

Aluminum-Catalyzed Selective Hydroboration of Alkenes and Alkynylsilanes

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Supporting Information

ABSTRACT: An efficient aluminum-catalyzed selective hydroboration of alkenes and alkynylsilanes is reported. A wide variety of alkenes and alkynylsilanes bearing various functional groups and heterocyclic substituents were converted to boronic ester products in good yields with high selectivity. Mechanistically, density functional theory calculations favored a mechanism involving the insertion of the double bond into the Al–H species followed by C–Al/B–H metathesis.

KEYWORDS: aluminum catalysis, hydroboration, alkenes, alkynylsilanes, main-group metals

I n order to develop a new generation of sustainable and environmentally benign catalysts for important organic transformations, catalysis by main-group metals is widely recognized as a promising alternative to transition metal catalysis.^{1,2} Transformations catalyzed by main-group metals, however, are almost entirely limited to the reduction of unsaturated polar bonds found in aldehydes, ketones, and imines (Scheme 1a).³ Aluminum, the most abundant metallic

Scheme 1. Main-Group-Metal-Catalyzed Hydroboration

a) Main-group metal catalyzed hydroboration of carbonyl compounds

$$\begin{array}{c} X \\ R^{1} \\ R^{2} \\ X = 0, N \end{array} + HBpin \qquad \begin{array}{c} AI, Mg, Ca, etc. \\ \hline well \ developed \end{array} \qquad \begin{array}{c} X \\ R^{1} \\ R^{2} \end{array}$$

b) Al-catalyzed hydroboration of alkynes or alkenes

$$R^1 \xrightarrow{---} R^2$$
 + HBpin $\xrightarrow{Al cat.} R^1 \xrightarrow{R^2} R^2$

c) Al-catalyzed hydroboration of alkenes and alkynylsilanes

$$\begin{array}{c} R^{1} & \xrightarrow{\text{AlEt}_{3} \text{ or } AlMe_{3}} \\ \text{or} & \xrightarrow{\text{HBpin}} & R^{1} & \xrightarrow{\text{Bpin}} & \text{or} & \xrightarrow{\text{H}} & \xrightarrow{\text{Bpin}} \\ R^{1} & \xrightarrow{\text{SiR}_{3}} & \text{this work} \end{array}$$

element, is essentially confined to the role of a simple Lewis acid catalyst in reactions that employ it in substoichiometric quantities.⁴ The development of other catalytic applications and roles for aluminum would greatly expand the utility of this widely available element, and reactions in which this maingroup element mimics and takes the place of transition metal catalysts are especially desirable.²

Hydroboration of alkenes and alkynes is a fundamental approach to the preparation of organoboron compounds, which are versatile building blocks for organic synthesis.³ Numerous hydroboration reactions catalyzed by transition metals, both noble and earth-abundant, have been reported.^{6,7} However, there have been only a few examples of aluminumcatalyzed hydroboration of unsaturated hydrocarbons, and the scope of this transformation was limited to simple alkynes as substrates (Scheme 1b).8 Although the stoichiometric hydroalumination of alkenes is well-known,⁹ a more efficient catalytic reaction was disclosed only recently.¹⁰ Considering the low toxicity, low cost, and sustainable nature of aluminum catalysts, further expansion of the substrate scope for aluminum catalysis and elucidation the mechanism of this chemistry are still attractive. Herein, as a continuation of our efforts on hydroboration reactions,¹¹ we report the development of an efficient aluminum-catalyzed hydroboration of alkenes and alkynylsilanes (Scheme 1c).

To begin our investigation of the aluminum-catalyzed hydroboration of alkenes, we chose 4-phenyl-1-butene (1a) as the model substrate and HBpin as the boron source (Table 1). After extensive optimization, we found that 10 mol % AlEt₃ efficiently promoted the hydroboration reaction, affording the linear boronic ester 2a with excellent regioselectivity in high isolated yield (86%) (entry 1). In the absence of AlEt₃, only a 6% yield of the product was obtained (entry 2), which illustrates the critical role of the aluminum catalyst for this transformation. Compared with ether and halogenated

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Table 1. Reaction Optimization

