

Neosilyllithium-catalyzed hydroboration of alkynes and alkenes in the presence of pinacolborane (HBpin)

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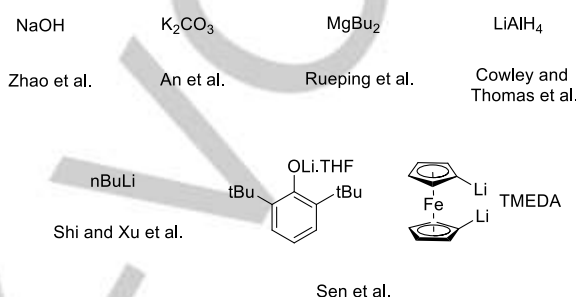
Abstract: We report here a novel protocol for the hydroboration of alkynes and alkenes, which in the presence of neosilyllithium ($\text{LiCH}_2\text{SiMe}_3$) (5 mol %) and pinacolborane efficiently results in the formation of corresponding alkenyl and alkyl boronate ester products in good yields. The electron-donating and electron-withdrawing substituents on the aromatic rings of alkynes and alkenes converted smoothly to the desired products. When we extended the scope of reactivity to various aliphatic alkynes and styrenes using similar conditions, the alkenyl and alkyl boronate ester products were again formed in good yields. We also performed intramolecular and intermolecular reactions to check the reactivity of different functional groups on the phenyl ring. Experimental investigations and DLPNO-CCSD(T) calculations reveal mechanistic insights from the $\text{LiCH}_2\text{SiMe}_3$ -catalyzed alkyne hydroboration.

Introduction

Hydrofunctionalization of unsaturated bonds plays an important role in organic transformations and syntheses of natural products and is also beneficial to the pharmaceutical industry.^[1,2] Alkylboronates are useful synthons in organic chemistry, used in the construction of element-to-element bonds such as C–C, C–O, C–N, and C–P links, which have various applications.^[3–8] The use of earth-abundant, relatively cheap, non-toxic, and environment-friendly metals as catalysts in the efficient hydroboration of unsaturated bonds is always challenging for chemists. In literature, several research groups have reported the use of transition-based metal catalysts such as Fe,^[9–11] Cu,^[12,13] Co,^[14–16] Ru,^[17,18] and Ir^[19,20] complexes in the hydroboration of alkynes and alkenes to form corresponding vinyl boronates and alkyl boronic products. Main group elements – both *s* and *p*-block metals – showed enormous catalytic efficiency (chemo- and regioselective) in synthetic transformations.^[21,22] However, there are a few reports on the development of *s*-block-catalyzed hydroboration of alkynes and alkenes.^[23–25] Use of the metal, lithium, as a catalyst in the hydroboration of alkynes and alkenes is very rare.^[26] However, lithium is very cheap, easily available, and abundant in the earth's crust. Alkyl boronic esters are very useful synthetic intermediates in the formation of C–B bonds, which are quite stable, easy to handle, and atom efficient. Hydroboration of unsaturated bonds, in the presence of organoborane reagents such as pinacolborane (HBpin) or catecholborane (HBcat), has been shown to be an atom-economical as well as an efficient process for the formation of various organoborane compounds.^[27,28] The use of HBpin as a boron reagent in the presence of various transition metals, as well as main group metal catalysts, in the hydroboration of unsaturated bonds is well documented.^[29]

Previous reports

Alkyne and alkene hydroboration



This work

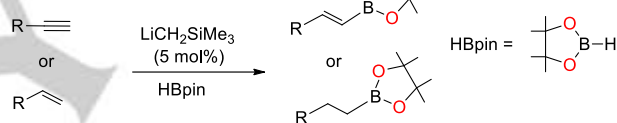


Figure 1. Selected examples of the hydroboration of alkynes and alkenes.

Zhao and co-workers developed the process of hydroboration of alkynes and alkenes using powdered NaOH as the promoter.^[30] Further, An *et al.* introduced K_2CO_3 as a catalyst in the hydroboration of alkenes in the presence of HBpin to form the alkyl boronate ester product in good yield.^[25] Rueping *et al.* reported the hydroboration of terminal and internal alkynes using a magnesium alkyl complex (MgBu_2) as an effective initiator.^[24] Cowley *et al.* introduced LiAlH_4 , which is easily handled, to the hydroboration of alkenes, during which in situ conversion of AlH_3 occurred through a reaction with HBpin, affording the corresponding boronate product in good yield.^[31] Shi *et al.* developed commercially available $n\text{BuLi}$ as a pre-catalyst for use in the hydroboration of α -alkenes, 1,1-di-substituted alkenes, and internal alkenes for the synthesis of alkylboronic esters.^[23] Recently, Sen *et al.* reported that easily accessible lithium compounds, 2,6-di-*tert*-butyl phenolate lithium, and 1,10-dilithioferrocene, could be used catalysts in the hydroboration of alkenes and alkynes, including conjugated terpenes.^[26] An *et al.*, also recently reported an alkyne hydroboration reaction in which no catalyst or solvent was used. However, relatively harsh conditions had to be employed to yield the alkyl boronic ester products.^[32] Nevertheless, limited catalysts have been reported where organolithium is used as an efficient catalyst in the hydroboration of alkenes and alkynes.

