Supported Lanthanum Borohydride Catalyzes CH Borylation Inside Zeolite Micropores

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Supporting Information  
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Abstract: The zeolite-supported lanthanide La(BH₄)ₓ-HYₓ catalyzes C–H borylation of benzene with pinacolborane (HBpin), providing a complementary approach to precious-metal catalyzed borylations. The sites for catalytic CH activation are generated from La grafted at the Brønsted acid sites (BAS) in micropores of the zeolite, whereas silanolate- and aluminoate-grafted sites are inactive under the reaction conditions. Under typical catalytic conditions, conversion to phenyl pinacolborane (PhBpin) is zero-order in HBpin concentration. A turnover number (TON) of 167 is accessed by capping silanols, selectively grafting at BAS sites, and adding HBpin slowly to the reaction.

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Experimental Procedures

Chemicals and Materials

All manipulations were performed under a dry argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox unless otherwise indicated. Dry and deoxygenated reagents were used throughout. Water and oxygen were removed from anhydrous toluene, pentane, and tetrahydrofuran (THF) purchased from Sigma Aldrich using an IT PureSolv System. 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (HBpin, 97%), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (PhBpin, 97%), chlorotriphenylsilane (TPSCI, 96%), NaBH₄ (99.99%), and 3,5-di-tert-4-butylhydroxytoluene (BHT, 99%) were purchased from Sigma Aldrich. LaCl₃ (99.9% anhydrous) was obtained from Strem. Benzene-d₆ and toluene-d₈ were heated to reflux over Na/K, and vacuum-transferred. Dichloromethane-d₆ was dried and deoxygenated by stirring over activated calcium hydride overnight, followed by distillation. SiO₂ (Aerosil® 380) was purchased from Evonik, Al₂O₃ was purchased from Strem, SiO₂/Al₂O₃ (grade 135) was purchased from Sigma Aldrich, and HY₃₀ (CBV760, Si/Al = 30) was purchased from Zeolyst. All metal oxides were treated at 500 °C for 5 h under dynamic vacuum and stored in a N₂-filled glovebox.

Characterization

Analysis of solutions. ¹H and ¹¹B NMR spectra were collected on a Bruker Avance NEO-400 spectrometer. Gas chromatography-mass spectrometry (GC-MS) analysis were performed using an Agilent 7890A GC and 5975C MS, equipped with a capillary Agilent J&W DB-5ht column.

Analysis of materials. Inductively coupled plasma - optical emission spectrometry (ICP-OES) was performed on an Optima 2100 DV to determine elemental composition (wt %) of lanthanum and boron in the catalysts. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) were collected using a Bruker VERTEX 80 IR spectrometer equipped with a Harrick “Praying Mantis” accessory, and spectra of samples were recorded within the 4000-400 cm⁻¹ wavenumber range. Samples were prepared in the glovebox under N₂ and sealed before measurements.

Solid-state (SS)NMR experiments were performed on a Varian NMR spectrometer operating at 9.4 T, equipped with a 1.7 mm, 3.2 mm and 5 mm dual-resonances MAS probes. All the samples are packed in MAS zirconia rotors in a glove box under nitrogen atmosphere and capped tightly. The samples were spun using N₂ gas to avoid oxygen/moisture contaminations. The detailed experimental conditions are summarized below using the following symbols: vR denotes the magic-angle spinning (MAS) rate, vRF(X) the magnitude of the radio frequency (RF) magnetic field applied to X spins, tCP the cross-polarization (CP) contact time; tRD the recycle relay; ns the number of scans.

| Spectrum | Experiment | Experimental Parameters |
|----------|------------|------------------------|
| Figure S2 (c) | ¹¹B DP MAS | vR = 20 kHz, vRF (11B) = 8.5 kHz for 15-degree pulse, tRD = 1 s, ns = 4000. |
| Figure S4 | ²⁹Si{¹H} CPMAS | vR = 5 kHz, tCP = 5 ms, vRF (1H) = 7.5 kHz for spinal-64 heteronuclear decoupling. tRD = 4 s, ns = 64000. |
| Figure S5 | ¹¹B MQ MAS | vR = 20 kHz, vRF (11B) = 83 kHz for the excitation and conversion pulse, vRF (11B) = 8.7 kHz for the z-filter selective pulse, vRF (1H) = 51 kHz for spinal-64 heteronuclear decoupling, tRD = 1 s, ns = 384. |
| Figure 2 | ¹¹B 15-degree pulse MAS | vR = 20 kHz, vRF (11B) = 8.5 kHz for 15-degree pulse, tRD = 1 s, ns = 8000. |