	+ HBpin AIEt ₃ (10 mol%)	Bpin
Pn ~	toluene (0.4 M)	· ·
1a (0.5 m	mol) 1.5 equiv 100 °C, 24 h	2a
entry	variation from the "standard" conditions	yield (%) ^a
1	none	93 (86)
2	without AlEt ₃	6
3	dioxane instead of toluene	75
4	DCE instead of toluene	83
5	AlMe ₃ instead of Et ₃ Al	91
6	DIBAL-H instead of Et ₃ Al	75
7	Al(OiPr)3 instead of Et3Al	83
8	Al(OtBu) ₃ instead of Et ₃ Al	27
9	AlMe ₂ Cl instead of Et ₃ Al	42
10	Using 5 mol % AlEt ₃	69
11	80 °C instead of 100 °C	55

^{*a*}Determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard; an isolated yield is shown in parentheses.

solvents, the use of toluene as the solvent delivered superior yield (entries 3 and 4). Diisobutylaluminum hydride, aluminum isopropoxide, and AlMe₃ all proved to have good catalytic activity, giving 2a in 75–91% yield (entries 5–7), while the use of more sterically hindered aluminum *tert*-butoxide decreased the yield dramatically (entry 8). The use of an aluminum catalyst with higher Lewis acidity (Me₂AlCl) afforded a lower yield (entry 9). In addition, decreased catalyst loadings and temperatures resulted in reduced yields of 2a (entries 10 and 11).

With the optimized conditions in hand, we then explored the scope of alkene substrates for this hydroboration reaction. We found that these simple but effective reaction conditions could convert a wide array of olefins into the corresponding linear boronic ester products in moderate to high yields with high regioselectivity (Table 2). Various functional groups were tolerated under the reaction conditions, including an alkyl chloride (2c), an alkyl bromide (2d), a dihaloaryl group (2w), a tertiary amine (2j), ethers (2f-j), a trifluoromethyl ether (2h), thioethers (2i and 3a), a silvl ether (2n), alkyl and aryl silanes (2k-m), and an arylboronic acid pinacol ester (2x). Compounds with an acidic proton, such as a free alcohol (2e)and a secondary amine (2z) were also competent substrates after in situ protection under the hydroboration conditions in the presence of an excess amount of HBpin. Moreover, terminal alkenes bearing heterocycles, including a furan (2y), an indole (3b), a pyrazole (3c), and a carbazole (3d), were also found to be compatible with our hydroboration protocol. In addition, electron-rich and electron-deficient styrenes also reacted smoothly to give boronic ester products (2o-u) in 55-79% yield with good to excellent anti-Markovnikov regioselectivity (all examples >9:1). Unsurprisingly, substrates bearing reducible functional groups, such as ester, nitrile, and carbonyl groups, were not tolerated under the conditions. Lastly, a gram-scale reaction (5 mmol) furnished product 2a in a similarly high yield.

To further demonstrate the generality of our protocol, we expanded it to the selective hydroboration of alkynylsilanes (Table 3a).¹² We found that the use of a 20% loading of AlMe₃ catalyst was effective to convert a broad array of alkynylsilanes to form trisubstituted olefins with C–Si and C–B bonds on the same carbon atom as single isomers. Alkyl- and aryl-substituted alkynylsilanes bearing different substituents on the

Table 2. Substrate Scope of Alkenes^a



^{*a*}Conditions: 0.5 mmol of alkene substrate, 0.75 mmol of HBpin, and 0.05 mmol of AlEt₃ in 1.25 mL of toluene at 100 °C for 24 h. Isolated yields are given. Unless otherwise indicated, a single regioisomer (>99:1) of the hydroborated product was obtained. Linear/branched ratios were determined by GC–MS analysis of the crude reaction mixtures and are shown in parentheses. ^{*b*}Using 3.0 equiv of HBpin.

silicon were competent substrates, delivering the corresponding products with high regio- and stereoselectivities. Moreover, a gram -scale reaction was successfully conducted to afford product **5a** in a similarly high yield, demonstrating the practicality of this hydroboration method. In addition, these boron- and silicon-difunctionalized alkenes are particularly attractive compounds because of their ability to be selectively manipulated through orthogonal cross-coupling reactions. To demonstrate this strategy, **5a** was readily transformed into stereodefined vinylsilane **7a** in high yield through a Suzuki– Miyaura reaction (Table 3b).¹³ Table 3. Substrate Scope of Alkynylsilanes and Selective Transformation of $5a^a$



"Isolated yields are given. The regio- and stereoselectivities were determined by NMR and GC analyses.

