

# C(sp<sup>3</sup>)–H Selective Benzylic Borylation by In Situ Reduced Ultrasmall Ni Species on CeO<sub>2</sub>

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**ABSTRACT:** Herein, we report that highly dispersed Ni hydroxide species supported on  $CeO_2$  act as an efficient heterogeneous catalyst for the selective borylation of benzylic  $C(sp^3)$ -H bonds of alkylarenes including secondary derivatives, using pinacolborane as the borylating agent. A thorough physicochemical analysis reveals that in situ reduced ultrasmall Ni species on  $CeO_2$  during the reaction are the actual active species responsible for the borylation.

**KEYWORDS**: benzylic borylation, ceria, C-H borylation, heterogeneous catalysis, nickel

C atalytic C–H borylation offers a simple route to valuable organoboron compounds from readily available hydrocarbons. To date, a number of effective catalysts have been reported for various types of C–H borylation reactions.<sup>1</sup> However, the direct transformation of alkylarenes into the corresponding benzylic boronate esters<sup>2</sup> is uncommon and challenging because  $C(sp^3)$ –H bonds need to be selectively borylated in the presence of aryl  $C(sp^2)$ –H bonds. Although significant progress on the borylation of primary benzylic  $C(sp^3)$ –H bonds of methylarenes has been made,<sup>3</sup> reports on the selective borylation of secondary benzylic  $C(sp^3)$ –H bonds to produce synthetically valuable secondary benzylic boronate esters are still scarce.<sup>4</sup>

The development of heterogeneous catalysts for liquid-phase organic transformations is becoming increasingly important.<sup>5</sup> However, heterogeneously catalyzed C-H functionalization has been less extensively investigated.<sup>6</sup> Particularly for benzylic  $C(sp^3)$ -H borylation, only few examples using heterogeneous catalysts have been reported (Scheme 1a).<sup>7,8</sup> In these systems, however, large excess amounts of alkylarenes with respect to the borylating agents were required, and the applicability to secondary benzylic borylation was very limited.<sup>7,8</sup> Meanwhile, Chatani and co-workers reported a  $C(sp^2)$ -H borylation of arenes in the presence of Ni(cod)<sub>2</sub> and NHC ligands (Scheme 1b).<sup>9</sup> In this system, when using methylarenes, the borylation was not selective, resulting in the formation of mixtures of  $C(sp^2)$ -H and  $C(sp^3)$ -H borylation products. Subsequently, Mandal and co-workers revealed by performing a series of controlled reactions and detailed spectroscopic studies that, in

the Ni(cod)\_2/NHC system, Ni nanoparticles formed during the reaction are the actual active species.  $^{10}$ 

In this study, we found that highly dispersed Ni hydroxide species supported on  $CeO_2$  (Ni(OH)<sub>x</sub>/CeO<sub>2</sub>) act as an excellent heterogeneous catalyst (precursor) for the  $C(sp^3)$ –H selective benzylic borylation of alkylarenes using pinacolborane (HBpin) as the borylating agent (Scheme 1c). Various physicochemical characterizations revealed that ultrasmall Ni species formed on  $CeO_2$  during the reaction are the actual active species. As mentioned above, previously reported Ni nanoparticle catalysts were unsuccessful in the selective benzylic borylation due to the concomitant progression of  $C(sp^3)$ –H and  $C(sp^2)$ –H bond borylation. In contrast,  $C(sp^3)$ –H bonds were preferentially borylated even in the presence of  $C(sp^2)$ –H bonds using the in situ reduced ultrasmall Ni species catalyst newly developed in this study.

We initially examined the reaction of heptylbenzene (1a) using various catalysts under the conditions shown in Table 1.  $Ni(OH)_x/CeO_2$ , which was prepared by a deposition—precipitation method, gave the desired benzylic boronate ester (2a) in 79% yield (Table 1, entry 1, Table S1) together

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# Scheme 1. C–H Borylation of Alkylarenes by Heterogeneous Catalysts<sup>7–10</sup>

a) C(sp<sup>3</sup>)–H benzylic borylation by heterogeneous catalysts



b) C-H borylation by in situ formed unsupported Ni nanoparticles



c) This work: C(sp<sup>3</sup>)–H selective benzylic borylation by in situ reduced ultrasmall Ni species on CeO<sub>2</sub>