Recently, our working group demonstrated successfully that an aluminum metal catalyst [κ^2 - $\{\text{C}_6\text{H}_4\text{NCH}_2\text{NP}(\text{Se})\text{Ph}_2\}\text{Al}(\text{Me})_2$] can

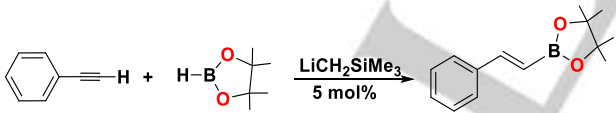
be employed for the chemoselective hydroboration of alkenes and alkynes under mild conditions.^[33] Later, our group also reported the use of a Ti^{IV} complex, [(Ph₂P(BH₃)N)₂C₆H₄Ti(NMe₂)₂], as an efficient catalyst in the facile hydroboration of terminal alkynes under mild conditions to yield corresponding alkenyl borane products in good quantity.^[34] Here, we report the use of an easily accessible, non-toxic, and environment-friendly catalyst, neosilyllithium (LiCH₂SiMe₃), in the hydroboration of alkynes and alkenes in the presence of HBpin to generate a broad scope of alkyl boronic ester products in excellent yields under lenient conditions. We also performed intramolecular and intermolecular reactions to study the efficiency of the catalyst. Further, we explored the mechanistic details using computational studies, and report our findings here.

Results and discussion

Hydroboration of alkynes:

Initial reactions were carried out using phenylacetylene as a prototypical substrate. The reaction of phenylacetylene (1 mmol) with HBpin (1.2 mmol) in the presence of catalyst LiN(SiMe₃)₂ (2 mol %) yielded 55% of the corresponding boronate ester (Table 1, entry 1). Higher loading of LiN(SiMe₃)₂ (5 mol %) afforded 71% of the exclusive boronate ester (Table 1, entry 2). The use of NaN(SiMe₃)₂ and KN(SiMe₃)₂ as catalysts in the presence of HBpin under neat conditions yielded 74% and 78% of the corresponding boronate products respectively (Table 1, entries 3–4). However, using the catalyst LiCH₂SiMe₃ (2 mol %) in solvent-free conditions afforded 70% of the anti-Markovnikov product exclusively after 8 hours (Table 1, entry 5). The increased amount of catalyst used (5 mol % of LiCH₂SiMe₃) afforded 92% of the boronic ester (Table 1, entry 6). Toluene, THF, and hexane were also used as solvents to examine which of them is most effective during the catalytic reaction. This resulted in a slight decrease in the quantity of boronate ester products obtained (Table 1, entries 7–9).

Table 1. Optimization table for catalytic hydroboration of terminal alkynes in presence of LiCH₂SiMe₃.

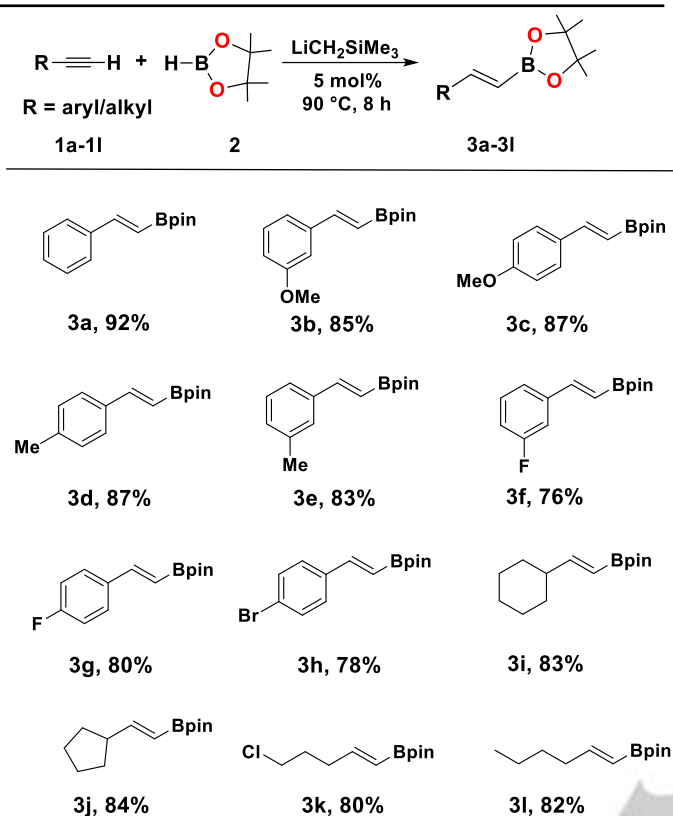


Entry	Catalyst	Cat mol%	Medium	Time (h)	Isolated Yield (%) ^a
1	LiN(SiMe ₃) ₂	2	Neat	8	55
2	LiN(SiMe ₃) ₂	5	Neat	8	71
3	NaN(SiMe ₃) ₂	5	Neat	8	74
4	KN(SiMe ₃) ₂	5	Neat	8	78
5	LiCH ₂ SiMe ₃	2	Neat	8	70
6	LiCH₂SiMe₃	5	Neat	8	92
7	LiCH ₂ SiMe ₃	5	Toluene	8	90
8	LiCH ₂ SiMe ₃	5	THF	8	82
9	LiCH ₂ SiMe ₃	5	Hexane	8	88

Reaction conditions: phenylacetylene (1 mmol), HBpin (1.2 mmol) in a specified solvent at 90 °C. ^aIsolated yields.