To understand the catalytic role of the aluminum catalyst, we explored the hydroboration with density functional theory calculations at the M06-2X/6-311+G(d,p)-SMD(toluene)// B3LYP/6-31G(d)-SMD(toluene) level¹⁴ using 1a as the model substrate and AlMe₃ as the model catalyst. Consistent with the reported mechanism of aluminum-catalyzed hydroboration of alkynes,^{8b} we believe that HAlMe₂ acts the catalyst in the hydroboration of alkenes (Scheme 2). Compared with the Lewis acid-base complex of AlMe₃ and HBpin (8), the separated species lie 6.7 kcal/mol higher in free energy (Scheme 2a). AlMe₃ can further undergo σ -bond metathesis with HBpin to generate HAlMe2 and MeBpin. This process has a free energy barrier of 26.5 kcal/mol relative to 8 and is endergonic by 5.6 kcal/mol (Scheme 2a). Under the experimental conditions, the three forms of aluminum (8, 9, and 10) can be considered to be in equilibrium, favoring the Lewis acid-base complex 8.

The hydridoalane $HalMe_2$ (10) is a feasible active catalyst for the hydroboration, as demonstrated by the calculated free energy changes of the catalytic cycle are shown in Scheme 2b. From 10, hydroalumination of 1a occurs via TS2, leading to alkylaluminum intermediate 12. Subsequent σ -bond metathesis between 12 and HBpin proceeds through TS3, which generates the hydroboration product and regenerates HAlMe₂ for the next catalytic cycle. On the basis of the calculated free energy changes, the on-cycle resting state is alkylaluminum intermediate 12, and the turnover-limiting step is the σ -bond metathesis via TS3 with an overall barrier of 20.3 kcal/mol.¹⁵

We wish to emphasize that the barrier for the generation of the active catalyst 10 via TS1 is 26.5 kcal/mol. Therefore, the overall rate-determining step is the catalyst initiation step, with trimethylaluminum acting as a precatalytic reservoir. Importantly, our computations indicate that an alternative mechanism in which $AlMe_3$ acts as a simple Lewis acid by coordination to the pinacolborane oxygen has a significantly higher overall energetic barrier, with the rate-determining transition state TS4 being 34.0 kcal/mol higher in free energy Scheme 2. Free Energy Changes for (a) σ -Bond Metathesis between AlMe₃ and HBpin, (b) the HAlMe₂-Catalyzed Hydroboration of Alkene 1a, and (c) the Lewis Acid (AlMe₃)-Catalyzed Hydroboration of 1a (Free Energies in kcal/mol Are Shown in Parentheses)



compared with 8 (Scheme 2c). In addition, the barrier for the uncatalyzed hydroboration is $42.1 \text{ kcal/mol.}^{16}$

In summary, a simple and general aluminum-catalyzed hydroboration method was developed that effectively transforms various alkenes and alkynylsilanes into versatile boronic ester products in good yields with high regioselectivity. Computational data favored a mechanism in which the π bond inserts into a catalytic Al–H species followed by C–Al/B–H σ -bond metathesis. In this process, aluminum performs a role similar to those of transition metals in catalytic hydroboration. We believe that the use of suitable chiralligand-bound aluminum catalysts will probably promote the asymmetric hydroboration of alkenes in the future, which may expand the applications of main-group metal catalysis.

EXPERIMENTAL SECTION

General Information. All of the reactions were carried out under an atmosphere of nitrogen with magnetic stirring unless otherwise indicated. Catalytic reactions were performed in 10 mL Schlenk tubes and gram-scale reactions in 25 mL Schlenk tubes. Reaction solvents, including anhydrous toluene, dioxane, dichloroethane (DCE), etc., were purchased from Energy Chemical Co. Ltd. or J&K Chemical Co. Ltd. and used as received. Alkene substrates were synthesized following known procedures or purchased from Energy Chemical Co. Ltd. or Tokyo Chemical Industry Co. Ltd. and used as received. HBpin, AlEt₃, and AlMe₃ were purchased from TCI Reagent Co. Ltd. and stored in the refrigerator. All new compounds were characterized by NMR spectroscopy, IR spectroscopy,

and high-resolution mass spectrometry. NMR spectra were recorded on an Agilent 400 or 600 MHz, Varian 400 MHz, or Bruker 400 MHz spectrometer and were calibrated using residual solvent as an internal reference (CDCl₃: 7.26 ppm for ¹H NMR and 77.16 ppm for ¹³C NMR). The carbons directly attached to the boron atoms were not detected because of quadrupolar relaxation. Melting points were measured on an SGW X-4 apparatus. All of the IR spectra were obtained on a Bruker TENSOR 27 FT-IR spectrometer. Electron ionization high-resolution mass spectrometry (EI-HRMS) was performed on a Waters Micromass G1540N/GCT Premier spectrometer, and electrospray ionization (ESI)-HRMS spectra were obtained on a Thermo Fisher Scientific LTO FT Ultra or an Agilent Technologies 6224 TOF LC/MS system. The GC-MS analysis was performed on a Shimadzu QP2010 SE instrument using a DB-5MS column (30 m, 0.25 mm i.d.).

