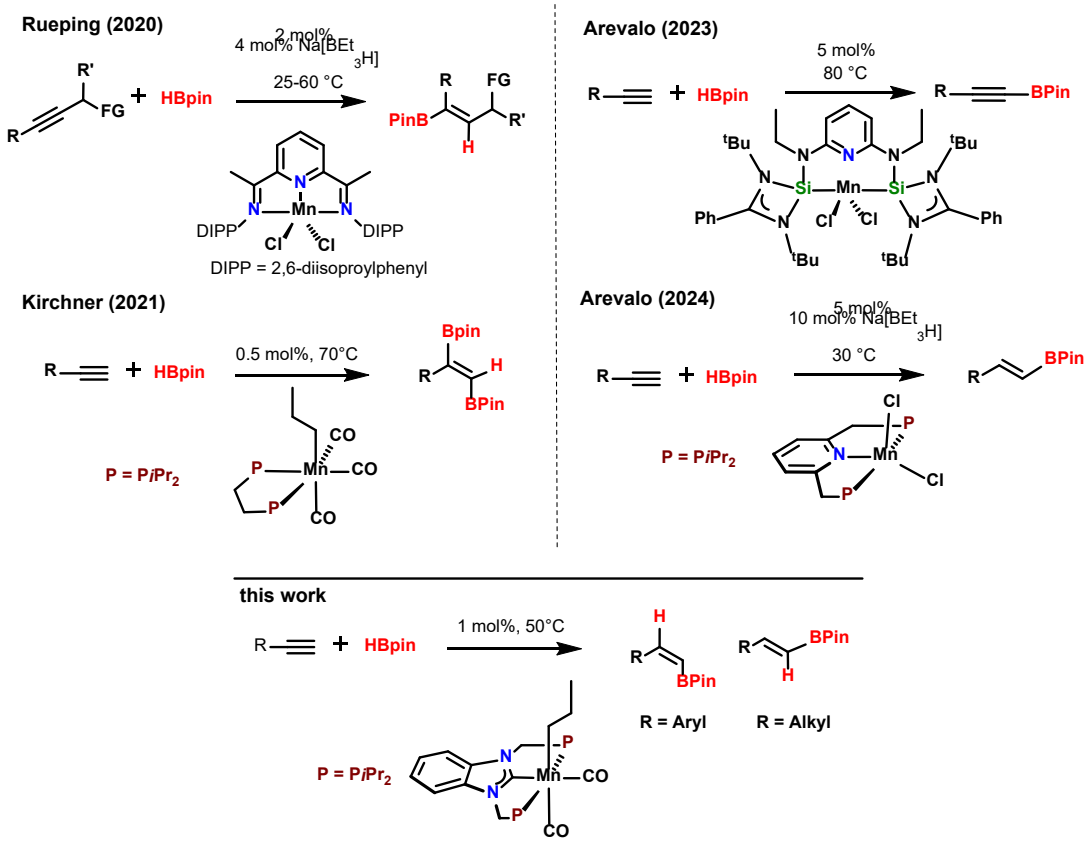
KEYWORDS: *Hydroboration, alkynes, manganese, alkyl complex, DFT calculations*

Introduction

The use of organoboron reagents especially in the field of cross-coupling chemistry has gained importance within the last few decades, in part due to the emergence of hydroboration catalysts which make these compounds easily accesible.[1,2] In this context, the use of dialkoxyboranes such as pinacolborane (HBPin) was introduced due to the stability of HBPin and the hydroborated products.[3] Transition-metal catalyzed hydroboration of C-C multiple bonds hereby displays a versatile and convenient route towards aforementioned organoboron species.[4] Catalysts with noble metal such as Rh[5] and Ir[6] are already well researched in the field of C-C multiple bond hydroboration. However, in the last years, non-precious metal catalysts based on for example Cu,[7] Ni,[8] Co[9] and Fe[10] were successfully applied for this reaction. As manganese is concerned, several examples for hydroborations of functional groups such as carbonyls,[11] nitriles,[12] CO_2[12b,13] and alkenes[11a,14] were reported. The first manganese-catalyzed hydroboration of alkynes was reported by Rueping and co-workers in 2020 (Scheme 1).[15] They reported the hydroboration of symmetrical internal alkynes to yield alkenylboronate esters from the *syn* addition of HBPin and the Mn(II) bis(imino)pyridine complex [Mn(PDI^{iPr})Cl_2] (PDI^{iPr} = 2,6-(2,6-^{i}Pr$_2$–C_6H_3–N=CMe)$_2C_5H_3N$) as pre-catalyst. as pre-catalyst. An *in situ* activation with Na[$HBEt_3$] triggered the catalytic activity of the Mn(II) complex. We described a Mn(I)-catalyzed 1,2-diboration

of terminal alkynes with HBPin.[16] The reaction proceeds with excellent *trans*-1,2-selectivity with no additives required (Scheme 1). The active pre-catalyst was the bench-stable alkyl bisphosphine Mn(I) complex *fac*-[Mn(dippe)(CO)$_3$(CH$_2$CH$_2$CH$_3$)] (dippe = 1,2-bis(di-*iso*-propylphosphino)ethane).[17] Arevalo *et al* showed that the Mn(II) complex [Mn(SiNSi)Cl$_2$] (SiNSi = 2,6-[^{Et}NSi(N*t*Bu)$_2$CPh]$_2$C$_5$H$_3$N) is an efficient catalyst for the chemoselective C(sp)–H borylation of terminal alkynes (Scheme 1).[18] Most recently, the same research group reported that the Mn(II) pincer complex [Mn(PNP-*i*Pr)Cl$_2$] (PNP-*i*Pr = 2,6-bis(diisopropylphosphinomethyl)pyridine) catalyzed the stereo- and regioselective hydroboration of terminal alkynes by employing HBPin and Na[HBEt$_3$] as activator affording exclusively *E*-alkenylboronate esters (Scheme 1).[19]

Scheme 1. Manganese-based Catalysts for the Hydroboration of Alkynes

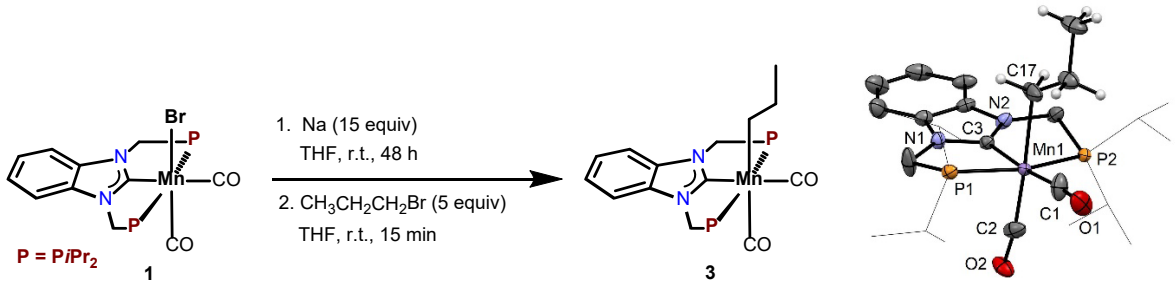


Here, we describe the activity of *cis*-[Mn(PCP-*i*Pr)(CO)$_2$(Br)] (**1**),[20] *cis*-[Mn(PCP-*i*Pr)(CO)$_2$(H)] (**2**), *cis*-[Mn(PCP-*i*Pr)(CO)$_2$(CH$_2$CH$_2$CH$_3$)] (**3**) and *cis*-[Mn(PCP-*i*Pr)(CO)$_2$(κ^2-H$_2$Bpin)] (**4**) as pre-catalysts for the stereo- and regioselective hydroboration of terminal alkynes. For this reaction, no additives are required. A plausible reaction mechanism based on detailed experimental and theoretical studies is presented.