Table 1. Effect of Catalyst on the Borylation of Heptylbenzene  $(1a)^{a}$ 

		Bpin			
R = (CH 1a (0.2	R cat. (3.6 mol%) HBpin (4 eq.) methylcyclohexane 1 <sub>2)4</sub> CH <sub>3</sub> 120°C, 4 h mmol)	2a pinB $\frac{1}{1}$	2a R 2a"	R Bpin	
		yield (%)			
entry	catalyst	2a	2a'	2a''	
1	$Ni(OH)_x/CeO_2$	79	5	2	
2	$Ni(OH)_x/Al_2O_3$	<1	<1	<1	
3	$Ni(OH)_x/TiO_2$	<1	<1	<1	
4	Ni(OH) <sub>x</sub> /HAP	<1	<1	<1	
5 <sup>b</sup>	$Ni(OH)_x/Al_2O_3 + CeO_2$	<1	<1	<1	
6	NiO/CeO <sub>2</sub>	<1	<1	<1	
7	Ni(OH) <sub>2</sub>	<1	<1	<1	
8	NiO	<1	<1	<1	
9	NiCl <sub>2</sub>	<1	<1	<1	
10	$Ni(OAc)_2 \cdot 4H_2O$	2	<1	<1	
11	$Ni(cod)_2$	<1	<1	<1	
12 <sup>c</sup>	CeO <sub>2</sub>	<1	<1	<1	
13	$Ni(OH)_x/CeO_2$ -HBpin	65	6	1	
14	$Ni(OH)_x/CeO_2-H_2$	1	<1	<1	

<sup>*a*</sup>Conditions: **1a** (0.2 mmol), HBpin (0.8 mmol), catalyst (Ni: 3.6 mol %), methylcyclohexane (1 mL), 120 °C, Ar (1 atm), 4 h. Yields were determined by GC. <sup>*b*</sup>Ni(OH)<sub>*x*</sub>/Al<sub>2</sub>O<sub>3</sub> (Ni: 3.6 mol %) and CeO<sub>2</sub> (32 mg). <sup>*c*</sup>CeO<sub>2</sub> (32 mg). HAP = hydroxyapatite.

with the homobenzylic borylation product 2a' (5%). The total yield of aryl C(sp<sup>2</sup>)-H borylation products 2a'' was only 2%. Thus, the selectivity to the C(sp<sup>3</sup>)-H borylation (benzyl + homobenzyl) reached up to 98%, which contrasts with the

previously reported borylation using Ni nanoparticles.<sup>9,10</sup> The generation of H<sub>2</sub> gas during the reaction was confirmed by GC–MS analysis. No reaction proceeded when other supports were used (Table 1, entries 2–4). In addition, the physical mixture of Ni(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>, a supported NiO catalyst, and Ni compounds barely showed catalytic activity (Table 1, entries 5–11). Meanwhile, other 3d transition metal hydroxide species were not effective (Table S2). The observed catalysis of Ni(OH)<sub>x</sub>/CeO<sub>2</sub> was determined to be heterogeneous by the hot filtration test (see SI). The reusability of Ni(OH)<sub>x</sub>/CeO<sub>2</sub> was also examined, but a significant loss of its catalytic activity was observed in the reuse experiment (see SI).

Immediately after the reaction started, the color of  $Ni(OH)_r/CeO_2$  turned from pale yellow to black (Figure S1). In a separate experiment, we obtained a similar black color by treating the catalyst with HBpin under nearly identical conditions to those of the reaction (henceforth referred to as  $Ni(OH)_x/CeO_2-HBpin$ ).  $Ni(OH)_x/CeO_2-HBpin$  also promoted the borylation of 1a (Table 1, entry 13). Therefore, Ni(OH)<sub>r</sub>/CeO<sub>2</sub>-HBpin was subjected to detailed characterizations to elucidate the active species generated during the reaction. The Ni K-edge XANES spectrum of Ni(OH),/CeO<sub>2</sub> was similar to that of  $Ni(OH)_2$  (Figure 1a, Figure S2). The partial reduction of the Ni(II) species in Ni(OH)<sub>x</sub>/CeO<sub>2</sub> upon HBpin treatment was evidenced by comparing the XANES spectra of  $Ni(OH)_x/CeO_2$  and  $Ni(OH)_x/CeO_2$ -HBpin (Figure 1a).<sup>11</sup> The XPS spectrum of Ni(OH)<sub>x</sub>/CeO<sub>2</sub>-HBpin displayed two Ni 2p3/2 peaks at 855.4 and 852.4 eV ascribable to Ni(OH)<sub>2</sub> and Ni(0) species, respectively (Figure 1b, Figure S3). The  $k^3$ -weighted Fourier-transformed Ni K-edge EXAFS spectra are shown in Figure 1c (Figure S4, Table S3).  $Ni(OH)_x/CeO_2$  exhibited strong Ni–O scattering in Ni-(OH)<sub>2</sub>, whereas Ni-Ni scattering in Ni(OH)<sub>2</sub> was hardly observed. Meanwhile, Ni(OH)<sub>x</sub>/CeO<sub>2</sub>-HBpin exhibited weak Ni-Ni scattering in Ni metal as well as strong Ni-O scattering. The Ni-Ni scattering of Ni(OH)<sub>v</sub>/CeO<sub>2</sub>-HBpin appeared at a slightly longer distance compared with that of Ni metal. This was possibly caused by the contribution of Ni-Ce scattering at the interface between Ni species and CeO<sub>2</sub>.<sup>12</sup>