With 5 mol % of LiCH₂SiMe₃, the temperature of 90 °C, and 8 hours of reaction time being identified optimized conditions, we first explored the scope of various terminal alkynes with electron-donating as well as electron-withdrawing substituents on aromatic moieties in the presence of HBpin. The addition of HBpin to different alkynes using 5 mol% of LiCH₂SiMe₃ confirms the formation of anti-Markovnikov products in good yields (Table 2). The electron-donating groups on aromatic rings, such as 3-methoxyphenylacetylene, 4-methoxyphenylacetylene, 4-methylphenylacetylene, and 3-methylphenylacetylene converted efficiently to the desired products in excellent yields within 8 hours of reaction time (Table 2, entries **3b–3e**). Furthermore, when we extended the scope of reactivity to electron-withdrawing substituents, such as 3-fluorophenylacetylene, 4-fluorophenylacetylene, and 4-bromophenylacetylene, they successfully converted into the anti-Markovnikov products in good yields (Table 2, entries **3f–3h**).

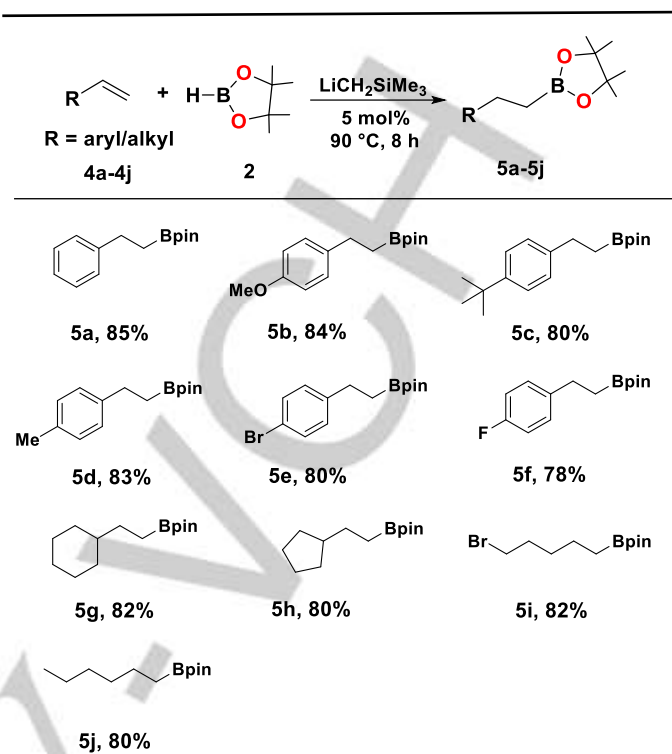
After successfully utilizing the aromatic acetylenes, we extended the scope of reactivity to various aliphatic alkyne moieties, such as ethynyl cyclohexane, ethynyl cyclopentane, and 5-chloropentyne. These were smoothly converted to corresponding boronate ester products with yields of 83%, 84%, and 80% respectively (Table 2, entries **3i–3k**). The use of 1-hexyne also resulted in smooth conversion, yielding 82% of the product under optimal reaction conditions (Table 2, entries **3l**).

Table 2. The scope of catalytic hydroboration of alkynes with HBpin in presence of $\text{LiCH}_2\text{SiMe}_3$.

Reaction conditions: alkyne (1 mmol), HBpin (1.2 mmol); all reactions were carried out at 90 °C under neat conditions for 8 h. ^aIsolated yields.

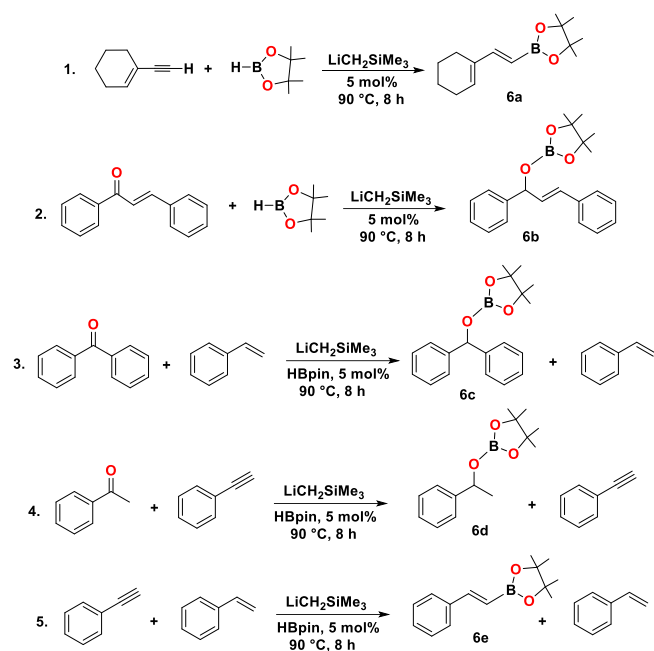
Hydroboration of alkenes:

