THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Hidden Boron Catalysis: Nucleophile-Promoted Decomposition of HBpin

Citation for published version:

Bage, AD, Hunt, TA & Thomas, SP 2020, 'Hidden Boron Catalysis: Nucleophile-Promoted Decomposition of HBpin', *Organic letters*. <https://doi.org/10.1021/acs.orglett.0c01168>

Digital Object Identifier (DOI):

[10.1021/acs.orglett.0c01168](https://doi.org/10.1021/acs.orglett.0c01168)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Organic letters

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

Hidden Boron Catalysis: Nucleophile-Promoted Decomposition of HBpin

Andrew D. Bage,[§] Thomas A. Hunt[‡] and Stephen P. Thomas^{*§}

[§]EaStCHEM School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh, EH9 3FJ, United Kingdom.

[‡]Medicinal Chemistry, Early Oncology, AstraZeneca, Unit 310, Cambridge Science Park, Milton Road, Cambridge, CB4 0WG, United Kingdom.

Supporting Information

ABSTRACT: Simple nucleophiles, with structural similarities to known hydroboration catalysts, can readily mediate the formation of BH₃ and borohydride species from pinacolborane (HBpin). Alkyne and alkene hydroboration reactions were successfully mediated by nucleophiles through BH₃ generation, with BH₃-catalyzed hydroboration found to dominate catalysis. NMR spectroscopy and kinetic analyses showed that the nucleophiles NaO^tBu, Na[N(SiMe₃)₂], ⁿBu₂Mg and ⁿBuLi only promoted the formation of BH₃ and were not ‘true’ hydroboration catalysts.

The need for sustainable catalysis has necessitated the development of a wide range of first-row transition metal and main-group complexes for catalysis with the hydroboration of carbonyls, imines, alkynes and alkenes with pinacolborane (HBpin) or catecholborane (HBcat) acting as an exemplar reaction.¹⁻⁴ However, the formation of BH₃ has been observed in metal-catalyzed hydroborations with HBcat, where hydroboration by BH₃ competed with the metal-catalyzed reaction.

In rhodium-catalyzed alkene hydroboration reactions with HBcat, the phosphine ligand of the catalyst was found to initiate the decomposition of HBcat to BH₃ (Scheme 1A).⁵⁻⁸ In other cases, the ‘catalysts’ were proposed to only mediate the decomposition of HBcat to BH₃.⁹⁻¹² BH₃ has been used to catalyze the hydroboration of alkynes with HBcat,¹³ and alkynes and alkenes with HBpin (Scheme 1B).¹⁴ Whilst the nucleophile-promoted formation of BH₃ from HBcat has received significant attention and is routinely controlled for,⁶⁻¹² the formation of BH₃ from HBpin is not. The inherent differences in stability of HBcat and HBpin prevents the extrapolation of HBcat decomposition to HBpin and very rarely have control reactions been performed for BH₃ when using HBpin.¹⁵ As the majority of new catalytic hydroboration systems contain nucleophilic motifs, it is necessary to exclude nucleophile-promoted BH₃ formation from ‘true’ catalysis by the metal/metalloid species. The nucleophilic motifs can be separated into three classes: pre-catalyst activators,¹⁵⁻²² sacrificial ligands²³⁻²⁵ and inherent nucleophilic catalysts (Scheme 1C).²⁶⁻³¹ To distinguish between ‘true’ catalysis and BH₃ catalysis for reactions using HBpin it was necessary to:

1. Identify nucleophile-promoted BH₃ formation.
2. Determine if BH₃ forms under catalysis conditions.
3. Compare the rate of reaction to that of BH₃ catalysis.

Scheme 1. The Roles of Nucleophiles and BH₃ in Hydroboration Catalysis

A. Phosphine-promoted Decomposition of HBcat

B. BH₃-catalyzed Hydroboration

C. Types of Nucleophilic Catalysis used for Hydroboration

D. This work: Identifying Hidden BH₃ Catalysis

We began by screening nucleophiles with similar motifs to known hydroboration systems to determine their ability to mediate the decomposition of HBpin to BH₃ (Table 1). Ti(OⁱPr)₄ was used by Burgess to question the veracity of the Ti-catalyzed hydroboration of alkenes with HBcat.¹¹ Reaction of Ti(OⁱPr)₄ with HBpin gave 0.30 M BH₃ as observed by ¹¹B NMR spectroscopy (Entry 1). Sodium and potassium *tert*-butoxide have been shown to form BH₃ when mixed with HBpin and have been used as activators in hydroboration catalysis.¹⁵⁻¹⁸ All metal alkoxides gave similar amounts of BH₃ formation (Entries 2-4).

