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Hydrogenolysis of Haloboranes: from Synthesis of Hydroboranes to Formal Hydroboration Reactions

Guilhem Zwart,^[a] Alexis Mifleur,^[a] Gabriel Durin,^[a] Emmanuel Nicolas,^[a] and Thibault Cantat*^[a]

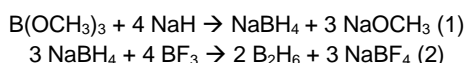
[a] G. Zwart, Dr. A. Mifleur, Dr. G. Durin, Dr. E. Nicolas, Dr. T. Cantat
CEA, IRAMIS, NIMBE, CNRS UMR 3299
91191 Gif-sur-Yvette (France)
E-mail: thibault.cantat@cea.fr

Supporting information for this article is given via a link at the end of the document.

Abstract: Hydroboranes are versatile reagents in synthetic chemistry but their synthesis relies on energy-intensive processes. Herein, we report a new method for the preparation of hydroboranes from hydrogen and the corresponding haloboranes. Triethylamine (NEt₃) form with dialkylchloroboranes a Frustrated Lewis Pair (FLP) able to split H₂ and afford the desired hydroborane with ammonium salts. Unreactive haloboranes were unlocked using a catalytic amount of Cy₂BCl, enabling the synthesis of commonly used hydroboranes such as pinacolborane or catecholborane. The mechanisms of these reactions have been examined by DFT studies, highlighting the importance of the base selection. Finally, the system's robustness has been evaluated in one-pot B-Cl hydrogenolysis/hydroboration reactions of C=C unsaturated bonds.

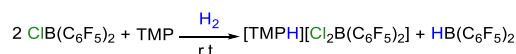
Hydroboranes are reagents of interest for numerous applications in synthetic chemistry. Their role in the hydroboration of alkenes allows for the regioselective functionalization of olefins, leading to the formation of alcohols.^[1-3] Metal-catalyzed C-H borylation of arenes with pinacolborane economically provides aryl boronates which are widely employed for the Suzuki-Miyaura cross-coupling reaction.^[4] Moreover, hydroboranes act as useful hydride sources for the reduction of organic molecules, under mild conditions. The redox potential E⁰(B(OH)₃,H⁺/B₂H₆): -0.52 V (vs NHE) is typical of hydroboranes and shows that B-H groups are amenable to the reduction of a wide range of carbonyl-based functions, including CO₂ and polyesters.^[5]

The synthesis of common substituted hydroboranes relies on borane (BH₃) as a precursor.^[3] BH₃ itself, or its dimer, is obtained from a two-step sequence where trimethylborate is reduced with NaH, following the energy-intensive Brown-Schlesinger process (Eq. 1),^[6] and the resulting sodium borohydride is reacted with BF₃, leading to a 43 % loss of boron atoms (Eq. 2).^[7] Alternative pathways to alkyl- or aryl- hydroboranes rely on the use of potent reductants such as LiAlH₄,^[8] and sometimes hydrosilanes,^[9] on borate derivatives or haloboranes.^[10] The latter being produced from the action of halogenated agents such as BCl₃ or PCI₅ to sophisticated boronic esters^[11] or by functionalization of boron trihalides with organometallic reagents.^[12] As such, all current methods for the synthesis of hydroboranes necessitate the use of stoichiometric amounts of highly reducing agents, which come with a significant overpotential, leading to energy and material wastage.