The direct observation of Ni species by HAADF-STEM was quite difficult (Figure 1d,e); however, EDS mapping showed that they were highly dispersed on CeO<sub>2</sub> (Figure 1f,g). In addition, the XRD patterns of Ni(OH)<sub>x</sub>/CeO<sub>2</sub> and Ni(OH)<sub>x</sub>/CeO<sub>2</sub>-HBpin were the same as that of CeO<sub>2</sub>; no signals due to Ni metal, oxides, or hydroxides were observed (Figure 1h, Figure S5). These results indicate that highly dispersed ultrasmall Ni species were formed on CeO<sub>2</sub> by HBpin treatment.

Meanwhile, the XANES and XPS spectra of Ni(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> were almost unchanged even after HBpin treatment, indicating that Ni(II) species in Ni(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> was hardly reduced by HBpin (Figure 1a,b). As can be extracted from Table 1, only Ni(OH)<sub>x</sub>/CeO<sub>2</sub> served as the effective catalyst. Considering that the occurrence of a charge transfer from CeO<sub>2</sub> to Ni species, which facilitates the reduction of Ni species, has been reported,<sup>13</sup> it seems reasonable to assume that there is a metal–support interaction in the Ni(OH)<sub>x</sub>/CeO<sub>2</sub> catalyst, in which CeO<sub>2</sub> enables the reduction of Ni(II) hydroxide species to Ni(0) by HBpin under mild reaction conditions using HBpin. In addition, Ni–Ni scattering in Ni(OH)<sub>2</sub> appeared prominently in the EXAFS spectrum of Ni(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> in contrast with that of Ni(OH)<sub>x</sub>/CeO<sub>2</sub> (Figure 1c), indicating



**Figure 1.** Characterization of catalysts: (a) Ni K-edge XANES spectra; (b) Ni 2p XPS spectra; (c)  $k^3$ -weighted Fourier-transformed Ni K-edge EXAFS spectra; (d,e) HAADF-STEM images of Ni(OH)<sub>x</sub>/CeO<sub>2</sub>-HBpin; (f,g) STEM-EDS mappings of Ni(OH)<sub>x</sub>/CeO<sub>2</sub>-HBpin, showing the distributions of Ni in yellow (panel (f)) and Ce in cyan (panel (g)); (h) XRD patterns.

that  $CeO_2$  had a higher dispersion of Ni(II) hydroxide species than  $Al_2O_3$ .<sup>14</sup>

We also prepared Ni(OH)<sub>x</sub>/CeO<sub>2</sub>-H<sub>2</sub> by treating Ni-(OH)<sub>x</sub>/CeO<sub>2</sub> with H<sub>2</sub> at 400 °C, and its performance in the borylation of **1a** was evaluated. However, despite having a XANES spectrum similar to that of Ni(OH)<sub>x</sub>/CeO<sub>2</sub>-HBpin (Figure S2), the reaction with Ni(OH)<sub>x</sub>/CeO<sub>2</sub>-H<sub>2</sub> hardly proceeded (Table 1, entry 14). At a difference with Ni(OH)<sub>x</sub>/  $CeO_2$ -HBpin, both Ni-Ni scatterings due to Ni metal and Ni(OH)<sub>2</sub> appeared prominently in the EXAFS spectrum of Ni(OH)<sub>x</sub>/CeO<sub>2</sub>-H<sub>2</sub> (Figure S4). Therefore, the transformation of Ni(II) hydroxide species on CeO<sub>2</sub> into highly dispersed reduced Ni species was more efficient with HBpin than with H<sub>2</sub>.