Organolithium and Grignard reagents have been used as pre-catalyst activators.¹⁹⁻²⁰ Reaction of MeLi and MeMgBr with HBpin both showed formation of BH₃ (Entries 5 and 6). Likewise, NaHBEt₃ has been used as an activator and was observed to promote BH₃ formation (Entry 7).²¹⁻²² Alkoxides, amides, NaOH, ⁿBu₂Mg, ⁿBuLi and LiAlH₄ have all been proposed to be active hydroboration catalysts²⁶⁻³¹ or used as sacrificial ligands.²³⁻²⁵ All promoted BH₃ formation (Entries 8-13). [BH₃] was shown to remain constant after 2 hours by using ⁿBuLi as an exemplar (SI, Table S1). Only NaOTf did not form BH₃ (Entry 15).

Table 1. Quantifying BH₃ Formation from the Reaction of Nucleophiles with HBpin

$\text{H-Bpin} \xrightarrow[\text{Ar atm.}]{\text{Nucleophile (0.50 M), Toluene, SMe}_2, 60^\circ\text{C, 20 min.}} \text{BH}_3$		
Entry	Nucleophile / Catalyst	[BH ₃] (M)
1	Ti(O ⁱ Pr) ₄	0.30
2	KO ⁱ Bu	0.02
3	NaO ⁱ Bu	0.02
4	LiO ⁱ Bu	0.03
5	MeLi	0.02
6	MeMgBr	0.01
7	NaHBEt ₃	0.03
8	Na[N(SiMe ₃) ₂]	0.02
9	LDA	0.06
10	NaOH	0.01
11	ⁿ Bu ₂ Mg	0.07
12	ⁿ BuLi	0.04
13	LiAlH ₄	0.18
14	LiBH ₄	0.01
15	NaOTf	0.00

Conditions: Nucleophile (0.12 mmol, 0.50 M), HBpin (1.8 mmol, 7.5 M), SMe₂ (0.12 mmol), toluene (0.24 mL), 60 °C, 20 min. Conversion determined by ¹¹B NMR spectroscopy.

Whilst an extensive range of nucleophiles reacted with HBpin to give BH₃, their ability to form sufficient amounts to catalyze a hydroboration reaction required confirmation. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) **3** forms air- and moisture stable mono- and bis-adducts with BH₃,³² so would serve as a BH₃ indicator; the adducts were observable by ¹¹B NMR spectroscopy even after work-up. The H₃B·SMe₂-catalyzed (10 mol%) hydroboration of phenylacetylene **1** gave the alkenylboronic ester **2** in 94% yield (Table 2, Entry 1, left). The addition of TMEDA **3** (10 mol%) significantly inhibited hydroboration (Entry 1, right). The H₃B·TMEDA adducts were poor catalysts for the hydroboration at 60 °C, compared to H₃B·SMe₂ (SI, Table S2). Control experiments showed no interaction between TMEDA **3** and HBpin at 60 °C (see SI). Nine nucleophiles were found to mediate the hydroboration of phenylacetylene **1** with HBpin (Entries 2-10). In all cases TMEDA **3** was found to effectively inhibit alkyne hydroboration and H₃B·TMEDA was observed by ¹¹B NMR spectroscopy in all cases.

Table 2. Inhibition of Alkyne Hydroboration by TMEDA

$\text{Ph-C}\equiv\text{C-H} + \text{H-Bpin} \xrightarrow[\text{Ar atm.}]{\text{Nucleophile (10 mol%), 60 }^\circ\text{C, 4 h}} \text{Ph-CH=CH-Bpin}$			
Entry	Nucleophile / Catalyst	2 (%)	
		No TMEDA 3 (0 mol%)	+ TMEDA 3 (10 mol%) ^a
1	H ₃ B·SMe ₂	94	10
2	NaHBEt ₃	61	3 ^b
3	LiAlH ₄	51	3
4	NaOH	41	1
5	NaO ⁱ Bu	59 ^c	1 ^c
6	Na[N(SiMe ₃) ₂]	29	0
7	MeMgBr	60	1
8	ⁿ BuLi	53	1 ^d
9	Ti(O ⁱ Pr) ₄	51	5 ^d
10	ⁿ Bu ₂ Mg	81	11 ^d

Conditions: **1** (1.0 mmol), nucleophile (0.10 mmol), HBpin (1.5 mmol). Yields determined by ¹H NMR spectroscopy using an internal standard (1,3,5-trimethoxybenzene). ^aTMEDA **3** (0.10 mmol). ^bTMEDA (0.60 mmol). ^c18 hours. ^dTMEDA (0.30 mmol).