Results and Discussion

The alkyl Mn(I) complex *cis*-[Mn(PCP-*i*Pr)(CO)$_2$(CH$_2$CH$_2$CH$_3$)] (**3**) was obtained in 57% isolated yield by reacting *cis*-[Mn(PCP-*i*Pr)(CO)$_2$(Br))] with Na (15 equiv) at room temperature for 48 h and subsequent addition of CH$_3$CH$_2$CH$_2$Br (Scheme 2). This complex is bench-stable for at least one weeks

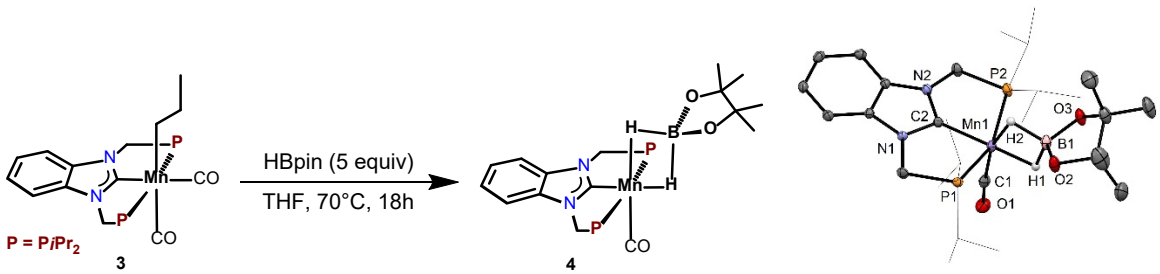
Scheme 2. Synthesis of *cis*-[Mn(PCP-*i*Pr)(CO)$_2$(CH$_2$CH$_2$CH$_3$)] (3) and Structural View of 3 Showing 50% Ellipsoids (most H atoms Omitted for Clarity).[a]



[a]Selected bond distances (Å) and angles (°): Mn1-C1 1.807(3), Mn1-C2 1.781(3), Mn1-C3 1.952(3), Mn1-C17 2.214(3), Mn1-P1 2.284(1), Mn1-P2 2.284(1), P1-Mn1-P2 160.52(3), C1-Mn1-C3 173.4(1), C2-Mn2-C17 175.8(1).

in the presence of air. Treatment of **3** with HBpin (5 equiv) for 18 h at 70 °C afforded *cis*-[Mn(PCP-*i*Pr)(CO)$_2$(κ^2-H$_2$Bpin)] (**4**) in 33 % isolated yield (Scheme 3). This complex features a κ^2-bound H$_2$Bpin ligand. While **3** is stable under an inert atmosphere of argon, in solution this compound starts decomposing within a few minutes. Complexes **3** and **4** were fully characterized by ^{1}H, ^{11}B{^{1}H}, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR and IR spectroscopy, and high-resolution mass spectrometry. In addition, the molecular structures of both complexes were determined by X-ray crystallography. Structural views are depicted in Schemes 2 and 3 with selected bond distances and angles given in the captions.

Scheme 3. Synthesis of *cis*-[Mn(PCP-*i*Pr)(CO)(κ^2-H$_2$Bpin)] (4) with Structural View of 4 Showing 50% Ellipsoids (most H atoms Omitted for Clarity).[a]

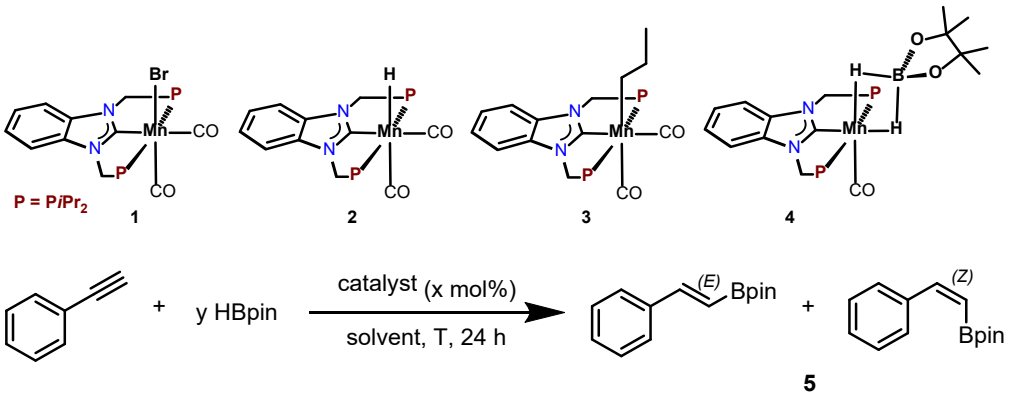


[a] Selected bond distances (Å) and angles (°): Mn1-C1 1.779(2), Mn1-C2 1.935(2), Mn1-H1 1.60(3), Mn1-H2 1.63(1), Mn1-P1 2.2480(8), Mn1-P2 2.2661(8), P1-Mn1-P2 155.94(3)

The catalytic performance of the known Mn(I) complexes **1**, **2** and complexes **3** and **4** was then investigated for the hydroboration of phenylacetylene as model substrate. Optimization experiments are depicted in Table 1. At 50 °C under solvent free conditions complex **1** was catalytically inactive. With complex **2** the corresponding boronic ester **5** was obtained in 41% yield with an *E/Z* ratio of 5/95, thus, being highly *Z*-selective (Table 1, entries 1 and 2). Under the same reaction conditions, complexes **3** and **4** afforded **5** in essentially quantitative yield with *E/Z* ratios of 3/97and 1/99, respectively (Table 1, entries 3 and 4). Due the higher stability of **3** we focused in the following on the catalytic activity of **3**. Lowering the catalyst loading to 0.5 mol reduced to yield of **5** to 87% with an *E/Z* ratio of 25/75 (Table 1, entry 5). By using a catalyst loading of 2 mol% at 25 °C the yield of 5 was significantly reduced to 40% which was also associated with a poorer *E/Z* ratio of 16/84 (Table 1, entry 6). If the catalytic reactions were performed in the solvents THF and toluene with a catalyst loading of 2 mol%, the yield of **5** was 94 and 93%, respectively, with an *E/Z* ratio of 1/99. In the CH$_2$Cl$_2$ the yield of **5** dropped to

27% (Table 1, entry 9). Notably, no additives were required to activate either **3** or **4**. In the absence of catalyst, no conversion of phenylacetylene to **5** was observed (Table 1, entry 10).