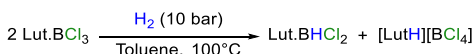


Dihydrogen is an attractive reductant, and developing efficient methods to generate hydroboranes from H₂ would be appealing to improve the energy efficiency of hydroboration chemistry. Yet, H₂ has a mild redox potential (E⁰(H⁺/H₂): 0.00 V vs. NHE), which translates into unfavorable thermodynamics for the direct hydrogenolysis of haloboranes (R₂B-X) to hydroboranes (R₂B-H). As such, the formation of B-H bonds from the splitting of H₂ has been mostly explored in Frustrated Lewis Pairs (FLPs) chemistry,^[13,14] in particular for the generation of reactive borohydride species in the presence of stoichiometric amounts of a suitable base. This approach, however, has barely been described for the synthesis of hydroboranes (Scheme 1). Camaioni *et al.* obtained a 1:1 mixture of Lut-BHCl₂ (Lut : lutidine) and [LutH][BCl₄] by heating the Lut-BCl₃ Lewis pair under H₂ pressure at elevated temperature (T = 100 °C).^[15] Berke and co-workers have reported similar reactivity with ClB(C₆F₅)₂ in presence of 2,2,6,6-tetramethylpiperidine (TMP), they observed the formation of the hydroborane HB(C₆F₅)₂ in mixture with the chloroborate [TMPH][Cl₂B(C₆F₅)₂].^[16] The authors assumed the formation of a transient chloroborohydride species reacting with a second molecule of ClB(C₆F₅)₂.

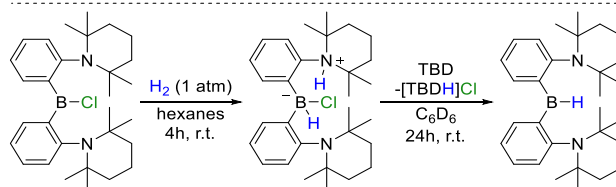
Observation of H₂ splitting in boron-based FLPs



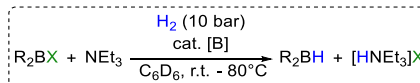
TMP = 2,2,6,6-Tetramethylpiperidine Berke, 2009



Lut = Lutidine : 2,6-dimethylpyridine Camaioni, 2015



This work: generation of hydroboranes by (catalytic) hydrogenolysis



cat. [B] = boron catalyst (Cy₂BCl, 9-BBN)

X = Cl, I, OTf

R = alkyl, aryl, alkoxy, aryloxy

Scheme 1. State of the art on chloroboranes hydrogenolysis

Chloroborohydrides intermediates have been isolated from sophisticated intramolecular Lewis pairs where diarylchloroborane is decorated with tetramethylpiperidine (TMP) side arms.^[17,18] Treatment of the [(TMP-Ar)₂BHCl] isolated by Fontaine with a strong base (TBD) affords the hydroborane (TMP-Ar)₂B-H.^[17]

To unlock a versatile synthesis of hydroboranes from (pseudo-)haloborane precursors and H₂, we have thought to exploit the ability of borane derivatives to split H₂ in the presence of a suitable base. The careful selection of the base should indeed both ensure a frustrated Lewis Pair character and favour the thermodynamics of the hydrogenolysis reaction by trapping the released acid.

Recently, our group reported on the hydrogen activation by an *inverse* frustrated Lewis pair BTPP/Cy₂B-Cl (BTPP: *tert*-butyliminotri(pyrrolidino)phosphorane) for the hydrogenolysis of chlorosilane to hydrosilane.^[19] During the reaction, the precatalyst Cy₂B-Cl rapidly evolves into Cy₂BH in the presence of H₂ and BTPP. Motivated by these observations, we aimed to tackle the hydrogenolysis of B-Cl bonds and we report herein a new pathway for the synthesis of common hydroboranes.

The reactivity of the commercially available chloroborane Cy₂B-Cl was first investigated in the presence of one equivalent of the bulky base BTPP and an atmosphere of H₂. As depicted in Eq. 1 and under 10 bar H₂, the dimer [Cy₂BH]₂ was formed in 41 % yield after 18 h in CD₂Cl₂ at room temperature (RT).

$$\text{Cy}_2\text{B-Cl} + \text{BTPP} + \text{H}_2 \text{ (10 bar)} \rightarrow \frac{1}{2} [\text{Cy}_2\text{BH}]_2 + [\text{BTPPH}]\text{Cl} \quad (3)$$