We expanded the scope of our procedure to hydroboration of alkenes using 5 mol% of $\text{LiCH}_2\text{SiMe}_3$ and HBpin. With the optimal conditions being 5 mol% of the Li-catalyst, 90 °C, and 8 hours of reaction time, we reviewed catalyst efficiency in the case of diverse aromatic and aliphatic alkenes (Table 3). To begin with, the reaction was carried out using styrene in presence of $\text{LiCH}_2\text{SiMe}_3$ and HBpin, yielding 85% of the corresponding boronate product (Table 3, entry 5a). Aromatic alkenes with electron-releasing groups on the aryl ring, such as *p*-methoxy, *p*-*tert*-butyl, and *p*-methyl styrenes contributed to the desired alkyl boronate ester products in excellent yields (Table 3, entries 5b–5d). Similarly, electron-withdrawing substituents on phenyl rings, such as *p*-bromo styrene and *p*-fluoro styrenes also underwent smooth transformations to yield corresponding alkyl boronate ester products in good quantities (80% and 78%, respectively) (Table 3, entries 5e–5f). Additionally, cyclic styrenes, such as cyclohexyl and cyclopentyl styrenes, also reacted smoothly to form the yielding 82% and 80% of the corresponding products, respectively (Table 3, entries 5g–5h). Further, aliphatic substrates such as 5-bromo-1-pentene and hex-1-ene reacted readily in the presence of $\text{LiCH}_2\text{SiMe}_3$ and HBpin to form their alkenyl boronate products in good yields (Table 3, entries 5i–5j).

Table 3. The scope of catalytic hydroboration of alkenes with HBpin in presence of Li-catalyst.

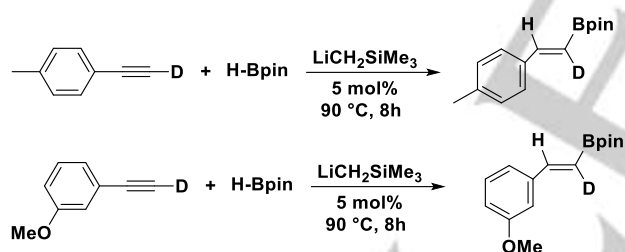
Reaction conditions: styrene (1 mmol), HBpin (1.2 mmol); all reactions were carried out at 90 °C in 0.5 mL of toluene for 8 h. ^aIsolated yields.

To examine the reactivity of the Li-alkyl catalyst on various functional groups, we carried out intra- and intermolecular hydroboration of different substrates (Scheme 1, entries 1–5). The reaction of 1-ethynylcyclohex-1-ene with $\text{LiCH}_2\text{SiMe}_3$ selectively reduces the terminal alkyne over the internal alkene (Scheme 1, entry 1). Further, we performed the hydroboration of *trans*-chalcone with HBpin in which the ketone functional group is reduced preferentially with a yield of 94% due to the higher reactivity of the carbonyl group over the alkene moiety (Scheme 1, entry 2). Similarly, the reaction between benzophenone and styrene in the presence of Li-catalyst selectively reduces the former over the latter at 90 °C in a reaction time of 8 hours (Scheme 1, entry 3). Under analogous reaction conditions involving acetophenone and phenylacetylene, acetophenone showed ideal reduction with a yield of 95% over phenylacetylene (Scheme 1, entry 4). Finally, phenylacetylene and styrene reacted in the presence of $\text{LiCH}_2\text{SiMe}_3$ and HBpin to reduce the alkyne (Scheme 1, entry 5).



Scheme 1. Intra- and intermolecular hydroboration of various functional groups.

The reaction between a deuterium-labeled methyl derivative of phenylacetylene-d1 and HBpin in the presence of $\text{LiCH}_2\text{SiMe}_3$ (5 mol %) authenticated the exclusive formation of an anti-Markovnikov product. Analogous outcomes were achieved when a methoxy derivative of deuterium-labeled phenylacetylene was used, confirming the regio-selectivity of the lithium metal catalyst (Scheme 2).