Table 1. Catalyst Screening and Optimization for the Hydroboration of Phenylacetylene[a]



entry	Catalyst (x mol%)	Solvent	Temp. (°C)	Yield (%)	*E*/*Z* ratio
1	**1** (1)	neat	50	<1	-
2	**2** (1)	neat	50	41	5/95
3	**3 (1)**	**neat**	**50**	**>99**	**3/97**
4	**4** (1)	neat	50	>99	1/99
5	**3** (0.5)	neat	50	87	25/75
6	**3** (2)	neat	25	40	16/84
7	**3** (2)	THF	50	94	1/99
8	**3** (2)	toluene	50	93	1/99
9	**3** (2)	CH_2Cl_2	50	27	1/99
10	-	neat	50	<1	-

[a]Reaction conditions: Phenylacetylene (0.25 mmol, 1 equiv), HBpin (0.26 mmol, 1.1 equiv), catalyst (x mol%), Temp., 24 h, conversion and *E*/*Z* ratio determined by GC-MS

Having established the optimal reaction conditions, the scope and limitations were examined (Table 2). In this context, a variety of aromatic and aliphatic alkynes with both electron-withdrawing and electron-donating moieties were tested. Most aromatic substrates react in the presence of 1 mol% catalyst to yield the corresponding alkenes with excellent *E*/*Z* ratios up to 1/99 (Table 2, **5a**-**5q**). Likewise, also in the case of 3-ethynylthiophene, trimethylsilylacetylene and 1-ethynylcyclohexene almost exclusively the *Z*-isomers were formed (Table 2, **5r**-**5t**). In the case of 4-ethynylbenzaldehyde and 1-(4-ethynylphenyl)ethenone) featuring formyl and acyl moieties, respectively, both functional groups were hydroborated as well yielding the respective *Z*-alkenylboronate esters in 77 and 72% isolated yields (Table 2, **5i**, **5j**). *Ortho*-substituted alkynes required higher temperatures to be fully converted (Table 2, **5k**-**5n**). 1,3-Diethynylbenzene was hydroborated to afford **5o** in 75% isolated yield showing that also two triple bonds could be directly converted to the *Z*-alkenylboronate ester (Table 2).

Surprisingly, when aliphatic alkynes were hydroborated the *E*/*Z* ratio was reversed and stereoselectively *E*-alkenylboronate esters were formed in very good yields. (Table 2, **5u**-**5x**). Higher reaction temperature of 70 °C was required. Alkynes bearing nitro- and hydroxy groups could not be converted to the alkenylboronate esters **5y** and **5z** (Table 2). Finally, it has to be also noted that internal alkynes were not hydroborated (Table 2, **5aa**).

Moreover, we showed that the obtained borylated products can be used as substrates for the stereochemically controlled synthesis of disubstituted olefins. For this purpose, the obtained solution of vinylboronate **5a** was applied without work-up in a Suzuki-Miyaura cross-coupling with 4-bromoanisole in the presence of 5 mol % of $Pd(PPh_3)_4$ (3 mol%) in the presence of Na_2CO_3 at 50 °C for 24 h which resulted in76% (*E*/*Z*: 9/91) of isolated product (Scheme 4).

Scheme 4 Synthetic Application of the Obtained Vinylboronates

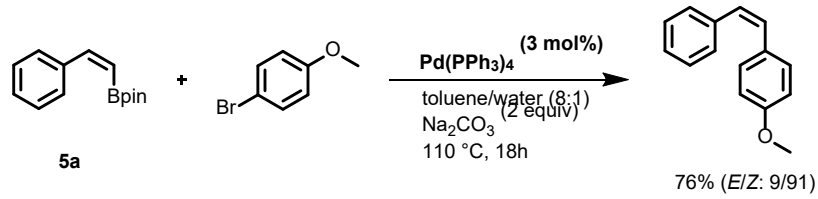
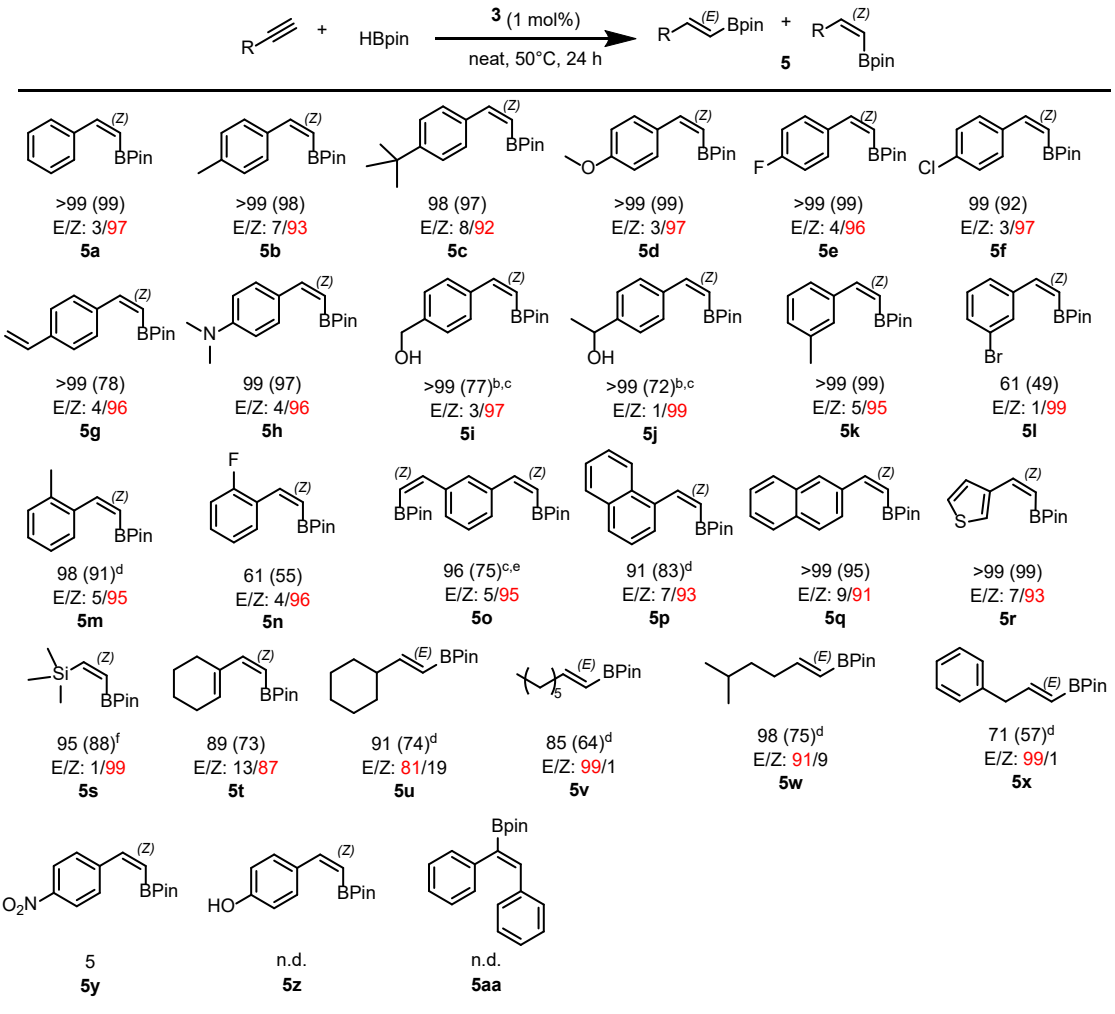