This promising result led us to investigate the effect of the base on the reactivity. Various common organic bases, with different properties (basicity and nucleophilicity), were tested in the same conditions. We observed good yields in the desired hydroborane with trialkylamines such as triethylamine (75 %), N,N-diisopropylethylamine (60 %) and N,N-dicyclohexylmethylamine (72 %). However, no reaction occurred with pyridine derivatives

(pyridine, lutidine), 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) or guanidines such as 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD), 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (Me-TBD) and 2-*tert*-Butyl-1,1,3,3-tetramethylguanidine (BTMG) (Figure 1). To better understand the key role of the base, DFT calculations were performed to determine the influence of the nature of the base on the outcome of the reaction. Prior research conducted in our laboratory, consistent with the literature,^[15] indicate that the H₂ cleavage is likely to occur through a FLP-type mechanism. As such, it is necessary to avoid the formation of stable adducts between the base and the chloroborane reagent. Thus, the Gibbs free energies for the formation of such base→CyBCl adducts have also been computed (Figure 1). Strikingly, while DBU, pyridine and guanidines form stable adducts ($\Delta G = -12.1$ kcal.mol⁻¹ with TBD) which prevents the hydrogenolysis, BTPP and the trialkylamines do not interact with Cy₂B-Cl ($\Delta G > 23$ kcal.mol⁻¹), explaining their good activities in the hydrogenolysis reaction.

Further optimization of the reaction conditions was carried out, using NEt₃ as the base (Table 1). The reaction performed well in various solvents. Using dichloromethane (entry 1) yielded 75% of [Cy₂BH]₂ after 18 hours at RT under 10 bar of H₂. Under the same conditions, aromatic solvents slightly improved the yield to 83 % and 80 % in C₆D₆ and C₆D₅Cl, respectively (entries 2 and 3). In toluene (entry 4), the reaction yielded only 63 %, and using cyclohexane (entry 5) gave 61 %. More polar solvents decreased reactivity: in THF-d₈ (entry 6) only 27 % of [Cy₂BH]₂ were formed, and no product was obtained in MeCN-d₃ (entry 7). In anisole, considered a green alternative to aromatic solvents,^[20] the reaction yielded 63 %, similar to toluene (entry 8). A large excess of base neither significantly helped nor hindered the reaction, and using NEt₃ as the solvent yielded [Cy₂BH]₂ in 69 % after 18 hours (entry 9). We chose benzene as the preferred solvent and investigated the effects of temperature and H₂ pressure.

