

An Aluminum Dihydride Working as a Catalyst in Hydroboration and Dehydrocoupling

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S Supporting Information

ABSTRACT: The well-defined aluminum dihydride LAIH_2 ($\text{L} = \text{HC}(\text{CMeNAr})_2$, $\text{Ar} = 2,6\text{-Et}_2\text{C}_6\text{H}_3$) (**1**) operates in catalysis like a transition metal complex. The catalytic activity of **1** for hydroboration of terminal alkynes was investigated. Furthermore, catalyst **1** effectively initiated the dehydrocoupling of boranes with amines, thiols, and phenols, respectively, to form compounds with B–E bonds ($\text{E} = \text{N}, \text{S}, \text{O}$) under elimination of H_2 . Quantum mechanical calculations indicate that hydroboration and dehydrocoupling reactions occur via three consecutive cycloaddition reactions involving the activation of the X–H ($\text{X} = \text{Al}, \text{B}, \text{C}, \text{and O}$) σ -bonds.

In quest of a new generation of commercial useful and environmentally benign catalysts for important chemical transformations, main group compounds are promoted as viable alternatives to transition metal catalysts.¹ Organoboron compounds are versatile precursors in organic synthesis due to their application as nucleophilic reagents in C–C bond forming reactions.² Consequently, great efforts have been accomplished on the development of tools for the preparation of organoborane derivatives.³ A number of research groups have investigated catalytic hydroboration reactions with transition metal complexes, in order to reduce the cost of the hydroboration catalysts, to complement the selectivity of the late transition metals systems, and to discover new catalytic pathways.⁴ Recently, Chirik et al. reported on alkyl compounds with low-coordinate cobalt and iron dinitrogen complexes, respectively, as catalyst for alkene and alkyne hydroboration.⁵ Nikonov and co-workers described the catalytic addition of HBCat with nitriles to form the bis(borylated) amines $\text{RCH}_2\text{N}(\text{BCat})_2$.⁶ These methods directly add the borane only to unsaturated precursors for the reason that an initial oxidative addition of the B–H bond to the metal center is followed by the π -coordination of the unsaturated $\text{C}\equiv\text{C}$ and $\text{C}\equiv\text{N}$ bond, respectively, to the metal center. In 2015 Hill et al. reported on dehydrocoupling reactions between deactivated boranes (HBPIn or 9-borabicyclo[3.3.1]nonane) with a number of amines and anilines to form aminoboranes by an alkaline-earth metal catalyst.⁷ Sadow et al. published magnesium-catalyzed ester hydroboration reactions, which rapidly and efficiently provide alkoxy borane products via ester cleavage.⁸

Nolan and co-workers used a ruthenium based catalyst that demonstrated a great ability to catalyze the coupling of thiols with boranes.⁹ However, all of the reported methods focus on transition and alkaline-earth metals, while the related catalytic reactions with group 13 elements have not been mentioned.