Table 2. Hydroboration of Various Terminal Alkynes Catalyzed by 3[a]

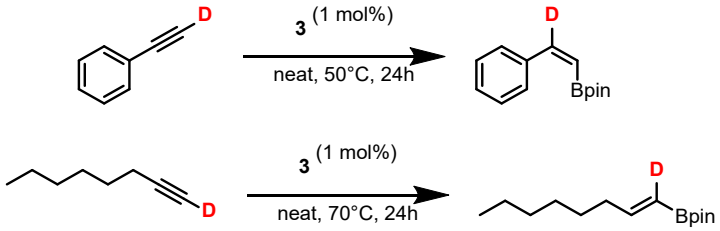


[a]Reaction conditions: Alkyne (0.50 mmol, 1 equiv), HBpin (0.55 mmol, 1.1 equiv), **3** (1 mol%), 50 °C, 24 h, conversion determined by GC-MS, *E*/*Z* ratio determined by ^{1}H NMR spectroscopy, isolated yield in parentheses. [b]**3** (1.5 mol%). [c]HBpin (1.05 mmol, 2.1 equiv). [d]70 °C. [e]**3** (2 mol%). [f]Conversion determined by ^{1}H NMR spectroscopy.

In order to get some mechanistic insights several experiments were carried out employing phenylacetylene as substrate under standard reaction conditions (Table 2). The homogeneity of the system was proven upon addition of one drop of Hg which did not lead to a loss of productivity. On the other hand, addition of 1 equiv of PMe_3 resulted in only 15% conversion. This indicates that the reaction proceeds *via* an inner-sphere reaction since PMe_3 blocks the vacant coordination site of the actual catalyst.

Furthermore, in order to gain a deeper understanding of the different stereoselectivities of aromatic and aliphatic alkynes, phenylacetylene-d_1 and octyne-d_1 were used as substrates (Scheme 5). In the case of phenylacetylene-d_1, upon hydroboration the deuterium ended up exclusively at the benzylic position indicating that C-D bond cleavage is taken place in the course of the reaction. In contrast, with octyne-d_1 no deuterium migration occurred. These findings reveal that two diverging reaction pathways depending on the acidity of the C-H bond of the alkyne can occur.

Scheme 5. Hydroboration of Deuterated Alkynes Catalyzed by 3[a]



[a]Reaction conditions: alkyne (0.25 mmol, 1 equiv), HBpin (0.28 mmol, 1.1 equiv), 2 (1 mol%), 50 - 70°C, 24 h, position of deuterium determined by ^{2}H-NMR spectroscopy.

The stereo- and regioselective hydroboration of terminal alkynes catalyzed by **3** ($\mathbf{A}^{\mathbf{C}}$ in the calculations) was investigated by DFT calculations[21] using HC≡CPh and HC≡CCH_3 as model substrates aiming plausible mechanisms that corroborate the experimental results discussed above. The detailed free energy profiles obtained are provided in the SI (Figures S3-S8) while simplified catalytic cycles are depicted in Schemes 6 and 7 with only key intermediates shown.

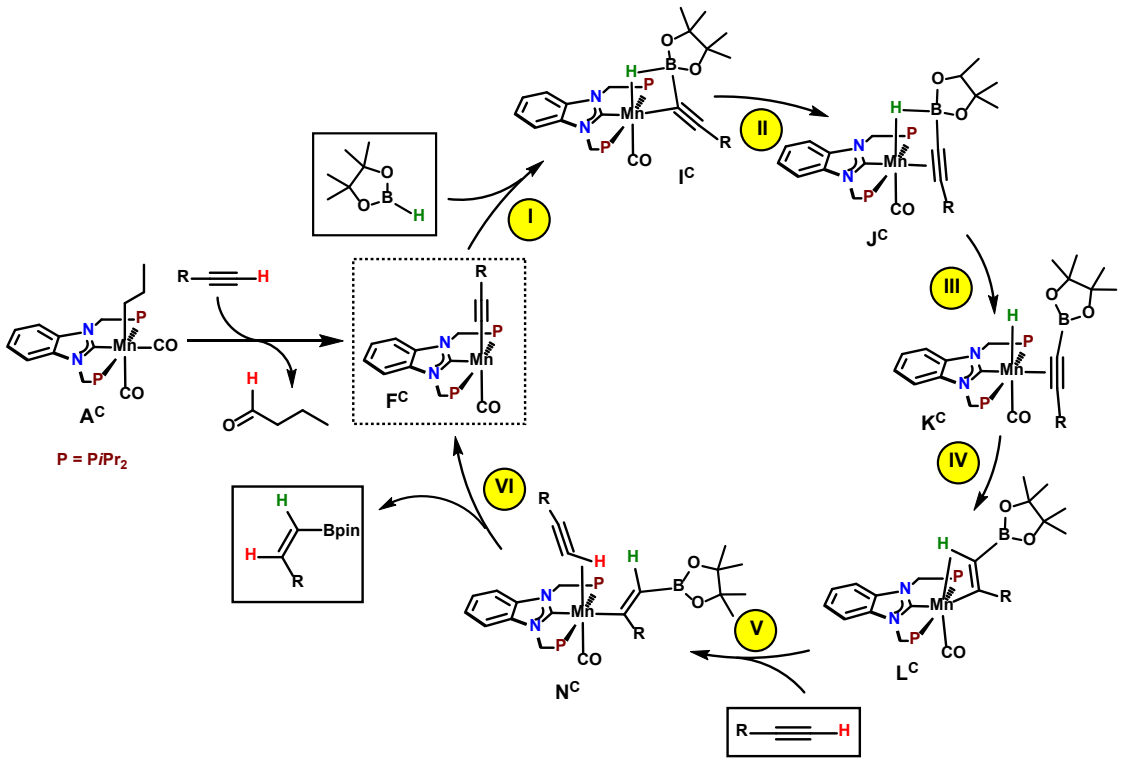
The experimental data suggest clearly that the hydroboration takes place via two different mechanisms depending on the substituents on the carbon-carbon triple bond, i.e., aromatic versus aliphatic groups. It has to be noted that the acidity of the terminal C-H bond of aromatic and aliphatic alkynes is different (pK_a (aromatic) ≈ 23, pK_a (aliphatic) ≈ 25).[22] Accordingly, the order of C-H and B-H bond activation steps of alkyne and HBpin, respectively, in the catalytic cycles may be the decisive factor as selectivity control is concerned.