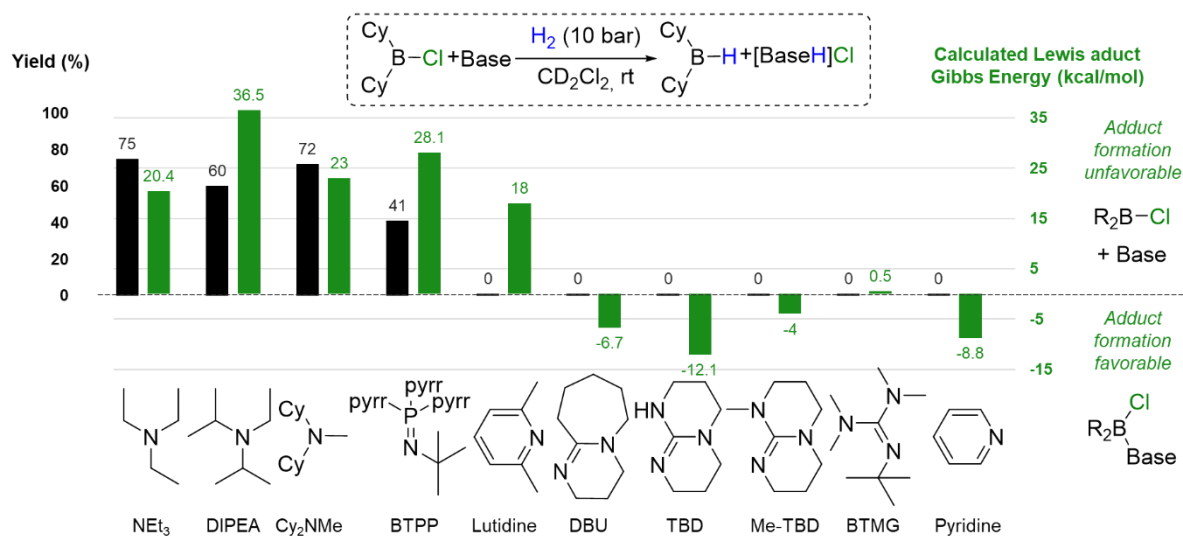


Figure 1. Base screening and calculation formation of adducts. Conditions: Cy₂B-Cl (0.1 mmol), CD₂Cl₂ (0.33 mol.L⁻¹), base (0.11 mmol, 1.1 eq.), H₂ (10 bar). Mesitylene as internal standard. NMR yields after titration by 4-octyne (See ESI for details). DFT Calculations: MN15L/Def2TZVP/W06, SMD (solvent: benzene). Pyrr = Pyrrolidino

After 4 hours at RT, the reaction yielded 71 % of hydroborane (entry 10), but increasing the temperature unexpectedly lowered the yields: at 70 °C and 120 °C, the yields were 7 % and 4 % respectively, after 4 hours in C₆D₆ (entries 11 and 12). As expected, we noticed that the yield in hydroborane was directly linked to the H₂ pressure: reducing or increasing the pressure to 5 or 15 bar led to yields of 57 % and 79 % respectively (entries 13 and 14).

Table 1. Optimization of the reaction conditions

Entry	Solvent	T (°C)	H2 (bar)	Time	Yield
1	CD ₂ Cl ₂	rt	10	18 h	75 %
2	C ₆ D ₆	rt	10	18 h	83 %
3	PhCl- <i>d</i> ₅	rt	10	18 h	80 %
4	Toluene- <i>d</i> ₈	rt	10	18 h	63 %
5	C ₆ D ₁₂	rt	10	18 h	61 %
6	THF- <i>d</i> ₈	rt	10	18 h	27 %
7	MeCN- <i>d</i> ₃	rt	10	18 h	0 %
8	Anisole	rt	10	18 h	63 %
9	NEt ₃	rt	10	18 h	69 %
10	C ₆ D ₆	rt	10	4 h	71 %
11	C ₆ D ₆	70	10	4 h	7 %
12	C ₆ D ₆	120	10	4 h	4 %
13	C ₆ D ₆	rt	5	4 h	57 %
14	C ₆ D ₆	rt	15	4 h	79 %

Conditions: Cy₂BCl (0.1 mmol), NEt₃ (0.11 mmol, 1.1 eq.), solvent (0.33 mol.L⁻¹), H₂ Mesitylene as internal standard. NMR yields after titration by 4-octyne.

To shed some light on the mechanism behind the hydrogenolysis of Cy₂BCl to [Cy₂BH]₂, DFT calculations were carried out at the MN15L/Def2TZVP/W06 level of theory, using the SMD model to account for the solvation in benzene (Figure 2) (see SI for details). Overall, the reaction proceeds through the cleavage of H₂ by Cy₂BCl and NEt₃, followed by the decoordination of the chloride anion and the final dimerization of Cy₂BH. The splitting of H₂ is rate determining and proceeds via a first transition state, **TS1**, in line with an FLP-type reactivity.^[21] The corresponding energy barrier of $\Delta G^\ddagger = 25.4 \text{ kcal.mol}^{-1}$ is consistent with the energies proposed by Roy et al. and Camaioni et al. for an organoborane amine pair.^[15,22] The resulting chloroborohydride/ammonium salt [Cy₂BClH][HNEt₃] (**Int1**, $\Delta G = 14.6 \text{ kcal.mol}^{-1}$) is not the final product as it evolves to Cy₂BH after a barrier-less decoordination of the chloride anion. Finally, [Cy₂BH]₂ is formed through a dimerization step with a low lying transition state **TS2** ($\Delta G^\ddagger = 17.9 \text{ kcal.mol}^{-1}$, $\Delta\Delta G^\ddagger = 3.4 \text{ kcal.mol}^{-1}$). The reaction profile is consistent with the absence of any observable