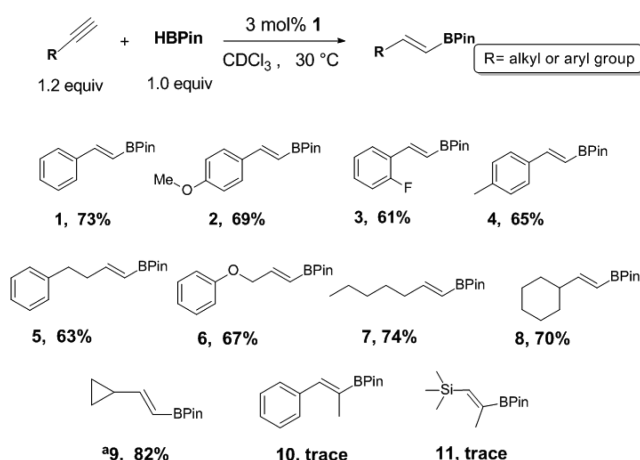
Recently, Stephan and co-workers reported on the Lewis acidic phosphonium salt $[(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$ which functioned as a main group catalyst effecting the dehydrocoupling of silanes with amines, thiols, phenols, and carboxylic acids, to form compounds containing the Si–E bond ($\text{E} = \text{N}, \text{S}, \text{O}$) by elimination of H_2 .¹⁰ Our group revealed the hydridic reactivity of $\text{LAIH}(\text{OTf})$ ($\text{L} = \text{HC}(\text{CMeNAr})_2$, $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$) with carbonyl compounds featuring the electrophilic Al center, which interacted with a polar σ -bond of the substrates.¹¹ In 2012, we reported on three structures containing the Al–E–C moiety using just the reverse polarity of the hydrides in LAIH_2 and the proton in C–EH compounds ($\text{E} = \text{N}, \text{S}, \text{O}$).¹² Previously, the reactions of aluminum(III) hydrides with alkynes and their application for bond activation have been proposed.¹³ Inspired by these results, we used the LAIH_2 compound as the catalyst for the formation of compounds with B–E ($\text{E} = \text{C}, \text{N}, \text{S}, \text{O}$) bonds. Herein, we report on the main group metal hydride catalyzed addition of HBPIn to compounds with the carbon–carbon triple bond and the dehydrocoupling of boranes with amines, thiols, and phenols, individually, with LAIH_2 (**1**) ($\text{L} = \text{HC}(\text{CMeNAr})_2$, $\text{Ar} = 2,6\text{-Et}_2\text{C}_6\text{H}_3$) as a precatalyst (Scheme S1).

At the outset of this investigation, the stoichiometric reaction of **1** with HBPIn and the terminal alkyne (PhCCH), separately, was carried out as a feasibility study for the proposed catalytic protocol.¹⁴ Encouraged by this result, the initial catalytic experiments were conducted with LAIH_2 (**1**) showing the utility of the hydroboration with a variety of alkynes. Stirring an anhydrous CDCl_3 solution containing a 1.2:1 mixture of phenylacetylene and HBPIn in the presence of 3 mol % of **1** at 30 °C for 12 h produced a 73% conversion to the (*E*)-vinylboronate ester arising from anti-Markovnikov addition of the borane (Scheme 1, product 1). Good yield and (*E*) selectivity were observed for the propargyl ethers, propargyl aryl-, and alkyl-substituted alkynes (Scheme 1, products 2–9). More electron-rich alkynes with secondary alkyl substituents

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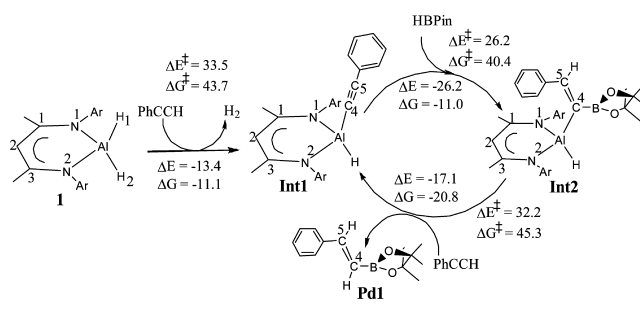
Scheme 1. Hydroboration of Alkynes Catalyzed by **1**^a

^aHydroboration of terminal alkynes with LAIH₂. Reaction conditions: 3 mol % of LAIH₂, 30 °C, in CDCl₃, 12 h. The *E* selectivity was determined by NMR spectroscopy. Reported numbers are the NMR yields. (a) Reaction time 32 h with neat substrate.

underwent slower hydroboration and required neat conditions and a reaction time of 32 h. Aryl substituted alkynes with electron-donating (*p*-OMe) and electron-withdrawing (*m*-F) groups maintained high (*E*) selectivity and produced good yields (Scheme 1, products 2 and 3). Under the same conditions, aliphatic alkynes showed higher yields than those of aromatic alkynes in the catalytic system, while they failed to react with internal alkynes to produce single hydroboration products (Scheme 1, products 10 and 11).