For the formation of *Z*-alkenylboronate esters from aromatic alkynes, catalyst initiation starts with migratory insertion of the propyl ligand into a Mn-CO bond, in $\mathbf{A}^{\mathbf{C}}$, to form an acyl species stabilized by an agostic C-H bond. This was reported previously for *fac*-[Mn(dippe)$(CO)_3(CH_2CH_2CH_3)$].[23] Addition of HC≡CPh followed by activation of the terminal C-H bond gives the 16e acetylide catalyst [Mn(PCP-*i*Pr)(CO)(C≡CPh)] ($\mathbf{F}^{\mathbf{C}}$) together with liberated butanal (hydroborated under these conditions) (see SI Figure S3). The highest barrier for the C-H bond activation and cleavage process is 27.8 kcal/mol corresponding to HC≡CPh coordination ($\mathbf{TS}^{\mathbf{C}}_{\mathbf{CD}}$, in Figure S3). For comparison, the equivalent barrier for the same process with HC≡CCH_3 is somewhat higher, $\Delta G^{\ddagger}$ = 30.8 kcal/mol, in agreement with the less acidic C-H bond as compared to HC≡CPh (see SI Figure S4).

Addition of HBPin to $\mathbf{F}^{\mathbf{C}}$ results in the formation of intermediate $\mathbf{I}^{\mathbf{C}}$ where both new B-C and Mn-H bonds are formed while the B-H bond remains almost intact. An η^1 to η^2 rearrangement of the alkyne moiety leads to $\mathbf{J}^{\mathbf{C}}$. This corresponds to steps **I** and **II** in the cycle of Scheme 6 (see SI Figure S5). The

highest barrier along the path is $\Delta G^{\ddagger}$ = 8.7 kcal/mol measured from intermediate $\mathbf{F^C}$ to $\mathbf{TS^C_{HI}}$ corresponding to the addition of HBPin to the metallic moiety. The reaction from $\mathbf{J^C}$ to $\mathbf{K^C}$ proceeds with B-H bond cleavage forming a metal-hydride and an η^2-coordinated alkyne in a facile process requiring merely 2.9 kcal/mol ($\mathbf{TS^C_{JK}}$ in Figure S6). Insertion of the C-C triple bond into the Mn-H bond of $\mathbf{K^C}$ affords the vinylboryl species $\mathbf{L^C}$ featuring a stabilizing agostic C-H bond. Addition of another HC≡CPh molecule to $\mathbf{L^C}$ leads to intermediate $\mathbf{M^C}$ and to the final step in the mechanism with protonation of the vinylboryl ligand and release of the final product, the respective *Z*-alkenylboronate ester. The acetylide ligand is regenerated to form $\mathbf{O^C}$. The barrier associated to this process from $\mathbf{M^C}$ via the alkyne complex $\mathbf{N^C}$ to the acetylide complex with the *Z*-alkenylboronate ester $\mathbf{O^C}$ is $\Delta G^{\ddagger}$ = 12.2 kcal/mol ($\mathbf{TS^C_{NO}}$) and the step is clearly favorable from the thermodynamic point of view with ΔG = –13.8 kcal/mol (corresponding to steps **V** and **VI** in the cycle of Scheme 6, see SI Figure S6). Liberation of the coordinated *Z*-alkenylboronate ester closes the catalytic cycle reforming thereby $\mathbf{F^C}$, with a favorable free energy balance of ΔG = –1.2 kcal/mol and an overall barrier for the catalytic cycle of $\Delta G^{\ddagger}$ = 12.2 kcal/mol, measured from the vinyl intermediate with HC≡CPh, $\mathbf{M^C}$, to the transition state for vinyl protonation and formation of the product $\mathbf{TS^C_{NO}}$.

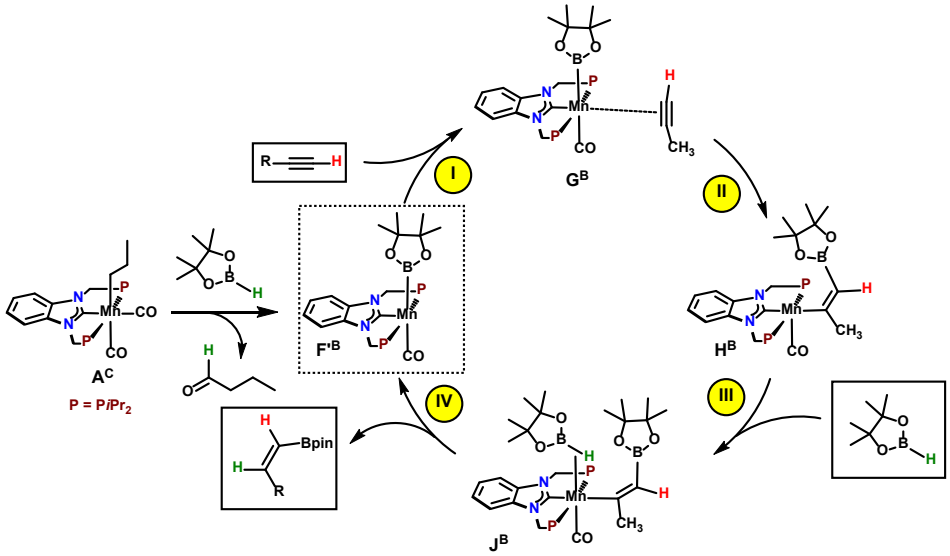
Scheme 6. Simplified Catalytic Cycle for the Hydroboration of Terminal Alkynes (Initiation by C-H Activation)