Catalyst Preparation and Characterization

Synthesis of La(BH₄)₃(THF)₃. La(BH₄)₃(THF)₃ was synthesized via reported method.[¹] LaCl₃ (2.455 g, 10.01 mmol) and excess sodium borohydride (1.515 g, 40.05 mmol) were heated at reflux in dry THF for 5 d. The solution was filtered using a cannula filtration to remove the residual NaBH₄ and NaCl. The filtrate was then evaporated under vacuum, giving a solid residue that was extracted
with toluene. The extracts were concentrated and then cooled to −30 °C, giving La(BH₄)(THF)₃ as a colorless powder that was isolated and stored under N₂ in a glovebox. The ¹H and ¹¹B NMR (see Figure S2) and DRIFTS spectra (see Figure S4) match the literature.[⁵] ¹H NMR (toluene-d₈, 400 MHz, 25 °C): δ 1.35 (t, 12 H, THF-CH₂), 1.73 (br q, 12 H, ¹Jₘ = 80 Hz, BH₄), δ 3.82 (t, 12 H, THF-OCH₂). ¹¹B NMR (toluene-d₈, 400 MHz, 25 °C): δ 19.03 (p, ¹Jₘ = 85 Hz, BH₄). DRIFTS of La(BH₄)(THF)₃ (cm⁻¹): 3100-2850 (m, vBH), 2500-2050 (m, vSiOH), 1900-1750 (m, vterminal BH₄). ¹H NMR (toluene-d₈, 400 MHz): 3.82 (t, 12 H, THF-OCH₂), 1.73 (br q, 12 H, ¹Jₘ = 80 Hz, BH₄), δ 1.35 (t, 12 H, THF-CH₂). ¹¹B NMR (toluene-d₈, 400 MHz): δ 19.03 (p, ¹Jₘ = 85 Hz, BH₄). DRIFTS of La(BH₄)(THF)₃ (cm⁻¹): 3100-2850 (m, vBH), 2250-2050 (m, vterminal BH₄). ¹H NMR (toluene-d₈, 400 MHz): 3.82 (t, 12 H, THF-OCH₂), 1.73 (br q, 12 H, ¹Jₘ = 80 Hz, BH₄), δ 1.35 (t, 12 H, THF-CH₂). ¹¹B NMR (toluene-d₈, 400 MHz): δ 19.03 (p, ¹Jₘ = 85 Hz, BH₄). DRIFTS of La(BH₄)(THF)₃ (cm⁻¹): 3100-2850 (m, vBH), 2250-2050 (m, vterminal BH₄).

Preparation of TPS-HY₃₀. In a typical small-scale synthesis, TPSCI (0.065 g, 0.22 mmol) was dissolved in pentane (5 mL), and HY₃₀ (0.300 g) was added. The mixture was stirred at room temperature for 24 h. The supernatant was decanted, the solid was washed with pentane (3 × 5 mL), and the isolated material was dried under dynamic vacuum (10⁻⁴ mbar) at room temperature for 24 h.

In a typical moderate scale synthesis, TPSCI (0.435 g, 1.48 mmol) was dissolved in pentane (30 mL). HY₃₀ (2.00 g) was added, and the mixture was stirred at room temperature for 48 h. The supernatant was decanted, the solid was washed with pentane (3 × 30 mL), and the solid was dried under dynamic vacuum (10⁻⁴ mbar) at room temperature for 24 h.

General procedure for grafting of La(BH₄)(THF)₃ onto supports. A toluene solution of La(BH₄)(THF)₃ (0.040 g, 0.10 mmol, 5 mL) was added to the support (0.300 g). The mixture was stirred at room temperature for 20 h. The supernatant was decanted, the solid was washed with toluene (3 × 5 mL), and the material was dried under dynamic vacuum (10⁻⁴ mbar) at room temperature for 20 h. The isolated materials were characterized by DRIFTS (see Figure S4), and La loading was determined by ICP-OES (see Table S3). La(BH₄)(THF)₃·SiO₂/Al₂O₃ (cm⁻¹): 3735 (w, vSiOH) 3100-2850 (m, vCH), 2445 (s, vBH-terminal), 2250-2050 (m, vterminal BH₄). La(BH₄)(THF)₃·Al₂O₃ (cm⁻¹): 3720 (w, vAlOH) 3100-2850 (m, vCH), 2450 (s, vBH-terminal), 2250-2050 (m, vterminal BH₄).