A mechanism for the aluminum catalyzed hydroboration of terminal alkynes at the M06/Def2-TZVPP//BP86/Def2-SVP level of theory¹⁵ is presented in Scheme 2 (Figure S3). The

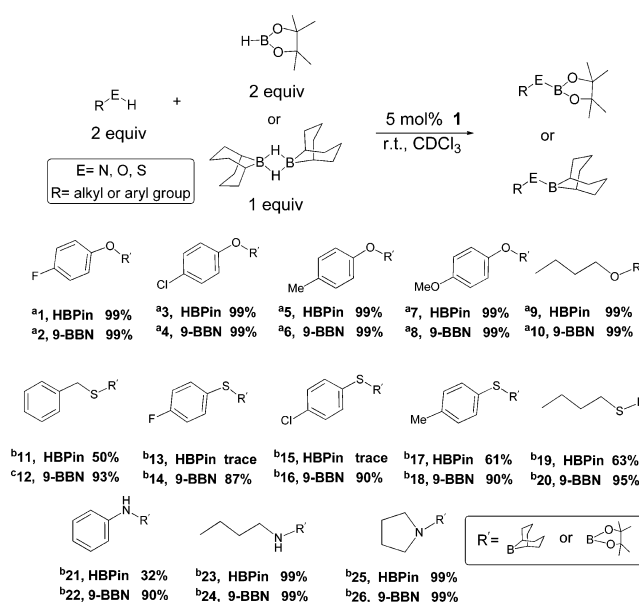
Scheme 2. Reaction Mechanism for the Hydroboration of Phenylacetylene



molecular electrostatic potential (Figure S2c) and NBO charge analysis (Table S2) on **1** show that the Al atom (*q*_{Al} = 1.40 e) is electrophilic and hydrogen atoms (*q*_H = -0.41 e) connected to the Al center are nucleophilic (Table S2). Note that hydrogen atom connected to the sp hybridized carbon in phenylacetylene is acidic (*q*_H = 0.23 e) and the hydrogen atom connected to boron in HBPIn is basic (*q*_H = -0.11 e). Accordingly, the first step is the σ -bond metathesis reaction via concerted $[2\sigma + 2\sigma]$ cycloaddition of H-C_{CCPh} of phenylacetylene across the Al-H bond leading to the aluminum acetylide (Int1) and H₂. Even though this step demands a high kinetic energy barrier ($\Delta E^\ddagger = 33.5$ and $\Delta G^\ddagger = 43.7$ kcal/mol), it is exothermic by 13.4 and exergonic by 11.1 kcal/mol. Int1 acts as the active species for the catalyst cycle.¹⁶ The second

step ($\Delta E = -26.2$ and $\Delta G = -11.0$ kcal/mol) is $[2\sigma + 2\pi]$ cycloaddition reaction where the B-H bond of pinacolborane (HBPIn) adds to the C≡C bond of Int1. The energy barrier for the formation of the resulting intermediate (*Z*)-alkene (Int2) is very high ($\Delta E^\ddagger = 26.2$ and $\Delta G^\ddagger = 40.4$ kcal/mol). The Al-C bond in Int2 is highly polarized (*q*_{Al} = 1.65 e and *q*_C = -0.89 e) as compared to the Al-H bond in **1**, which in turn favors the σ -bond metathesis $[2\sigma + 2\sigma]$ reaction by the addition of the Al-C bond with the H-C_{CCPh} bond of the second molecule of phenylacetylene resulting in the product (*E*)-alkene (Pd1) and the active catalyst Int1. Similar to the previous two cycloaddition steps, the final step is also thermodynamically favorable but involves a high kinetic energy barrier. This is consistent with the longer reaction time of the hydroboration reactions (Scheme 1). The overall reaction proceeds through three successive metathesis reactions and the energetics indicate that the formation of the aluminum acetylide (Int1) is the overall rate-determining step (Figure S3).

In 2014 Jones et al. reported that Ge(II) and Sn(II) hydride complexes can be efficient catalysts for the hydroboration of carbonyl compounds.¹⁷ The carbonyl compound was used as substrate, and the first step involves the addition of the metal hydride to the C=O bond. Jones proposed that the metal alkoxide acts as the intermediate and then undergoes a σ -bond metathesis with HBPIn to generate a borate ester by returning the catalyst. We found that aluminum hydride LAIH₂ (**1**) can react with phenol to form the metal alkoxide under elimination of H₂.¹² **1** was also used to catalyze the dehydrocoupling of boranes with phenols. The reactions were carried out in CDCl₃ with 5 mol % loading of the catalyst at ambient temperature. Scheme 3 (products 1–10) summarizes the investigation of **1** to catalyze the dehydrocoupling of phenols with HBPIn and 9-BBN, respectively. Moreover, we also observed that both 9-BBN and less Lewis acidic HBPIn exhibit high reactivity