intermediate during the hydrogenolysis of Cy₂BCl, in contrast with the findings of Fontaine and co-authors, who could monitor the formation of a chloroborohydride intermediate (Scheme 1).^[17] Interestingly, the overall reaction is computed to be endergonic ($\Delta G = +9.0 \text{ kcal.mol}^{-1}$), although it proceeds at room temperature in good yields. In fact, both products, [Cy₂BH]₂ and [HNEt₃]Cl, are insoluble in the reaction mixture and their precipitation is likely the driving force of an overall exergonic reaction. This is consistent with the observation of the effect of temperature during the optimization process. It was shown that increasing the temperature led to a significant decrease of reactivity (Table 1 Entries 11 and 12) probably because it increases the solubility of the products, preventing the reaction to proceed.

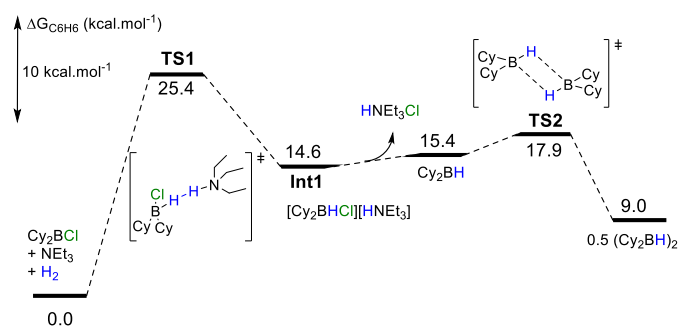





Figure 2. Computed mechanism for the synthesis of [Cy₂BH]₂ from Cy₂BCl, NEt₃ and H₂. DFT Calculations: MN15L/Def2TZVP/W06, SMD (solvent: benzene).

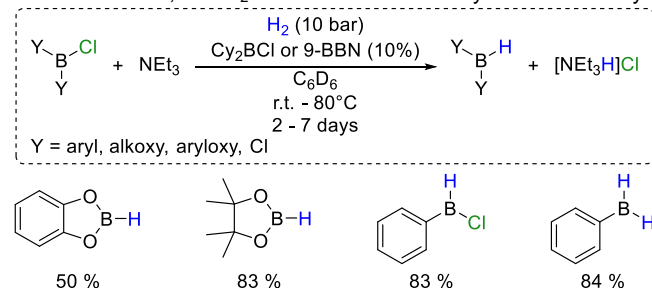
To explore the robustness of the methodology, the hydrogenolysis of a variety of B–X bond-containing compounds was tested (Table 2). [Cy₂BH]₂ was obtained by treatment of the Cy₂BCl with NEt₃ under 10 bar of H₂ with 92 % yield with a longer reaction time from the optimized conditions (46 h) (entry 1), while no reactivity was observed starting from Cy₂BI (entry 2). Hydrogenolysis of the chloro- and triflate-9-BBN derivatives afforded 9-BBN dimer in 85 % and 67 % yields, after 18 h and 46 h, respectively (entries 4 and 5). These conditions did not afford the desired product from I-9-BBN in acceptable yields (6 % after 120 h, entry 6). However, substituting the NEt₃ base with the bulkier tertiary amine Cy₂NMe unlocked the reactivity of the iodoboranes, providing [Cy₂BH]₂ and 9-BBN in 84 and 50 % yields, respectively, after 45 h and 21 h (entries 3 and 7). Moreover, the use of Cy₂NMe led to an increased reactivity with the triflate derivatives (entry 8). The efficiency of the method was illustrated with the synthesis of the commonly used 9-BBN hydroborane on a 1 mmol scale (entry 9): using anisole as a sustainable solvent, 9-BBN dimer was isolated in 84 % yield after a 48 h hydrogenolysis of the chloroborane with NEt₃ and 15 bar H₂ and elimination of the ammonium by-product in THF (see SI). During the reactions involving iodoboranes, and in lesser extent triflate boranes, we observed the formation of side products by NMR. Reacting I-9-BBN with NEt₃ in C₆D₆ led to a major signal at δ : -0.2 ppm in boron NMR (vs BF₃OEt₂ at 0.0 ppm). Such a downfield shift is consistent with a tetracoordinate boron environment. Interestingly, the group of Vedejs reported a similar