Analysis of release of THF per La during grafting. La(BH₄)(THF)₃ (0.010 g, 0.025 mmol) and 1,3,5-trimethoxybenzene (TMB; 0.005 g, 0.03 mmol) were dissolved in benzene-d₆ (1.0 mL) in a J. Young NMR tube. TPS-HY₃₀ (0.030 g) was added, and the mixture was agitated at room temperature for 20 h using an orbital shaker. Solution-phase ¹H NMR spectra of the mixture were acquired before and after the addition of TPS-HY₃₀. The concentrations of La(BH₄) and THF were determined by integration of these signals, the TMB signals, and the residual ¹H signal in the benzene-d₆ solvent.

Poisoning spectrochemical analysis experiments with BHT. BHT (0.005 g, 0.02 mmol) was dissolved in toluene (2.0 mL). La(BH₄)(THF)₃·HY₃₀ (0.100 g) or La(BH₄)(THF)₃·TPS-HY₃₀ (0.100 g) was added, and the reaction mixture was stirred at room temperature for 4 h. The solid materials were recovered, washed with anhydrous toluene (3 × 5 mL), dried under vacuum (10⁻⁴ mbar) overnight, and then analyzed by SS NMR spectroscopy.

Catalytic Borylation Experiments

Catalyst testing and optimization studies. In a typical experiment, an air-tight, Teflon valved, re-sealable glass reactor was charged with the precatalyst (~0.004 mmol La, 0.050-0.150 mg, see Table 1), benzene (1.0 mL), and HBpin (0.30 mL, 2.1 mmol) in the glovebox. The reaction vessel heated in a preheated oven for 2.0 h at room temperature for 24 h. The reaction mixture was cooled, the solution was removed from the solid catalyst, and then the reaction mixture was characterized by calibrated GC-MS and ¹¹B NMR spectroscopy. Each experiment was repeated at least two times.

Kinetic investigations. The time-resolved studies of benzene borylation catalyzed by La(BH₄)(THF)₃·TPS-HY₃₀ were performed by heating the catalyst (0.050 g, 0.0025 mmol La), benzene (1.0 mL), and HBpin (0.30 mL, 2.1 mmol) at 120 °C. The experiments were then stopped (cooled) after 2, 4, 6, 8, 10, 12, 16, or 24 h. The TON was determined by calibrated GC-MS analysis. Each time point was a separate experiment.

Product analysis. The yield of PhBpin in the above experiments was determined using calibrated GC-MS. An aliquot of the reaction solution (0.100 g) was withdrawn and mixed with TMB in benzene (100 mM, 0.20 mL). This mixture was then diluted to 1.0 mL solution by adding benzene.

Quantification was achieved using external calibration with TMB. A calibration curve for quantifying PhBpin was constructed by plotting the molar amount of PhBpin as a function of peak area between PhBpin and TMB to obtain the response factor (RF). The amount of PhBpin obtained with the calibration curve, using the following equation:

\[
\text{Molar amount of PhBpin} = \frac{\text{Peak Area (PhBpin)}}{\text{Peak Area (TMB)}} \times \text{RF} \times \frac{\text{weight (total reaction mixture)}}{\text{weight (withdrawn reaction mixture)}}
\]

The conversion of HBpin was monitored with solution ¹H and ¹¹B NMR spectroscopy. Typically, 0.100 g reaction solution was added and mixed with 0.4 mL CD₂Cl₂ to measure NMR spectra. The recycle delay for to obtain quantitative ¹¹B NMR spectra is 20 s. The production of PhBpin was further confirmed using ¹¹B NMR spectroscopy by spiking the reaction solution with authentic PhBpin (Figure S8).
Results