General Procedure for 0.5 mmol-Scale Catalytic Hydroboration of Alkenes. In a nitrogen-purged Schlenk tube containing a magnetic stirring bar, the alkene substrate (0.5 mmol), toluene (1.25 mL), HBpin (109 μ L, 0.75 mmol, 1.5 equiv), and AlEt₃ (1 M in toluene, 50 μ L, 0.05 mmol, 10 mol %) were added sequentially. The reaction mixture was stirred at 100 °C for 24 h, cooled to room temperature, and quenched by addition of HCl in dioxane (4 M, 0.5 mL). The resulting mixture was then filtered through a short pad of silica gel, eluting with EtOAc. The solvent was removed in vacuo. The linear/branched ratio of the crude product mixture was determined at this stage by ¹H NMR and GC analyses. The crude residue was purified via column chromatography to afford the desired product.

Gram-Scale Synthesis of 2a. In a nitrogen-purged Schlenk tube containing a magnetic stirring bar, alkene substrate **1a** (661.1 mg, 5.0 mmol), toluene (12.5 mL), HBpin (1.09 mL, 7.5 mmol, 1.5 equiv), and AlEt₃ (1 M in toluene, 500 μ L, 0.5 mmol, 10 mol %) were added sequentially. The reaction mixture was stirred at 100 °C for 24 h, cooled to room temperature, and quenched by addition of HCl in dioxane (4 M, 5.0 mL). The resulting mixture was then filtered through a short pad of silica gel, eluting with EtOAc. The solvent was removed in vacuo. The linear/ branched ratio of the crude product mixture was determined at this stage by ¹H NMR and GC analyses. The crude residue was purified via column chromatography to afford the product **2a** as a colorless liquid (1.1 g, 84% yield).

General Procedure for 0.2 mmol-Scale Catalytic Hydroboration of Alkynylsilanes. In a nitrogen-purged Schlenk tube containing a magnetic stirring bar, the alkynylsilane substrate (0.2 mmol), toluene (0.2 mL), HBpin (58 μ L, 0.4 mmol, 2.0 equiv), and AlMe₃ (2 M in toluene, 20 μ L, 0.04 mmol, 20 mol %) were added sequentially. The reaction mixture was stirred at 80 °C for 24 h, cooled to room temperature, and quenched by addition of HCl in dioxane (4 M, 0.4 mL). The resulting mixture was then filtered through a short pad of silica gel, eluting with EtOAc. The solvent was removed in vacuo. The crude product was determined to be a single isomer at this stage by NMR and GC analyses. The crude residue was purified via column chromatography to afford the desired product.

Gram-Scale Synthesis of 5a. In a nitrogen-purged Schlenk tube containing a magnetic stirring bar, alkynylsilane substrate 4 (0.91 g, 5.0 mmol), toluene (5.0 mL), HBpin (1.45 mL, 10.0 mmol, 2.0 equiv), and AlMe₃ (2 M in toluene, 500 μ L, 1.0 mmol, 20 mol %) were added sequentially. The

reaction mixture was stirred at 80 °C for 24 h, cooled to room temperature, and quenched by addition of HCl in dioxane (4 M, 7.5 mL). The resulting mixture was then filtered through a short pad of silica gel, eluting with EtOAc. The solvent was removed in vacuo. The crude product was determined to be a single isomer at this stage by NMR and GC analyses. The crude residue was purified via column chromatography to afford the product **5a** as a colorless liquid (1.32 g, 85% yield).

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.oprd.9b00205.

Experimental procedures, spectroscopic data, and NMR spectra of all products (PDF)

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Notes

The authors declare no competing financial interest.

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(14) Full computational details and complete references for Gaussian 09 and computational methods are included in the Supporting Information.

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(16) Details are included in the Supporting Information.