Table 2. Examples of catalyzed chloroboranes hydrogenolysis

Entry	R ₂ BX	Base	Time	Products	Yield
1	Cy ₂ BCl	NEt ₃	46 h		92 %
2	Cy ₂ BI	NEt ₃	120 h	[Cy ₂ BH] ₂	0 %
3	Cy ₂ BI	Cy ₂ NMe	45 h		84 %
4	Cl-9-BBN	NEt ₃	18 h		85 %
5	OTf-9-BBN	NEt ₃	46 h		67 %
6	I-9-BBN	NEt ₃	120 h		6 %
7	I-9-BBN	Cy ₂ NMe	21 h		50 %
8	OTf-9-BBN	Cy ₂ NMe	18 h		73 %
9 ^[a]	Cl-9-BBN	NEt ₃	48 h		84 % ^[b]

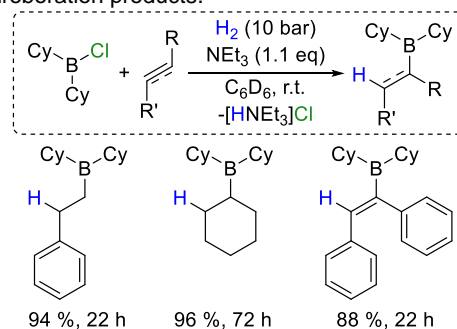
1 Conditions: R₂BX (0.1 mmol), Base (0.11 mmol, 1.1 eq.), C₆D₆ (0.33 mol.L⁻¹)
 2 H₂ (10 bar), room temperature. Mesitylene as internal standard. NMR yields
 3 after titration by 4-octyne. [a] R₂BX (1 mmol), NEt₃ (1.1 mmol, 1.1 eq.), Anisole
 4 instead of C₆D₆ (0.5 mol.L⁻¹), H₂ (15 bar), room temperature. [b] Isolated yield
 5 reaction between the 9-borabicyclo[3.3.1]nonane bis-triflimide
 6 (NTf₂-9-BBN) and NEt₃ in CD₂Cl₂, with a ¹¹B NMR signal assigned
 7 to the corresponding borenium (δ: 85.1 ppm).^[23] Mixing OTf-9-
 8 BBN with NEt₃ in CD₂Cl₂ resulted to an equivalent shift
 9 (δ: 84.8 ppm), which evolved after 17h to the signal at δ: -0.3 ppm.
 10 A reasonable interpretation of these findings is the formation of a
 11 boronium salt [(C₈H₁₅)B(NEt₃)₂]OTf, which occurs in the presence
 12 of a good leaving group such as a iodide or triflate anion and limits
 13 the hydrogenolysis step. In our case, the steric hindrance of the
 14 cyclohexyl group on the Cy₂NMe might reduce the formation of
 15 such by-products (borenium or boronium) and favor the
 16 hydrogenolysis reaction.
 17 Notably, no reaction was observed when the less Lewis acidic B-
 18 chloro-catecholborane (catBCl) or B-chloropinacolborane
 19 (pinBCl) were used in place of Cy₂BCl. Indeed, although the
 20 hydrogenolysis of catBCl is thermodynamically possible
 21 (ΔG = +6.4 kcal.mol⁻¹), the transition state for the splitting of H₂
 22 with catBCl and NEt₃ was computed at 33 kcal.mol⁻¹ (instead of
 23 26 kcal.mol⁻¹ for Cy₂BCl), which is not accessible at room
 24 temperature. However, it has been reported that substituents on
 25 boron can exchange through transborylation,^[24,25] and we
 26 envisioned a system where Cy₂BH is used as an intermediate to
 27 transfer its hydride to catBCl. DFT calculations were performed,
 28 and demonstrated that the hydrogen transfer from Cy₂BH to
 29 catBCl is thermodynamically favorable (ΔG = -9.1 kcal.mol⁻¹)
 30 through a low energy transition state (TS3, ΔG[‡] = 17.4 kcal.mol⁻¹)
 31 which corresponds to the redistribution of the H and Cl
 32 substituents *via* σ-bond metathesis (see SI, Figure 21). The
 33 hydrogenolysis of catBCl was hence tested in the presence of
 34 10 mol% Cy₂BCl and 2 equivalents of triethylamine at 60 °C
 35 Under these conditions, catBH was slowly formed in 50 % yield
 36 within 7 days (Scheme 2). Similarly, B-chloro-pinacolborane
 37 (pinBCl) afforded 83 % of pinBH in 2 days at RT. The reaction with