Table S1. HBpin decomposition with metal oxide supports

| Entry | Support | C\textsubscript{6}H\textsubscript{6} (mL) | HBpin (mL) | T (°C) | t (h) | Conversion of HBpin (%) |
|-------|---------|-----------------|-------------|--------|------|------------------------|
| 1     | HY\textsubscript{30} | 1.0             | 0.5          | 120    | 2    | 100                    |
| 2     | SiO\textsubscript{2} | 1.0             | 0.5          | 120    | 2    | 0                      |
| 3     | Al\textsubscript{2}O\textsubscript{3} | 1.0             | 0.5          | 120    | 2    | 0                      |
| 4     | SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} | 1.0             | 0.5          | 120    | 2    | 100                    |
| 5     | TPS-HY\textsubscript{30} | 1.0             | 0.5          | 120    | 2    | 100                    |

Table S2. Concentration of La and B in precatalysts measured by ICP-OES

| Entry | Catalyst | La (wt %) | La (mmol/g) | B (wt %) | B (mmol/g) | B/La |
|-------|----------|-----------|-------------|----------|------------|------|
| 1     | La(BH\textsubscript{4})\textsubscript{2}(THF)\textsubscript{n}-SiO\textsubscript{2} | 2.01 | 0.14 | - | - | - |
| 2     | La(BH\textsubscript{4})\textsubscript{2}(THF)\textsubscript{n}-Al\textsubscript{2}O\textsubscript{3} | 0.33 | 0.02 | - | - | - |
| 3     | La(BH\textsubscript{4})\textsubscript{2}(THF)\textsubscript{n}-SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} | 1.28 | 0.09 | - | - | - |
| 4     | La(BH\textsubscript{4})\textsubscript{2}(THF)\textsubscript{3}-HY\textsubscript{30} | 1.01 | 0.07 | 0.22 | 0.20 | 2.9 |
| 5     | La(BH\textsubscript{4})\textsubscript{2}(THF)\textsubscript{3}-TPS-HY\textsubscript{30} | 0.75 | 0.05 | 0.18 | 0.16 | 3.2 |