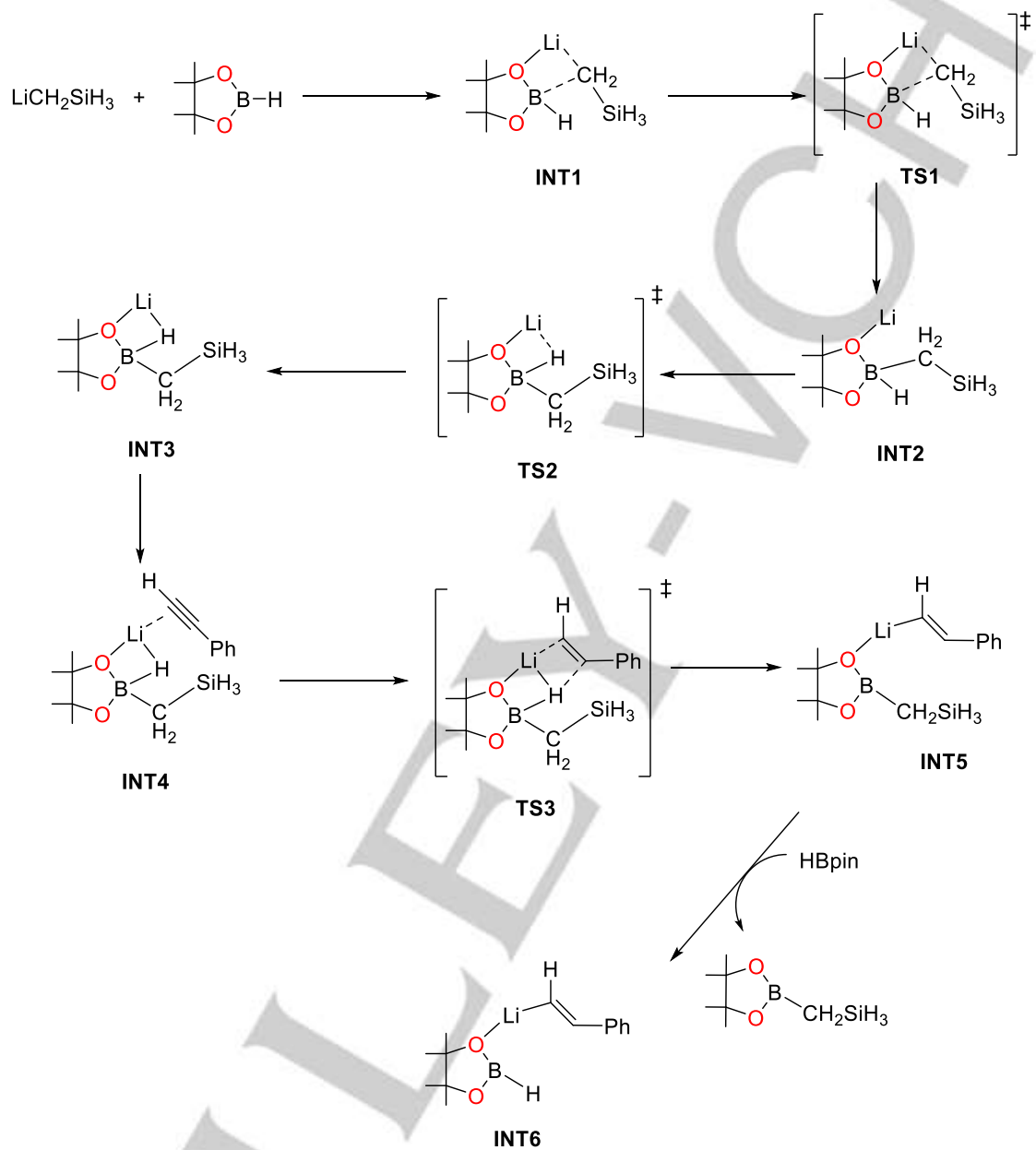
Scheme 2. Reaction with deuterium-labeled alkynes.