Scheme 3. Dehydrocoupling of Boranes with Amines, Phenols, and Thiols Catalyzed by **1**^a

^aReaction condition: 5 mol % of LAIH₂, at rt, in CDCl₃. Reported numbers are the yields by NMR. (a) Reaction time 1 h with neat substrate. (b) Reaction time 24 h. (c) Reaction time 18 h.

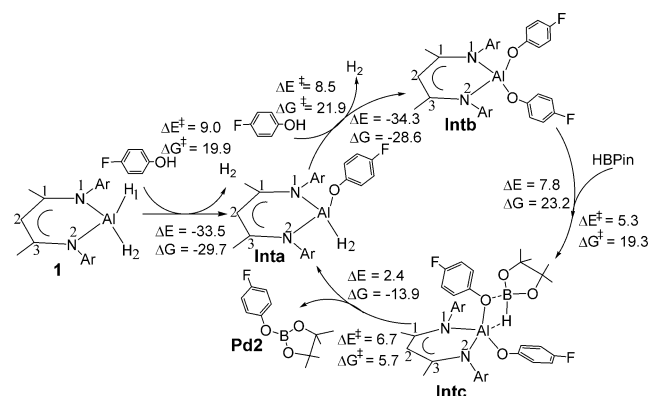
patterns. In general, these reactions were complete in 1 h with a noticeable bubbling of hydrogen.

This facile dehydrocoupling route to organoboranes can be used to access other useful compounds. For example, through the hydric (B–H) and the protic (E–H, E = N, O, S) properties of hydrogen atoms, the elimination of dihydrogen was observed. In this case, the Al center is attacked by the Lewis base (N, O, S) to generate the corresponding transient four-membered species. Initially, 5 mol % of **1**, C₆H₅CH₂SH, and HBPIn were allowed to react for 24 h to result in a 50% yield at rt (Scheme 3, product 11). Interestingly, when HBPIn was used instead of the enhanced Lewis acidic 9-BBN, the reaction was complete within 18 h to result in 93% conversion (Scheme 3, product 12). In contrast, HBPIn reactions with aryl substituted thiophenols bearing electron-withdrawing (*m*-F and *m*-Cl) groups are not yielding the desired products even by increasing the reaction time (Scheme 3, products 13 and 15). However, the more Lewis acidic 9-BBN provided, the higher yield and required neat conditions and longer reaction time (24 h) (Scheme 3, products 14 and 16). In case of the reaction of (*p*-Me) thiophenol with HBPIn and 9-BBN, dehydrocoupling of the SH group with borane resulted in 61% and 90% yield, respectively (Scheme 3, products 17 and 18). As shown in Scheme 3, under the same condition, butanethiol gave nearly the same yield compared to that of thiophenol (Scheme 3, products 19 and 20).

Aminoboranes are used in a variety of interesting transformations, although the activation of the N–H bond often relies on the oxidative addition of the N–H to a transition-metal center.¹⁸ Thus, the metal catalytic dehydrocoupling of amines and boranes is quite limited.⁴ Berben and co-workers reported on the heterolytic activation of amines by Al pincer complexes via a metal–ligand cooperative pathway.¹⁹ Herein, we used the aluminum hydride effect as the catalyst for the synthesis of aminoboranes from readily available amine and borane precursors. The reaction of *n*-butylamine with HBPIn gives a high yield of product within 24 h with 5 mol % loading of the catalyst at ambient temperature in CDCl₃. Encouraged by this result, we studied the scope of the aluminum-catalyzed dehydrocoupling reactivity. As shown in Scheme 3, the weak Lewis acid HBPIn was observed to couple readily with primary amine (aniline and butyl amine) and secondary amine, respectively (Scheme 3, products 21, 23, 25). However, it failed to perform in the reaction of 2 molar equiv of borane with 1 equiv of amine and aniline, respectively, providing conversion into the bisborylated amine, albeit with gentle heating and slightly extended reaction time. The same result can also be observed for the more Lewis acidic 9-BBN, while aromatic and aliphatic amines coupled readily with 1 molar equiv of 9-BBN resulting in higher yields than those of HBPIn under the same conditions (Scheme 3, products 22, 24, 26).