As the hydroboration of alkenes is also catalyzed by BH₃ (Table 3, Entry 1),¹⁴ the selected nucleophiles were tested in the hydroboration of *tert*-butylstyrene **4** with HBpin. Similar results were observed to those using phenylacetylene **1**. All nucleophiles efficiently promoted the hydroboration of *tert*-butylstyrene **4**, and hydroboration was inhibited by TMEDA **3** (Entries 2-10). H₃B·TMEDA was observed in all cases and, once again, the role of the nucleophile was to promote BH₃ formation.

Table 3. Inhibition of Alkene Hydroboration by TMEDA

$\text{tBu-C}_6\text{H}_4\text{-CH=CH}_2 + \text{H-Bpin} \xrightarrow[\text{Ar atm.}]{\text{Nucleophile (10 mol%), 60 }^\circ\text{C, 18 h}} \text{tBu-C}_6\text{H}_4\text{-CH}_2\text{-CH}_2\text{-Bpin}$			
Entry	Nucleophile / Catalyst	5 (%)	
		No TMEDA 3 (0 mol%)	+ TMEDA 3 (20 mol%) ^a
1	H ₃ B·SMe ₂	67	5
2	NaHBEt ₃	81	43
3	LiAlH ₄	81	5
4	NaOH	28	7
5	NaO ⁱ Bu	71	10
6	Na[N(SiMe ₃) ₂]	72	12
7	MeMgBr	55	21
8	ⁿ BuLi	30	26
9	Ti(O ⁱ Pr) ₄	73	10
10	ⁿ Bu ₂ Mg	85	22

Conditions: **4** (1.0 mmol), nucleophile (0.10 mmol), HBpin (1.5 mmol). Yields determined by ¹H NMR spectroscopy using an internal standard (1,3,5-trimethoxybenzene). ^aTMEDA **3** (0.20 mmol).

Figure 1. A. Calibration gradients of initial rates of reaction (v_0) plotted against $[BH_3]$ (M) for the hydroboration of **1 (left) and **4** (right). B. Comparison of the calculated and observed BH_3 concentrations.** Conditions: **1** or **4** (2.0 mmol, 5.0 M), nucleophile (0.20 mmol, 0.50 M, 10 mol%), HBpin (3.0 mmol, 7.5 M), SMe₂ (0.20 mmol, 0.50 M), toluene (0.40 mL), 60 °C, 20 min. prior to the addition of substrate **1** or **4** (then alkyne 1.5 h; alkene 22 h). Yields determined by ¹H NMR spectroscopy using an internal standard (1,3,5-trimethoxybenzene, 0.10 mmol).^a From Table 1. ^bEt₃B (0.09 M) and H₃B·SMe₂ (0.07 M).

The addition of TMEDA **3** to the hydroboration reactions clearly indicated that BH₃ was formed under reaction conditions. However, TMEDA **3** could also inhibit ‘true’ catalysis by coordination to the metal or by altering aggregation states.^{33–35} To distinguish ‘true’ catalysts from those which only decompose HBpin to BH₃, the rates of the BH₃-catalyzed hydroborations of alkynes and alkenes (v_0) were plotted against $[BH_3]$ loading to generate a calibration gradient (Figure 1A). The rates of the nucleophile-promoted hydroboration reactions were then measured and compared to this (Figure 1B). If the calculated BH₃ concentration ($[BH_3]_{calc}$) matched the observed BH₃ concentration ($[BH_3]_{obs}$, from Table 1), it would suggest that the nucleophiles were not active catalysts but simply promoting the decomposition of HBpin to BH₃. Direct comparison between Table 1 and Figure 1B was enabled by matching the reaction conditions and adding the substrate after 20 minutes; the same point at which $[BH_3]_{obs}$ was measured in Table 1.