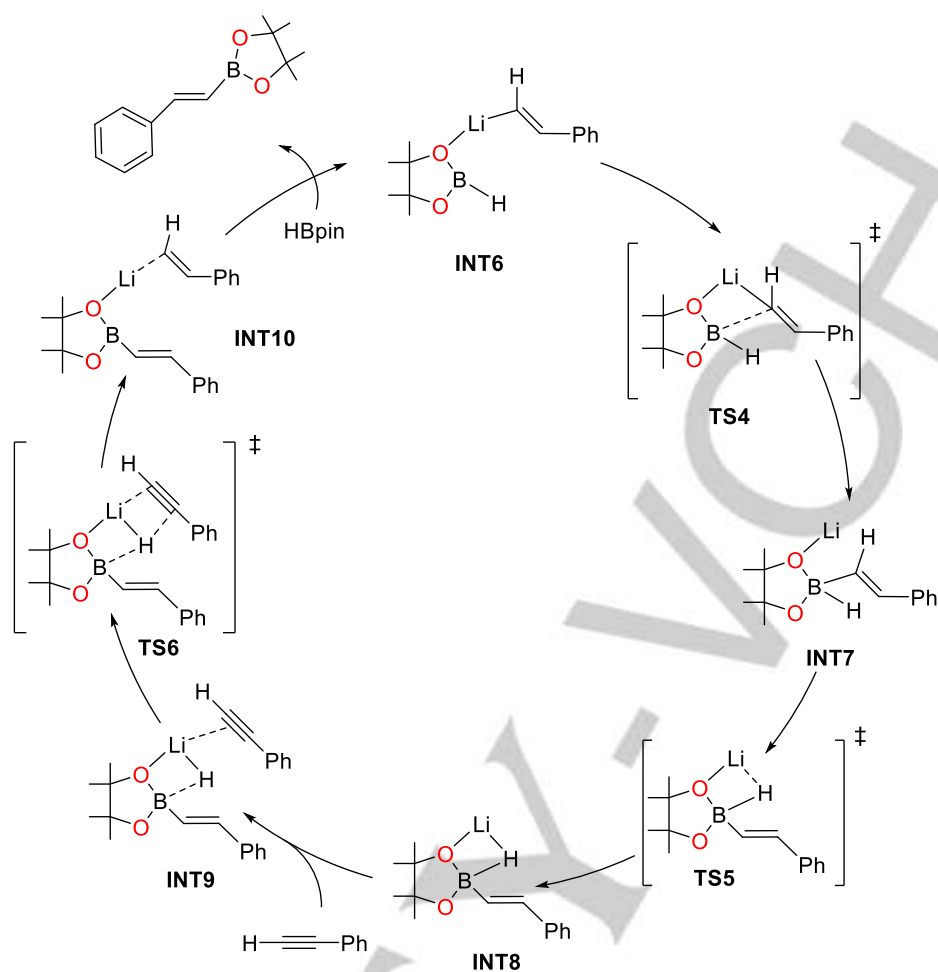
Computational study

To explore the mechanistic pathway for the $\text{LiCH}_2\text{SiMe}_3$ catalyzed hydroboration of alkynes, here we have carried out density functional theory (DFT) calculations using BP86/def2-SVP level of theory.^[24] Here, we have used a truncated model $\text{LiCH}_2\text{SiH}_3$ as a catalyst for computational modeling and explored the mechanistic pathway for hydroboration. Furthermore, DLPNO-CCSD(T) calculations with TightPNO settings were carried out on the DFT optimized structures to determine the accurate energetics of the reaction.^[35-37] (see Supporting information for details on Computational Methods). The DLPNO-CCSD(T) computed free energy profile pathway is provided in Figure 2.

In the first step, $\text{LiCH}_2\text{SiH}_3$ catalyst binds with HBpin through Li-O coordination and forms a stable intermediate ($\Delta G_{298} = -7.8$ kcal/mol; $\Delta H_{298} = -19.7$ kcal/mol). The formation of stable

intermediate INT1 indicates that the $\text{LiCH}_2\text{SiH}_3$ catalyst favors binding with HBpin.^[38-39] In the next step, INT1 undergoes intramolecular rearrangement where the silylmethyl group attacks the boron atom of HBpin via a four-membered transition state (TS1). The activation barrier for this rearrangement is 7.5 kcal/mol, and the observed product (INT2) is 8.2 kcal/mol stabilized compared to INT1. Natural bonding orbital analysis of TS1 reveals that the $2p_x$ orbital of the carbon atom of the silylmethyl group interacts with the vacant π^* $2p_x$ orbital of B-O bond (90% B + 10% O). Second-order perturbation analysis estimates this interaction to be -24.3 kcal/mol (see Figure 3), indicating the facile transfer of the silylmethyl group to HBpin. Subsequently, INT2 reorganizes via an intramolecular rearrangement to form INT3, where the latter form (INT3) represents the active form of the catalyst. In the next step, the phenylacetylene (PhAc) interacts with INT3 and forms a weakly coordinating intermediate INT4. Later, INT4 is rearranged through a six-membered ring transition state (TS3), where a hydride migration occurs from the boron atom to the carbon of PhAc, forming INT5.^[39-42] The activation barrier for this step is 16.9 kcal/mol ($\Delta H_{298} = 15.1$ kcal/mol). The structure of TS3, along with relevant structural parameters, is depicted in Figure 3. It is evident from Figure 3 that in TS3, the C-C bond length of PhAc is 1.266 Å, while the B-H/C-H bond lengths (involved in hydride migration) are 1.384 Å / 1.718 Å, respectively (see Figure 3). On the other hand, in INT4, the C-C bond length (PhAc) and B-H/C-H bonds lengths are 1.231 Å, and 1.318 Å / 3.300 Å, respectively. Comparing the structural data of INT4 and TS3 reveals that the B-H bond and the C-C bond of PhAc rupture simultaneously in TS3, indicating hydride migration (i.e., the formation of the C-H bond). Structural topology of TS3 reveals that the σ (B-H) bonding orbital (37%B + 62%H) aligns properly to interact with the π^* $2p_y$ orbital of C-C bond in PhAc, thus offering an ideal condition for hydride migration. Second-order perturbation analysis estimates this interaction to be -18.8 kcal/mol (see Figure 3). TS3 results in the formation of the desired anti-Markovnikov intermediate (INT5), which is thermodynamically more stable than all preceding intermediates. In the next step, ligand exchange occurs where the HBpin molecule takes out the silylmethyl group and forms INT6. Later, alkene migration occurs from the loosely bounded lithium to the boron of HBpin, forming the intermediate INT7, with an activation barrier of 6.7 kcal/mol ($\Delta H_{298} = 5.3$ kcal/mol). The observed INT7 is 15.6 kcal/mol more stable than the INT6, and this large stabilization is a consequence of the facile transfer of lone pair of alkene carbon to the vacant 2p orbital of the boron atom. Second-order perturbation estimates this interaction to be -27.8 kcal/mole in TS4 (see Figure 3). In the next step, an intramolecular rearrangement takes place, where the zwitterionic intermediate INT7 rearranges to INT8 (generating the active form of the catalyst) via TS5. In the next step, the second molecule of PhAc interacts with INT8 and forms INT9 (very similar to INT4), which undergoes the hydride migration via a six-membered transition state (TS6) and generates INT10. In the last step, another molecule of HBpin interacts with INT10 and forms the desired anti-Markovnikov product by ligand exchange and regenerates INT6 for the next catalytic cycle (see Figure 2).