Table S3. Comparison of activity of reported catalysts for borylation of benzene

| Reference | Catalyst | Boron reagent | T (°C) | t (h) | TON |
|-----------|----------|---------------|--------|------|-----|
| [3]       | (η\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{5})Rh(η\textsuperscript{4}-C\textsubscript{6}Me\textsubscript{6}) | HBpin | 150    | 45   | 328 |
| [4]       | (η\textsuperscript{5}-C\textsubscript{9}H\textsubscript{7})Ir(η\textsuperscript{4}-C\textsubscript{8}H\textsubscript{12}) + dmpe | HBpin | 150    | 61   | 4500 |
| [4]       | (η\textsuperscript{5}-C\textsubscript{9}H\textsubscript{7})Ir(η\textsuperscript{4}-C\textsubscript{8}H\textsubscript{12}) | HBpin | 150    | 18   | 3   |
| [4]       | (η\textsuperscript{5}-C\textsubscript{9}H\textsubscript{7})Ir(Bpin)\textsubscript{3} | HBpin | 150    | 15   | 3   |
| [5]       | [Ir(η\textsuperscript{5}-C\textsubscript{9}H\textsubscript{7})Cl\textsubscript{2} + 2,2'-bipyridine | B\textsubscript{2}Pin\textsubscript{2} | 80     | 16   | 8000 |
| [6]       | Pyrim-MOF-Co | B\textsubscript{2}Pin\textsubscript{2} | 85     | 48   | 114 |
| [7]       | mBPV-MOF-Ir | B\textsubscript{2}Pin\textsubscript{2} | 115    | 16   | 1000 |
| [7]       | mPT-MOF-Ir | B\textsubscript{2}Pin\textsubscript{2} | 115    | 18   | 1000 |
| [8]       | UiO-67-mix-Ir(III) | B\textsubscript{2}Pin\textsubscript{2} | 80     | 5    | 16   |
| [9]       | Ir-BPy-PMO | B\textsubscript{2}Pin\textsubscript{2} | 80     | 12   | 125 |
| [10]      | Ir-BPy\textsuperscript{110}-PMO | B\textsubscript{2}Pin\textsubscript{2} | 80     | 24   | 640 |
| [11]      | Ir-BPy-PMO | HBpin | 80     | 24   | 728 |
Figure S1. Representative structure of the zeolite HY₃₀, showing the major reactive surface sites.
Figure S2. (a) $^1$H and (b) $^{11}$B NMR spectra of La(BH$_4$)$_3$(THF)$_3$ in toluene-$d_8$; and (c) $^{11}$B DPMAS solid-state NMR spectrum of La(BH$_4$)$_3$THF$_3$. 
Figure S3. $^1\text{H}$ NMR spectra of the La(BH$_4$)$_3$(THF)$_3$ in benzene-$d_6$ solution before and after grafting on TPS-HY$_{30}$. Before grafting, there was 0.075 mmol of BH$_4^-$ and THF (corresponding to 0.025 mmol of La(BH$_4$)$_3$(THF)$_3$) added to the solution, as well as calculated from integrals of the TMB, BH$_4^-$, and THF signals. After grafting, the concentration decreased to 0.024 and 0.033 mmol, respectively. The concentration difference of BH$_4^-$ indicated 0.017 mmol La was taken up by the zeolite through grafting (or physisorption). 0.009 mmol of THF is in excess in the solution compared to the residual BH$_4^-$ in La(BH$_4$)$_3$(THF)$_3$. Therefore, about 0.5 equivalents of THF was released into solution per grafted La species.
Figure S4. DRIFTS spectra of partially dehydroxylated metal oxides (treated at 500 °C under vacuum), reactants for grafting and grafted materials (from the bottom). Bottom group: TPS-Cl, La(BH$_4$)$_3$(THF)$_3$, and La(BH$_4$)$_x$(THF)$_y$-HY$_{30}$. 2nd group from the bottom: SiO$_2$/Al$_2$O$_3$ and La(BH$_4$)$_x$(THF)$_y$-SiO$_2$/Al$_2$O$_3$. 3rd group from the bottom: Al$_2$O$_3$, La(BH$_4$)$_x$(THF)$_y$-Al$_2$O$_3$. Top group: SiO$_2$, and La(BH$_4$)$_x$(THF)$_y$-SiO$_2$ (from bottom to top).
Figure S5. $^{29}$Si[1H] CPMAS solid-state NMR spectrum of TPS-HY. The signal at −101 ppm is assigned to the Si Q$^3$ moiety Si(OH)(OSi)$_3$, corresponding to silanols that are inaccessible to reaction with Ph$_3$SiCl, either because they are too close to Ph$_3$Si–OSi$^-$ on the external surface and are sterically blocked, or they correspond to defects inside the micropores. The signal at −109 ppm is assigned to Si Q$^4$ site corresponding to Si(OSi)$_4$.$^{12}$ The broad peak at −20 ppm is assigned to Ph$_3$Si–OSi$^-$.$^{18}$
Figure S6. $^{11}$B MQMAS spectrum of La(BH$_4$)$_2$(THF)$_{2.5}$-TPS-HY$_{3.0}$. The signals centered at –22 ppm and –15 ppm appear along the chemical shift axis (red dashed line), indicating that two peaks observed in the MAS dimension (horizontal axis) are from two inequivalent boron species, and are not the singularities of the quadrupolar powder pattern resulting from a single species.
Figure S7. Plots of concentration of PhBpin (red line) and HBpin (black line) as a function of time. And fitting parameters of two plots were shown in the table. The zero-order rate constants for PhBpin formation and pseudo-first-order rate constant for HBpin consumption are labeled as $k_1$ and $k_2$, respectively. The term $a$ is a curve-fitting parameter.

| [PhBpin] = $k_1t$ | [HBpin] = $ae^{-k_2t} - k_1t$ |
|-------------------|---------------------------------|
| $10^3 \times k_1$ (mol L$^{-1}$ h$^{-1}$) | 9.7 ± 0.4 |
| $k_2$ (h$^{-1}$) | -- |
| $R^2$ | 0.99 |

$k_2$ (h$^{-1}$) = 0.16 ± 0.11
Figure S8. $^{11}$B NMR of reaction solution (black line) before (black) and after (red) it was spiked with 0.006 g (0.03 mmol) of PhBpin (red line). Reaction conditions to produce the black spectrum: 0.050 g La(BH$_4$)$_2$(THF)$_2$.5-TPS-HY$_{30}$ (0.05 g), benzene (1 mL), HBpin added in four portions (0.10 mL each portion, 2.7 mmol in total) heated at 120 °C for a total of 24 h (described in Figure 4).
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