NaO^tBu and Na[N(SiMe₃)₂] exhibited comparable $[BH_3]_{obs}$ and $[BH_3]_{calc}$ for both the alkyne and alkene hydroboration reactions (Figure 1B, Entries 2 and 3), suggesting these are not ‘true’ catalysts but promoters of HBpin decomposition to BH₃. For LiAlH₄, $[BH_3]_{calc}$ of alkyne hydroboration matched $[BH_3]_{obs}$, but

$[BH_3]_{calc}$ was higher than expected for alkenes (Entry 4). Presumably, AlH₃ is formed in this case,³⁶ introducing a complementary, additional, aluminum-catalyzed hydroboration.²⁶

When ⁿBu₂Mg was tested, $[BH_3]_{obs}$ was lower than $[BH_3]_{calc}$ (Entry 5) suggesting that ⁿBu₂Mg may be an active catalyst. However, ⁿBu₃B (0.09 M) was also observed by ¹¹B NMR spectroscopy. The sum of $[^nBu_3B]_{obs}$ and $[BH_3]_{obs}$ equaled $[BH_3]_{calc}$. Although trialkylboranes have not been reported to catalyze hydroboration reactions, they are known to redistribute to catalytically active dialkyl- and monoalkylboranes,^{37–38} e.g. ⁿBu₂BH and ⁿBuBH₂, in the presence of BH₃.³⁹ Hydroboration using Et₃B (10 mol%) was successful (Entry 7), presumably through redistribution with HBpin to form R_{3–n}BH_n species, albeit at a much lower rate than that using BH₃. Using a solution of BH₃ and Et₃B that mimicked the concentrations of BH₃ and ⁿBu₃B formed under catalysis conditions gave an equal rate of reaction to the ⁿBu₂Mg-mediated hydroboration of alkynes (Entry 8). Therefore, ⁿBu₂Mg is not a ‘true’ catalyst for the hydroboration of alkynes and alkenes but merely a nucleophile.

$[BH_3]_{obs}$ for ⁿBuLi was lower than $[BH_3]_{calc}$ and the hydroboration of alkynes had a higher $[BH_3]_{calc}$ compared to alkenes (Entry 6). Again, this suggested that ⁿBuLi was an active catalyst.

^{13}C NMR spectroscopy showed that $^n\text{BuLi}$ was fully consumed in the reaction of $^n\text{BuLi}$ with HBpin. Furthermore, LiBH_4 was observed by ^{11}B and ^7Li NMR spectroscopy and was the only lithium species present, inferring that the hydroboration reactions were not catalyzed by $^n\text{BuLi}$. $^n\text{BuH}_2\text{B}\cdot\text{SMe}_2$ was also observed by ^{11}B NMR spectroscopy, suggesting that $^n\text{Bu}_2\text{BH}$ and $^n\text{BuBH}_2$ were formed, along with $^n\text{Bu}_3\text{B}$. The difference between $[\text{BH}_3]_{\text{calc}}$ for alkynes and alkenes is presumably due to the different rates of hydroboration using mono- and dialkylboranes, and BH_3 (Entries 1 and 9).⁴⁰

Borane-catalyzed hydroboration is proposed to proceed by an initial hydroboration to give an alkenyl- or alkylborane intermediate which undergoes transborylation^{38,41} with HBpin to give the boronic ester product and regenerate the borane catalyst (Scheme 2).

Scheme 2. Proposed Borane-catalyzed Hydroboration Mechanism

Ketone hydroboration is often used as a basis to test new catalyst structures.²⁻⁴ However, Clark showed that ketone hydroboration with HBpin was mediated by NaO^tBu .¹⁷ Nucleophilic addition of NaO^tBu to HBpin gave a trialkoxyborohydride, which is known to reduce ketones.⁴² Borohydride addition to a ketone formally gives an alkoxide, which reacts with HBpin to form another trialkoxyborohydride, propagating the reaction. To confirm Clark's mechanism, and show its applicability to other nucleophiles, the hydroboration of acetophenone **6** was investigated. Whilst BH_3 would successfully mediate the hydroboration of acetophenone **6**, the yield was much lower than any of the nucleophile-mediated reactions (SI, Table S4). Therefore, nucleophile-mediated ketone hydroboration does not proceed by BH_3 catalysis. In the nucleophile-promoted decomposition reactions, borohydride species were observed in addition to BH_3 . Nucleophile-promoted decomposition of HBpin must proceed by the initial formation of a hydridic boron 'ate' species, from nucleophilic addition to HBpin (e.g. $[\text{NuHBpin}]^-$). Trialkoxyborohydride **8** (the product of hydride transfer to acetophenone) was prepared and shown to be an active catalyst for the hydroboration of acetophenone **6** (Scheme 3). This supports Clark's mechanism and demonstrates this mechanism is applicable to the other nucleophiles studied. It is possible that this mechanism is operative in the hydroboration of other carbonyl derivatives.