Scheme 3. A most plausible mechanism for the hydroboration of alkynes.

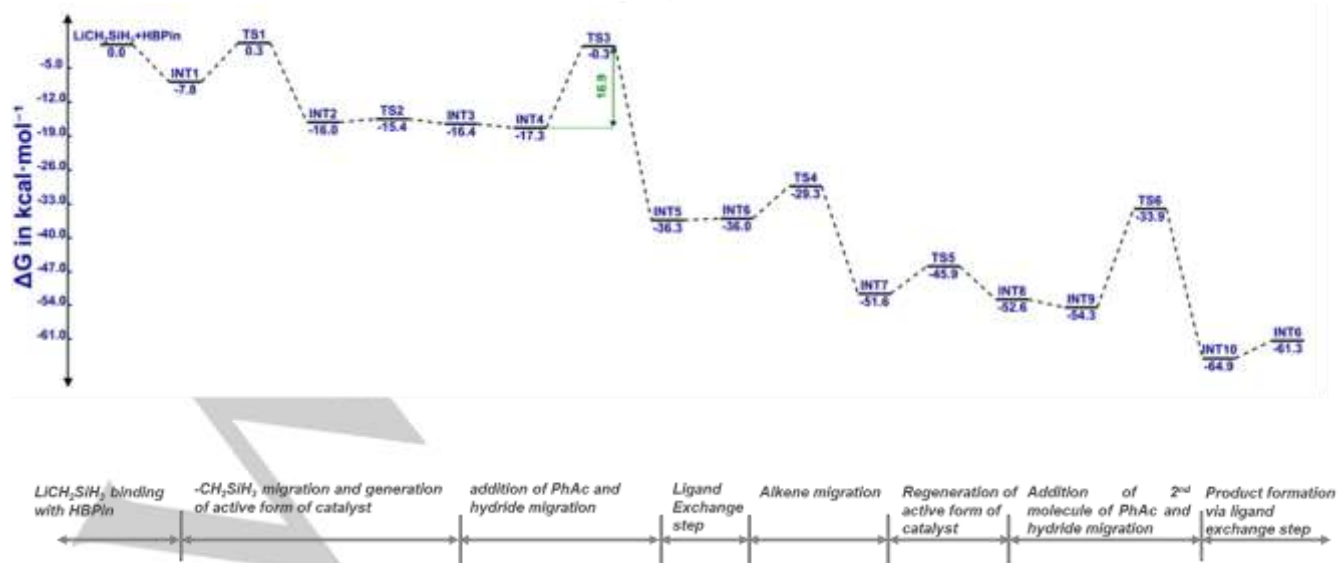


Figure 2. DLPNO-CCSD(T)-computed free energy profile (in kcal/mol) for the hydroboration of alkynes.