As the formation of *E*-alkenylboronate esters from aliphatic alkynes is concerned, catalyst initiation also starts from subsequent to migratory insertion of the propyl ligand into a Mn-CO bond $\mathbf{A^C}$ to afford $\mathbf{B^C}$ (see SI, Figure S7). Addition of HBPin to $\mathbf{B^C}$ leads, via intermediate $\mathbf{C^B}$, to the formation of acyl species $\mathbf{D^B}$ which subsequently, upon rotation of the acyl moiety about the Mn-C bond by ca. 80°, affords $\mathbf{E^B}$. Both $\mathbf{D^B}$ and $\mathbf{E^B}$ contain a κ^2-*B,H*-bound HBpin ligand. In $\mathbf{E^B}$, the HBpin ligand undergoes B-H bond cleavage accompanied by protonation of the acyl moiety to afford the boryl catalyst [Mn(PCP-*i*Pr)(CO)(Bpin)] ($\mathbf{F^B}$ as butanal adduct) that, upon addition of HC≡CCH$_3$ yields $\mathbf{G^B}$ together

with liberated butanal. The overall barrier for these steps, i.e. alkyl migration and B-H bond activation and cleavage, is 26.7 kcal/mol measured from the free reactants, HBPin and $\mathbf{A}^{C}$, to $\mathbf{TS}^{B}_{AB}$, the transition state for HBPin κ^2-coordination. For comparison, C-H bond activation of $HC{\equiv}CCH_3$ to form the putative acetylide species [Mn(PCP-*i*Pr)(CO)(C≡CCH_3)] requires a barrier of 30.8 kcal/mol which is 6.6 kcal/mol higher than the barrier for the formation of $\mathbf{F}^{B}$ via H-B bond cleavage (see SI Figures S4 and S7). Facile insertion of $HC{\equiv}CCH_3$ into the Mn-B bond affords the vinylboryl intermediate $\mathbf{H}^{B}$ (**II** in Scheme 7) in an almost barrierless ($\Delta G^{\ddagger}$ = 0.3 kcal/mol) and clearly favorable step (ΔG = –44.1 kcal/mol). Addition of HBpin to $\mathbf{H}^{B}$ leads to $\mathbf{I}^{B}$ and, then, to $\mathbf{J}^{B}$, a B-H κ^2-complex from which protonation of the vinylboryl ligand forms intermediate $\mathbf{K}^{B}$ with loosely bound *E*-alkenylboronate ester, the final product (see Figure S8). The previous process from $\mathbf{H}^{B}$ to $\mathbf{K}^{B}$, corresponds to steps **III** and **IV** in the cycle of Scheme 7. It is practically thermoneutral (ΔG = 0.5 kcal/mol) and has a barrier of $\Delta G^{\ddagger}$ = 22.7 kcal/mol (measured from $\mathbf{H}^{B}$ to $\mathbf{TS}^{B}_{JK}$) that is also the overall barrier of the catalytic cycle. Closing the cycle with liberation of the product, the *E*-alkenylboronate ester and regenerating $\mathbf{G}^{B}$, the boryl intermediate (plus a $HC{\equiv}CCH_3$ molecule) has a free energy balance of 5.6 kcal/mol.

Scheme 7. Simplified Catalytic Cycle for the Hydroboration of Terminal Alkynes (Initiation by B-H Activation)



Conclusion

In conclusion, the bench-stable alkyl Mn(I) complex *fac*-[Mn(PCP-*i*Pr)(CO)$_2$($CH_2CH_2CH_3$)] turned out to be an efficient catalyst for the additive-free stereo- and regioselective hydroboration of terminal alkynes with HBPin. Hydroboration takes place with a catalyst loading of 1 mol % at 50 – 70 °C with a high *Z*-selectivity in the case of aryl alkynes and essentially *E*-selectivity in the case of aliphatic alkynes. The catalytic process is initiated by migratory insertion of a CO ligand into the Mn-alkyl bond to yield an acyl intermediate which undergoes C-H activation of the terminal alkyne in the case of aromatic alkynes and B-H bond cleavage of HBPin for aliphatic alkynes. Thereby, the catalytically active 16e$^-$ Mn(I) acetylide and boryl species [Mn(PCP-*i*Pr)(CO)(C≡CR)] and [Mn(PCP-*i*Pr)(CO)(BPin)], respectively, are formed. A broad variety of aromatic and aliphatic alkynes were efficiently and selectively borylated. Mechanistic insights are provided based on experimental and computational studies. The functionalized alkenes can be used for further applications which has been demonstrated for a Suzuki-Miyaura cross-coupling reaction.

AUTHOR INFORMATION

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:
X-ray crystallographic data for ·**3** and **4** (CCDC 2308703 and 2308704). (CIF)
Synthetic procedures, ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{H\}$ NMR spectra of all compounds, crystallographic data and complete computational details (PDF) and corresponding references.
Cartesian coordinates for DFT-optimized structures (XYZ)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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References

(1) (a) Miyaura, N.; Yamada, K.; Suzuki, A. A New Stereospecific Cross-Coupling by the Palladium-Catalyzed Reaction of 1-Alkenylboranes with 1-Alkenyl or 1-Alkynyl Halides. *Tetrahedron Lett.* **1979**, *20*, 3437–3440. (b) Suzuki, A.; Miyaura, N. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. *Chem. Rev.* **1995**, *95*, 2457–2483. (c) Martin, R.; Buchwald, S. L. Palladium-Catalyzed Suzuki− Miyaura Cross-Coupling Reactions Employing Dialkylbiaryl Phosphine Ligands. *Acc. Chem. Res.* **2008**, *41*, 1461–1473. (d) Hooshmand, S. E.; Heidari, B.; Sedghi, R.; Varma, R. S. Recent Advances in the Suzuki–Miyaura Cross-Coupling Reaction Using Efficient Catalysts in Eco-Friendly Media. *Green Chem.* **2019**, *21*, 381–405.

(2) (a) Brown, H.; Rao, B. C. Communications-Hydroboration of Olefins. A Remarkably Fast Room-Temperature Addition of Diborane to Olefins. *J. Org. Chem.* **1957**, *22*, 1136–1137. (b) Brown, H. C.; Zweifel, G. Hydroboration. IX. The Hydroboration of Cyclic and Bicyclic Olefins—Stereochemistry of the Hydroboration Reaction. *J. Am. Chem. Soc.* **1961**, *83*, 2544–2551.

(3) Vogels, C. M.; Westcott, S. A. Recent Advances in Organic Synthesis Using Transition Metal-Catalyzed Hydroborations. *Curr. Org. Chem.* **2005**, *9*, 687–699.

(4) (a) Metal-Catalyzed Hydroboration Reactions. In: Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, 1998 (b) Contemporary Boron Chemistry (Eds.: M. G. Wade, K. Marder, A. K. Hughes), Royal Society of Chemistry, Cambridge, 2000.

(5) For selected examples for Rh-catalyzed hydroboration reactions see: (a) Kono, H.; Ito, K.; Nagai, Y. Oxidative Addition of 4,4,6-Trimethyl-1,3,2-Dioxaborinane and Benzo[1,3,2]Dioxaborole to Tris(Triphenylphosphine)Halogenorhodium. *Chem. Lett.* **1975**, *4*, 1095–1096 (b) Brown, J. M.; Hulmes, D. I.; Layzell, T. P. Effective Asymmetric Hydroboration Catalysed by a Rhodium Complex of 1-(2-Diphenylphosphino-1-Naphthyl) Isoquinoline. *J. Chem. Soc., Chem. Commun.* **1993**, 1673–1674. (c) Smith, J. R.; Collins, B. S. L.; Hesse, M. J.; Graham, M. A.; Myers, E. L.; Aggarwal, V. K. Enantioselective Rhodium(III)-Catalyzed Markovnikov Hydroboration of Unactivated Terminal Alkenes. *J. Am. Chem. Soc.* **2017**, *139*, 9148–9151.