Scheme 3. Trialkoxyborohydride-Mediated Acetophenone Hydroboration

Conditions: **6** (1.0 mmol), **8** (0.20 M in THF, 0.040 mmol), HBpin (1.5 mmol). Yield determined by ^1H NMR spectroscopy using an internal standard (1,3,5-trimethoxybenzene, 0.10 mmol).

The hydroboration of alkynes, alkenes and ketones with HBpin can be effectively mediated by simple nucleophiles. The results suggest that the reactions proceed through nucleophile-promoted decomposition of HBpin. BH_3 and borohydride species are formed by decomposition and these are active catalysts for the hydroboration of alkynes and alkenes, and ketones, respectively. For carbanion-containing systems, the decomposition is more complex, forming multiple borane species, all of which are potentially active hydroboration catalysts. Any future hydroboration catalysts should be rigorously tested to confirm that the decomposition of HBpin does not occur, particularly non-enantioselective catalysts and those that exhibit the same regioselectivity as BH_3 -catalyzed hydroboration or borohydride reduction. The addition of TMEDA and ^{11}B NMR spectroscopy both offer means of observing R_3B ($\text{R} = \text{H}$, alkyl or alkenyl) in catalyzed hydroboration reactions. However, it should be noted that, even in BH_3 -catalyzed reactions, observation of these intermediates may be challenging as transborylation from R_3B to RBpin is fast and results in very low R_3B concentrations.

ASSOCIATED CONTENT

Supporting Information. General experimental information, experimental setup and procedures, reaction monitoring, NMR spectra and associated references. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*stephen.thomas@ed.ac.uk

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

SPT thanks the Royal Society for a University Research Fellowship. SPT and ADB thank AstraZeneca and the EPSRC for an iCASE award.

REFERENCES

- (1) Obligation, J. V.; Chirik, P. J. Earth-abundant transition metal catalysts for alkene hydrosilylation and hydroboration. *Nat. Rev. Chem.* **2018**, *2*, 15-34.
- (2) Chong, C. C.; Kinjo, R. Catalytic Hydroboration of Carbonyl Derivatives, Imines, and Carbon Dioxide. *ACS Catal.* **2015**, *5*, 3238-3259.
- (3) Hill, M. S.; Liptrot, D. J.; Weetman, C. Alkaline earths as main group reagents in molecular catalysis. *Chem. Soc. Rev.* **2016**, *45*, 972-988.
- (4) Shegavi, M. L.; Bose, S. K. Recent advances in the catalytic hydroboration of carbonyl compounds. *Catal. Sci. Technol.* **2019**, *9*, 3307-3336.
- (5) Männig, D.; Nöth, H. Catalytic Hydroboration with Rhodium Complexes. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 878-879.
- (6) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T. New homogeneous rhodium catalysts for the regioselective hydroboration of alkenes. *J. Am. Chem. Soc.* **1992**, *114*, 8863-8869.
- (7) Burgess, K.; Van der Donk, W. A.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. Reactions of catecholborane with Wilkinson's catalyst: implications for transition metal-catalyzed hydroborations of alkenes. *J. Am. Chem. Soc.* **1992**, *114*, 9350-9359.
- (8) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. Nucleophile promoted degradation of catecholborane: consequences for transition metal-catalyzed hydroborations. *Inorg. Chem.* **1993**, *32*, 2175-2182.
- (9) Burgess, K.; Jaspars, M. Ruthenium-catalyzed hydroborations of alkenes. *Organometallics* **1993**, *12*, 4197-4200.