The reaction mechanism of the dehydrocoupling of *p*-fluorophenol with pinacolborane (HBPIn) at the M06/Def2-TZVPP//BP86/Def2-SVP level of theory (Scheme 4) was also explored.¹⁵ The first and second step of the reaction are the two consecutive [2σ + 2σ] σ-bond metathesis involving addition of each of the Al–H bonds of **1** across the O–H bond of two molecules of *p*-fluoro-phenol through a four-membered transition state (Scheme 4, Figure S5). The formation of the resultant intermediates **Inta** and **Intb** occurs with the liberation of H₂. The addition of more polar O–H bonds is thermodynamically and kinetically favorable as compared to the addition of the C–H bond of phenylacetylene to the Al–H

Scheme 4. Reaction Mechanism for the Dehydrocoupling of *p*-Fluoro-phenol with HBPIn



bond of **1** in the first step of hydroboration reaction (Scheme 2). In this reaction, the intermediate **Inta** can be considered as the active species for the catalytic cycle.²⁰ The next step is the [2σ + 2σ] cycloaddition of the H–B bond of pinacolborane to one of the Al–O bond in **Intb** resulting in an intermediate, **Intc**, having a four-membered Al–O–B–H ring. This step is slightly endothermic ($\Delta E = 7.8$ kcal/mol) and endergonic ($\Delta G = 23.2$ kcal/mol). The final step is the concomitant transfer of hydride of the HBPIn unit to the Al-center as well as the cleavage of the Al–O bond leading to the dehydrocoupling product **Pd2** and regeneration of the active catalyst **Inta**. This step is exergonic ($\Delta G = -13.9$ kcal/mol) and involves a low kinetic energy barrier ($\Delta E^\ddagger = 6.7$ and $\Delta G^\ddagger = 5.7$ kcal/mol). The overall energetics indicate that the formation of the active catalyst, **Inta**, from compound **1** is the rate-determining step. However, the slight endothermicity/endergonicity observed in the formation of the dehydrocoupling product is duly compensated by the subsequent formation of the stable intermediate, **Intb**. This can be correlated with the less reaction time of the dehydrocoupling reactions as compared to the hydroboration reactions.

In conclusion, an aluminum hydride catalyzed method for hydroboration of terminal alkynes and dehydrocoupling of boranes with amines, phenols, and thiols, separately, was developed. The quantum mechanical calculations indicate that the dehydrocoupling reaction is found to be kinetically more favorable than the hydroboration reaction.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b00032.

Complete experimental and computational details, representative NMR spectra (PDF)

Crystallographic data for **1** in a cif format (ZIP)

Cartesian coordinates of all calculated molecules (XYZ)

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Notes

The authors declare no competing financial interest.

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- (14) We assume that **I** is the active species in the stoichiometric and catalytic reactions reported herein (see Schemes S2–S5).
- (15) See Supporting Information for details of computational methodology.
- (16) We have explored the alternate reaction mechanisms. (a) The energetics of the reaction mechanism in which two Al–H bonds of the catalyst **I** are involved are found to be less favorable (Scheme S22 and Figure S4). (b) Scheme S4 depicts the activation of phenyl acetylene by metal–ligand cooperation, where both the metal and one nitrogen atom of the β -diketiminato ligand are involved for the activation process. The initial steps of this pathway are energetically less favorable as compared to those in Scheme 2 and also lead to the breakage of the Al–N bond of the catalyst (Scheme S24).
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- (20) The alternate reaction mechanism (Scheme S23 and Figure S6) involving an attack of the H–B bond of HBPIn to the Al–O bond of **Inta** gives **Intb'**, formation of which is thermodynamically less favorable as compared to the formation of **Intb**. The highly exothermic step **Inta** \rightarrow **Intb** governs the catalytic cycle and hence formation of the product.