PhBCl₂ gave 83 % of the monohydrogenolyzed product PhBHCl
 in 4 days at RT. However, the more hydridic 9-BBN, associated
 with an increased reaction temperature (80 °C), was necessary to
 push the hydrogenolysis towards the formation of PhBH₂. Using
 these variations, PhBH₂ was obtained in 84 % yield within 7 days.



Scheme 2. Examples of catalyzed chloroboranes hydrogenolysis

Finally, to evaluate the potential of this new method, we explored
 the possibility to promote the hydroboration of alkenes and
 alkynes, where the hydroborane is produced *in-situ* from a
 chloroborane, H₂ and a base. While no reaction was observed
 upon mixing Cy₂BCl with triethylamine and styrene, exposing this
 reaction mixture to a 10 bar pressure of H₂ led to the formation of
 the corresponding hydroboration product
 phenethyldicyclohexylborane in 94 % yield after 22 h (Scheme 3).
 When cyclohexene and diphenylacetylene were used,
 tricyclohexylborane and (*Z*)-dicyclohexyl(1,2-diphenylvinyl)-
 borane were obtained in 96 % and 88 % yields, respectively in
 72 h and 22 h. Interestingly, under these metal-free conditions, no
 hydrogenation of the C=C multiple bond was observed and the
 products of the alkene/alkyne were selectively transformed to
 their hydroboration products.



Scheme 3. Examples of alkenes and alkynes hydroboration from Cy₂BCl and H₂

In conclusion, we reported herein the synthesis of hydroboranes
 from (pseudo-)haloboranes using H₂ as a hydride source and a
 base, using either stoichiometric or catalytic paths. Experiments
 coupled with theoretical calculations highlighted the critical role of
 the base, which enables the activation of H₂ by Frustrated Lewis
 Pairs chemistry and ensures an overall exergonic hydrogenolysis
 through the precipitation of products. Trialkylamines, and
 especially NEt₃, led to the formation of dialkylborane derivatives
 in quantitative yields. Less reactive substrates were converted
 with the use of a catalytic amount of dialkylboranes, allowing us

1 to synthesize the valuable hydroboranes 9-BBN, catBH and
2 pinBH in good yields and mild conditions without relying on strong
3 hydridic reductants.

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12 **Keywords:** Hydroborane Synthesis • H₂ Activation • Frustrated
13 Lewis Pair • Hydrogenolysis

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