(6) For selected examples for Ir-catalyzed hydroboration reactions see: (a) Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. Reactions of Catecholborane with Iridium Complexes: Molecular Structure of *Trans*-IrHCl(CO)(Bcat)$(PPh_3)_2$. *Can. J. Chem.* **1993**, *71*, 930–936. (b) Iverson, C. N.; Smith, M. R. Stoichiometric and Catalytic B− C Bond Formation from Unactivated Hydrocarbons and Boranes. *J. Am. Chem. Soc.* **1999**, *121*, 7696–7697. (c) Ohmura, T.; Yamamoto, Y.; Miyaura, N. Rhodium- or Iridium-Catalyzed Trans-Hydroboration of Terminal Alkynes, Giving (Z)-1-Alkenylboron Compounds. *J. Am. Chem. Soc.* **2000**, *122*, 4990–4991. (d) Wang, G.; Liang, X.; Chen, L.; Gao, Q.; Wang, J.; Zhang, P.; Peng, Q.; Xu, S. Iridium-Catalyzed Distal Hydroboration of Aliphatic Internal Alkenes. *Angew. Chem. Int. Ed.* **2019**, *58*, 8187–8191.

(7) For selected examples for Cu-catalyzed hydroboration see: (a) Kerchner, H. A.; Montgomery, J. Synthesis of Secondary and Tertiary Alkylboranes via Formal Hydroboration of Terminal and 1,1-Disubstituted Alkenes. *Org. Lett.* **2016**, *18*, 5760–5763. (b) Iwamoto, H.; Kubota, K.; Ito, H. Highly Selective Markovnikov Hydroboration of Alkyl-Substituted Terminal Alkenes with a Phosphine–Copper (i) Catalyst. *Chem. Commun.* **2016**, *52*, 5916–5919. (c) Xi, Y.; Su, B.; Qi, X.; Pedram, S.; Liu, P.; Hartwig, J. F. Application of Trimethylgermanyl-Substituted Bisphosphine Ligands with Enhanced Dispersion Interactions to Copper-Catalyzed Hydroboration of Disubstituted Alkenes. *J. Am. Chem. Soc.* **2020**, *142*, 18213–18222.

(8) For selected examples for Ni-catalyzed hydroboration reactions see: (a) Pereira, S.; Srebnik, M. A Study of Hydroboration of Alkenes and Alkynes with Pinacolborane Catalyzed by Transition Metals. *Tetrahedron Lett.* **1996**, *37*, 3283–3286 (b) Touney, E. E.; Van Hoveln, R.; Buttke, C. T.; Freidberg, M. D.; Guzei, I. A.; Schomaker, J. M. Heteroleptic Nickel Complexes for the Markovnikov-Selective Hydroboration of Styrenes. *Organometallics* **2016**, *35*, 3436–3439; c) Li, J. F.; Wei, Z. Z.; Wang, Y. Q.; Ye, M. Base-Free Nickel-Catalyzed Hydroboration of Simple Alkenes with Bis(Pinacolato)Diboron in an Alcoholic Solvent. *Green Chem.* **2017**, *19*, 4498–4502 (d) Ulm, F.; Cornaton, Y.; Djukic, J.; Chetcuti, M. J.; Ritleng, V. Hydroboration of Alkenes Catalysed by a Nickel N-heterocyclic Carbene Complex: Reaction and Mechanistic Aspects. *Chem. Eur. J.* **2020**, *26*, 8916–8925.

(9) For selected examples for Co-catalyzed hydroboration reactions see: (a) Zhang, L.; Zuo, Z.; Leng, X.; Huang, Z. A Cobalt-Catalyzed Alkene Hydroboration with Pinacolborane. *Angew. Chem. Int. Ed.* **2014**, *53*, 2696–2700. (b) Tamang, S. R.; Bedi, D.; Shafiei-Haghighi, S.; Smith, C. R.; Crawford, C.; Findlater, M. Cobalt-Catalyzed Hydroboration of Alkenes, Aldehydes, and Ketones. *Org. Lett.*

2018, *20*, 6695–6700. (c) Léonard, N. G.; Palmer, W. N.; Friedfeld, M. R.; Bezdek, M. J.; Chirik, P. J. Remote, Diastereoselective Cobalt-Catalyzed Alkene Isomerization–Hydroboration: Access to Stereodefined 1, 3-Difunctionalized Indanes. *ACS Catal.* **2019**, *9*, 9034–9044. (d) Chen, C.; Wang, H.; Li, T.; Lu, D.; Li, J.; Zhang, X.; Hong, X.; Lu, Z. Cobalt-Catalyzed Asymmetric Sequential Hydroboration/Isomerization/Hydroboration of 2-Aryl Vinylcyclopropanes. *Angew. Chem., Int. Ed.* **2022**, *134*, e202205619.

(10) For selected examples for Fe-catalyzed hydroboration reactions see: (a) Tseng, K.-N. T.; Kampf, J. W.; Szymczak, N. K. Regulation of Iron-Catalyzed Olefin Hydroboration by Ligand Modifications at a Remote Site. *ACS Catal.* **2015**, *5*, 411–415. (b) MacNair, A. J.; Millet, C. R. P.; Nichol, G. S.; Ironmonger, A.; Thomas, S. P. Markovnikov-Selective, Activator-Free Iron-Catalyzed Vinylarene Hydroboration. *ACS Catal.* **2016**, *6*, 7217–7221. (c) Espinal-Viguri, M.; Woof, C. R.; Webster, R. L. Iron-Catalyzed Hydroboration: Unlocking Reactivity through Ligand Modulation. *Chem. Eur. J.* **2016**, *22*, 11605–11608. (d) Gorgas, N.; Alves, L. G.; Stöger, B.; Martins, A. M.; Veiros, L. F.; Kirchner, K. Stable, Yet Highly Reactive Nonclassical Iron(II) Polyhydride Pincer Complexes: Z-Selective Dimerization and Hydroboration of Terminal Alkynes. *J. Am. Chem. Soc.* **2017**, *139*, 8130–8133.

(11) (a) Zhang, G.; Zeng, H.; Wu, J.; Yin, Z.; Zheng, S.; Fettinger, J. C. Highly Selective Hydroboration of Alkenes, Ketones and Aldehydes Catalyzed by a Well-Defined Manganese Complex. *Angew. Chem. Int. Ed.* **2016**, *55*, 14369–14372. (b) Vijjamarri, S.; O'Denius, T. M.; Yao, B.; Kubátová, A.; Du, G. Highly Selective Hydroboration of Carbonyls by a Manganese Catalyst: Insight into the Reaction Mechanism. *Organometallics* **2020**, *39*, 3375–3383.