- (10) Burgess, K.; Jaspars, M. Hydroboration reactions mediated by bis(mesityl)niobium: Beware of the trojan horse. *Tetrahedron Lett.* **1993**, *34*, 6813-6816.
- (11) Burgess, K.; van der Donk, W. A. On Titanium-Promoted Hydroborations of Alkenes by Borohydride and by Catecholborane. *Organometallics* **1994**, *13*, 3616-3620.
- (12) Harder, S.; Spielmann, J. Calcium-mediated hydroboration of alkenes: "Trojan horse" or "true" catalysis? *J. Organomet. Chem.* **2012**, *698*, 7-14.
- (13) Suseela, Y.; Periasamy, M. Convenient method for the preparation of catecholborane and promotion of the formation of alkenyl catecholborane using BH_3 complexes. *J. Organomet. Chem.* **1993**, *450*, 47-52.
- (14) Ang, N. W. J.; Buettner, C. S.; Docherty, S.; Bismuto, A.; Carney, J. R.; Docherty, J. H.; Cowley, M. J.; Thomas, S. P. Borane-Catalysed Hydroboration of Alkynes and Alkenes. *Synthesis* **2018**, *50*, 803-808.
- (15) Jeong, E.; Heo, J.; Park, S.; Chang, S. Alkoxide-Promoted Selective Hydroboration of N-Heteroarenes: Pivotal Roles of *in situ* Generated BH_3 in the Dearomatization Process. *Chem. Eur. J.* **2019**, *25*, 6320-6325.
- (16) Docherty, J. H.; Peng, J.; Dominey, A. P.; Thomas, S. P. Activation and discovery of earth-abundant metal catalysts using sodium *tert*-butoxide. *Nature Chem.* **2017**, *9*, 595-600.
- (17) Query, I. P.; Squier, P. A.; Larson, E. M.; Isley, N. A.; Clark, T. B. Alkoxide-Catalyzed Reduction of Ketones with Pinacolborane. *J. Org. Chem.* **2011**, *76*, 6452-6456.
- (18) Wu, J.; Zeng, H.; Cheng, J.; Zheng, S.; Golen, J. A.; Manke, D. R.; Zhang, G. Cobalt(II) Coordination Polymer as a Precatalyst for Selective Hydroboration of Aldehydes, Ketones, and Imines. *J. Org. Chem.* **2018**, *83*, 9442-9448.
- (19) Greenhalgh, M. D.; Thomas, S. P. Chemo-, regio-, and stereoselective iron-catalysed hydroboration of alkenes and alkynes. *Chem. Commun.* **2013**, *49*, 11230-11232.
- (20) Zuo, Z.; Huang, Z. Synthesis of 1,1-diboronate esters by cobalt-catalyzed sequential hydroboration of terminal alkynes. *Org. Chem. Front.* **2016**, *3*, 434-438.
- (21) Tamang, S. R.; Findlater, M. Iron Catalyzed Hydroboration of Aldehydes and Ketones. *J. Org. Chem.* **2017**, *82*, 12857-12862.
- (22) Mandal, S.; Verma, P. K.; Geetharani, K. Lewis acid catalysis: regioselective hydroboration of alkynes and alkenes promoted by scandium triflate. *Chem. Commun.* **2018**, *54*, 13690-13693.
- (23) Weidner, V. L.; Barger, C. J.; Delferro, M.; Lohr, T. L.; Marks, T. J. Rapid, Mild, and Selective Ketone and Aldehyde Hydroboration/Reduction Mediated by a Simple Lanthanide Catalyst. *ACS Catal.* **2017**, *7*, 1244-1247.
- (24) Baishya, A.; Baruah, S.; Geetharani, K. Efficient hydroboration of carbonyls by an iron(II) amide catalyst. *Dalton Trans.* **2018**, *47*, 9231-9236.
- (25) Arrowsmith, M.; Hadlington, T. J.; Hill, M. S.; Kociok-Köhn, G. Magnesium-catalysed hydroboration of aldehydes and ketones. *Chem. Commun.* **2012**, *48*, 4567-4569.
- (26) Bismuto, A.; Cowley, M. J.; Thomas, S. P. Aluminum-Catalyzed Hydroboration of Alkenes. *ACS Catal.* **2018**, *8*, 2001-2005.
- (27) Wu, Y.; Shan, C.; Ying, J.; Su, J.; Zhu, J.; Liu, L. L.; Zhao, Y. Catalytic hydroboration of aldehydes, ketones, alkynes and alkenes initiated by NaOH. *Green Chem.* **2017**, *19*, 4169-4175.