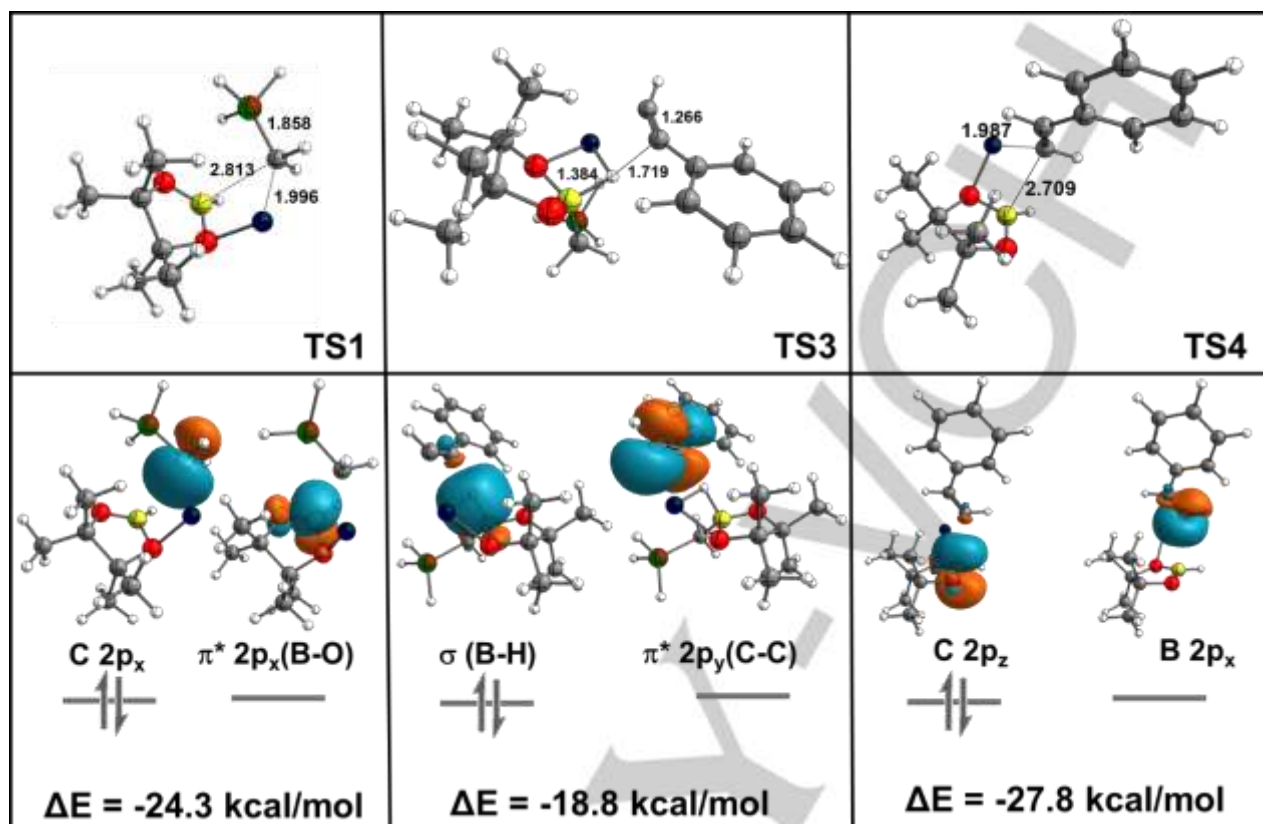


Figure 3. DFT optimized structure of **TS1**, **TS3**, and **TS4** along with relevant structural parameters (top). Three-dimensional contour plot of NBO representing the most stabilizing interactions involved in the transition state **TS1**, **TS3**, and **TS4** (bottom). The ΔE here represents the donor–acceptor interactions obtained from the second-order perturbation analysis. Colour code: B (yellow), O (red), C (grey), Li (blue), and H (white).

Conclusions

We have reported here a novel methodology for the catalytic hydroboration of alkynes or alkenes using neosilyllithium and pinacolborane. The efficacy of the Li-alkyl catalyst was examined using different substituents on the aromatic as well as aliphatic alkynes. Additionally, the catalyst proficiently converted various alkenes to the corresponding alkyl boronate ester products in quantitative yields under solvent-free conditions. In the reaction mechanism proposed, the formation of metal hydride plays an important role in the conversion of initial compounds to the desired products, which is also evidenced by DLPNO-CCSD(T) calculations.

Conflict of Interest

The authors have no conflicts of interest to declare.

Experimental Section

All manipulations involving air- and moisture-sensitive compounds were carried out under argon atmosphere, using the standard Schlenk

technique or argon-filled glove box. CDCl_3 was distilled and stored in the glovebox. ^1H NMR (400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz), and $^{11}\text{B}\{^1\text{H}\}$ (128.3 MHz) spectra were measured on a BRUKER AVANCE III-400 spectrometer. $\text{LiCH}_2\text{SiMe}_3$ was prepared as per reports in the literature.^[43] All the starting materials, including alkynes and alkenes, were purchased from Sigma Aldrich India, TCI chemicals, and used without further purification. HBpin was purchased from Sigma Aldrich India and distilled before use. Deuterated phenylacetylene was prepared according to the reported literature procedures.^[44]

General procedure for the synthesis of compounds (3a–3l) and (5a–5j)

$\text{LiCH}_2\text{SiMe}_3$ (5 mol%), alkynes (**1a–1l**) or alkenes (**4a–4j**) (1.0 mmol), and HBpin (1.2 mmol) were added into a 25 mL Schlenk flask inside an argon-filled glove box under an inert atmosphere. Thereafter, the reaction mixture was stirred at 90 °C for 8 hours under neat conditions (0.5 mL of toluene for styrene). The resulting boronic ester product was separated using silica-gel column chromatography with 2% EtOAc as an eluent (in the case of styrene). Further, removing the solvent under reduced pressure enabled the generation of the corresponding boronic ester products. NMR spectra of all the products were given in supporting information.

Supporting Information

Hydroboration of alkynes and alkenes with HBpin was performed in the presence of $\text{LiCH}_2\text{SiMe}_3$ under neat conditions at 90 °C. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{11}\text{B}\{^1\text{H}\}$ NMR for the final products as well as computational details are given in the supporting information (electronic format).

Acknowledgments

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Keywords: Hydroboration • lithium catalyst • alkynes • alkenes

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