(12) (a) Nguyen, T. T.; Kim, J. H.; Kim, S.; Oh, C.; Flores, M.; Groy, T. L.; Baik, M. H.; Trovitch, R. J. Scope and Mechanism of Nitrile Dihydroboration Mediated by a β-Diketiminate Manganese Hydride Catalyst. *Chem. Commun.* **2020**, *56*, 3959–3962. (b) Ghosh, P.; Jacobi von Wangelin, A. Manganese-Catalyzed Hydroborations with Broad Scope. *Angew. Chem., Int. Ed.* **2021**, *133*, 16171–16179. (c) Thenarukandiyil, R.; Satheesh, V.; Shimon, L. J. W.; de Ruiter, G. Hydroboration of Nitriles, Esters, and Carbonates Catalyzed by Simple Earth-Abundant Metal Triflate Salts. *Chem. Asian J.* **2021**, *16*, 999–1006.

(13) (a) Erken, C.; Kaithal, A.; Sen, S.; Weyhermüller, T.; Hölscher, M.; Werlé, C.; Leitner, W. Manganese-Catalyzed Hydroboration of Carbon Dioxide and Other Challenging Carbonyl Groups. *Nat. Commun.* **2018**, *9*, 4521. (b) Kostera, S.; Peruzzini, M.; Kirchner, K.; Gonsalvi, L. Mild and Selective Carbon Dioxide Hydroboration to Methoxyboranes Catalyzed by Mn (I) PNP Pincer Complexes. *ChemCatChem* **2020**, *12*, 4625–4631. (c) Kostera, S.; Weber, S.; Blaha, I.; Peruzzini, M.; Kirchner, K.; Gonsalvi, L. Base- and Additive-Free Carbon Dioxide Hydroboration to Methoxyboranes Catalyzed by Non-Pincer-Type Mn(I) Complexes. *ACS Catal.* **2023**, *13*, 5236–5244.

(14) (a) Carney, J. R.; Dillon, B. R.; Campbell, L.; Thomas, S. P. Manganese-Catalyzed Hydrofunctionalization of Alkenes. *Angew. Chem., Int. Ed.* **2018**, *57*, 10620–10624. (b) Weber, S.; Stöger, B.; Veiros, L. F.; Kirchner, K. Rethinking Basic Concepts—Hydrogenation of Alkenes Catalyzed by Bench-Stable Alkyl Mn(I) Complexes. *ACS Catal.* **2019**, *9*, 9715–9720. (c) Garhwal, S.; Kroeger, A. A.; Thenarukandiyil, R.; Fridman, N.; Karton, A.; De Ruiter, G. Manganese-Catalyzed Hydroboration of Terminal Olefins and Metal-Dependent Selectivity in Internal Olefin Isomerization–Hydroboration. *Inorg. Chem.* **2020**, *60*, 494–504.

(15) Brzozowska, A.; Zubar, V.; Ganardi, R.-C.; Rueping, M. Chemoselective Hydroboration of Propargylic Alcohols and Amines Using a Manganese(II) Catalyst. *Org. Lett.* **2020**, *22*, 3765–3769.

(16) Weber, S.; Zobernig, D.; Stöger, B.; Veiros, L. F.; Kirchner, K. Hydroboration of Terminal Alkenes and Trans-1,2-Diboration of Terminal Alkynes Catalyzed by a Manganese(I) Alkyl Complex. *Angew. Chem. Int. Ed.* **2021**, *60*, 24488–24492.

(17) Weber, S.; Kirchner, K. Manganese Alkyl Carbonyl Complexes: From Iconic Stoichiometric Textbook Reactions to Catalytic Applications. *Acc. Chem. Res.* **2022**, *55*, 2740–2751.

(18) Ahuja, H.; Kaur, H.; Arevalo, R. Chemoselective C(sp)–H borylation of terminal alkynes catalyzed by a bis(Nheterocyclicsilylene) manganese complex, *Inorg. Chem. Front.* **2023**, *10*, 6067–6076.

(19) Arroyo, V. D.; Arevalo, R. Tandem manganese catalysis for the chemo-, regio-, and stereoselective hydroboration of terminal alkynes: in situ precatalyst activation as a key to enhanced chemoselectivity *RSC Adv.* **2024**, *14*, 5514-5523.

(20) Zobernig, D. P.; Luxner, M.; Stöger, B.; Veiros, L. F.; Kirchner, K. Hydrogenation of Terminal Alkenes Catalyzed by Air-Stable Mn(I) Complexes Bearing an N-Heterocyclic Carbene-Based PCP Pincer Ligand. *Chem. Eur. J.* **2024**, *30*, e202302455.

(21) (a) Parr, R. G.; Yang, W. Density Functional Theory of Atoms and Molecules; Oxford University Press: New York, **1989**. (b) Free energy values were obtained at the PBE0-D3/6-311++G(d,p)//PBE0/(SDD,6-31G(d,p)) level using the Gaussian 09 package. A full account of the computational details and a complete list of references are provided as SI.

(22) Streitwieser, Jr., A., Reuben, D. E. Acidity of Hydrocarbons. XXXV. Equilibrium Acidities of Phenylacetylene and *tert*-Butylacetylene in Cyclohexylamine *J. Am. Chem. Soc.* **1971**, *93*, 1971-1975.

(23) (a) Weber, S.; Stöger, B.; Veiros, L. F.; Kirchner, K. Rethinking Basic Concepts - Hydrogenation of Alkenes Catalyzed by Bench-Stable Alkyl Mn(I) Complexes. *ACS Catal.* **2019**, *9*, 9715-9720. (b) Weber, S.; Glavic, M.; Stöger, B.; Pittenauer, E.; Podewitz, M.; Veiros, L. F.; Kirchner, K. Manganese-Catalyzed Dehydrogenative Silylation of Alkenes Following two Parallel Inner-Sphere Pathways. *J. Am. Chem. Soc.* **2021**, *143*, 17825-17832. (c) Weber, S.; Veiros, L. F.; Kirchner, K. Selective Manganese-Catalyzed Dimerization and Cross Coupling of Terminal Alkynes. *ACS Catal.* **2021**, *11*, 6474-6483. (d) Weber, S.; Veiros, L. F.; Kirchner, K. Old Concepts, New Application: Additive-free Hydrogenation of Nitriles Catalyzed by a Bench-Stable Alkyl Mn(I) Complex, *Adv. Synth. Catal.* **2019**, *361*, 5412-5420. (e) Weber, S.; Brünig, J.; Veiros, L. F.; Kirchner, K. Manganese-Catalyzed Hydrogenation of Ketones under Mild and Base-free Conditions *Organometallics* **2021**, *40*, 1388-1394.