- (28) Zhu, Z.; Wu, X.; Xu, X.; Wu, Z.; Xue, M.; Yao, Y.; Shen, Q.; Bao, X. *n*-Butyllithium Catalyzed Selective Hydroboration of Aldehydes and Ketones. *J. Org. Chem.* **2018**, *83*, 10677-10683.
- (29) Yan, D.; Wu, X.; Xiao, J.; Zhu, Z.; Xu, X.; Bao, X.; Yao, Y.; Shen, Q.; Xue, M. *n*-Butyllithium catalyzed hydroboration of imines and alkynes. *Org. Chem. Front.* **2019**, *6*, 648-653.
- (30) Wang, Z.-C.; Wang, M.; Gao, J.; Shi, S.-L.; Xu, Y. *n*-BuLi-promoted *anti*-Markovnikov selective hydroboration of unactivated alkenes and internal alkynes. *Org. Chem. Front.* **2019**, *6*, 2949-2953.
- (31) Magre, M.; Maity, B.; Falconnet, A.; Cavallo, L.; Rueping, M. Magnesium-Catalyzed Hydroboration of Terminal and Internal Alkynes. *Angew. Chem. Int. Ed.* **2019**, *58*, 7025-7029.
- (32) Gatti, A. R.; Wartik, T. Preparation and Properties of the Monoborane Adduct of *N,N,N',N'*-Tetramethylethylenediamine. *Inorg. Chem.* **1966**, *5*, 329-330.
- (33) Palenik, G. J. The crystal structure of the aluminum hydride-*N,N,N',N'*-tetramethylethylenediamine adduct. *Acta Cryst.* **1964**, *17*, 1573-1580.
- (34) Seebach, D.; Hässig, R.; Gabriel, J. ^{13}C -NMR-Spektroskopie von Organolithiumverbindungen bei tiefen Temperaturen. Strukturinformation aus der ^{13}C , 6Li -Kopplung. *Helv. Chim. Acta* **1983**, *66*, 308-337.
- (35) Gitlitz, M. H.; Considine, W. J. The preparation of di-*n*-butylmagnesium-*N,N,N',N'*-tetramethylethylenediamine complex from a non-etheral grignard. *J. Organomet. Chem.* **1970**, *23*, 291-292.
- (36) Nöth, H.; Rurländer, R. Metal tetrahydridoborates and (tetrahydridoborato)metalates. 10. NMR study of the systems aluminum hydride/borane/tetrahydrofuran and lithium tetrahydroaluminate/borane/tetrahydrofuran. *Inorg. Chem.* **1981**, *20*, 1062-1072.
- (37) Shirakawa, K.; Arase, A.; Hoshi, M. Preparation of (*E*)-1-alkenylboronic acid pinacol esters via transfer of alkenyl group from boron to boron. *Synthesis* **2004**, 1814-1820.
- (38) Nieto-Sepulveda, E.; Bage, A. D.; Evans, L. A.; Hunt, T. A.; Leach, A. G.; Thomas, S. P.; Lloyd-Jones, G. C. Kinetics and Mechanism of the Arase-Hoshi R_2BH -Catalyzed Alkyne Hydroboration: Alkenylboronate Generation via B-H/C-B Metathesis. *J. Am. Chem. Soc.* **2019**, *141*, 18600-18611.
- (39) Contreras, R.; Wrackmeyer, B. Application of ^{11}B nuclear magnetic resonance spectroscopy to the study of hydroboration—III. ^{11}B Nuclear magnetic resonance study of exchange reactions of triorganyl boranes with borane in tetrahydrofuran and dimethyl sulfide. *Spectrochim. Acta A* **1982**, *38*, 941-951.
- (40) Quantifying the amounts of dialkyl- and monoalkylborane formed was not possible due to overlap with the HBpin signal. A nucleophile-catalyzed pathway cannot be completely ruled out, however the similarity between $[BH_3]_{obs}$ and $[BH_3]_{calc}$ suggests that the contribution from this nucleophile-catalyzed pathway is negligible.
- (41) Docherty, J. H.; Nicholson, K.; Dominey, A. P.; Thomas, S. P. A Boron-Boron Double Transborylation Strategy for the Synthesis of *gem*-Diborylalkanes. *ACS Catal.* **2020**, *10*, 4686-4691.
- (42) Rickborn, B.; Wuesthoff, M. T. Kinetics, stereochemistry, and mechanism of the sodium borohydride reduction of alkyl-substituted cyclohexanones. *J. Am. Chem. Soc.* **1970**, *92*, 6894-6904.