Next, the substrate scope for the proposed  $Ni(OH)_r/CeO_2$ catalyzed borylation was investigated (Scheme 2a,b, Figure S6). Alkylbenzenes (1a-1d) and diphenylmethanes (1e-1g)were converted to the corresponding benzylic boronate esters. The reaction of toluene (1h) gave the corresponding gemdiborylatedproduct as the major product (Figure S7). Xylenes (1i-1k) and mesitylene (11) also gave the corresponding gemdiborylated products as the major products, whereas the yields of borylated compounds with the two methyl groups bearing boron substituents were very low (<10%). These results indicated that the benzylic Bpin substituent activated the remaining benzylic C-H bonds to give gem-diborylated products preferentially, as previously reported.<sup>3a,f</sup> The conversion of para-tert-butyl toluene (1m) was low. Toluenes with methoxy (1n), dimethylamino (1o, 1p), and Bpin (1q, 1r) groups were also applicable to the gem-diborylation. Meanwhile, the reactions of alkylarenes substituted with carbonyl groups or halogens, heteroaromatic compounds, and methylnaphthalene were unsuccessful (Scheme S1). The reaction of 4-propyltoluene (1s) gave the compound with the diborylated methyl group as the major product, indicating that the catalytic system preferred primary C-H bonds over secondary ones (see SI).

When using a large excess of methylarene substrates, the corresponding monoborylated products were obtained as the major products (Scheme 2c). To demonstrate the synthetic utility of the present catalytic system, we conducted the synthesis at larger scale, followed by functionalization of the borylation product (Scheme 2d). The larger-scale reaction of 1a (4.0 mmol) was successful, and 70% yield of 2a was isolated. Then, the synthesized product was employed in the Suzuki–Miyaura cross-coupling with iodobenzene, giving the arylated product 4a. Using NaOH and  $H_2O_2$ , 2a could be converted to the corresponding benzylic alcohol 5a. The one-carbon homologation of 2a using BrCH<sub>2</sub>Cl and *n*-BuLi was also successful, affording the corresponding homobenzylic boronate ester 6a.

Several experiments were performed to clarify the mechanism of the proposed borylation. First, a deuteriumlabeling experiment was conducted. The initial rates of 1a and dideuterated heptylbenzene at the benzylic position (1a- $d_2$ ) were almost the same ( $k_H/k_D = 1.0$ ; Figure S8), revealing that the benzylic C-H cleavage was not the rate-determining step. The changes in the GC-MS spectra of the remaining 1a- $d_2$  during the borylation with HBpin showed a rapid decrease in the deuterium content at the benzylic position (Figure S9), indicating that the benzylic C-D cleavage and the incorporation of a H atom from the external hydrogen source (i.e., HBpin) were very fast in the presence of Ni(OH)<sub>x</sub>/CeO<sub>2</sub>.

To get further information, the reaction of 1a with  $D_2$  instead of HBpin was also performed. When 1a was stirred in methylcyclohexane at 120 °C under  $D_2$  atmosphere for 4 h in the presence of Ni(OH)<sub>x</sub>/CeO<sub>2</sub>-HBpin, deuterium-labeling was observed at the benzylic (20%) and homobenzylic (3.5%) positions of 1a without aromatic C(sp<sup>2</sup>)-H deuteration (Scheme S2). It can be assumed that a Ni-H species was formed in the presence of an external hydrogen source such as

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<sup>*i*</sup>Yields were determined by GC (averages of 2–4 runs for 2a–2g, 3h–3s, 2h, 2o, and 2q), and the values in parentheses are the isolated yields. <sup>*a*</sup>Conditions: 1 (0.2 mmol), HBpin (0.8 mmol), Ni(OH)<sub>*x*</sub>/CeO<sub>2</sub> (Ni: 3.6 mol %), methylcyclohexane (1 mL), Ar (1 atm), 120 °C, 4 h. <sup>*b*</sup>Isolated with the homobenzylic boronate ester impurity. <sup>*c*</sup>Ni(OH)<sub>*x*</sub>/CeO<sub>2</sub> (Ni: 11 mol %). <sup>*d*</sup>Isolated with 8% yield of the regioisomer impurity. <sup>*c*</sup>Cyclopentyl methyl ether (CPME) was used instead of methylcyclohexane. <sup>*f*</sup>The values in parentheses are the isolated yields of the corresponding alcohols or aldehydes. <sup>*g*</sup>Conditions: 1 (0.2 mmol), HBpin (1.0 mmol), Ni(OH)<sub>*x*</sub>/CeO<sub>2</sub> (Ni: 3.6 mol %), methylcyclohexane (1 mL), Ar (1 atm), 100 °C, 8 h. <sup>*h*</sup>Borylated compounds with the two methyl groups bearing boron substituents were also formed (<10% GC yields). <sup>*i*</sup>120 °C. <sup>*j*</sup>HBpin (0.8 mmol), 120 °C, 4 h. Other borylated byproducts were also formed (see SI). <sup>*k*</sup>Conditions: 1 (2 mL), HBpin (0.4 mmol), Ni(OH)<sub>*x*</sub>/CeO<sub>2</sub> – HBpin (Ni: 1.8 mol %, Ni(OH)<sub>*x*</sub>/CeO<sub>2</sub> treated with HBpin before use), Ar (1 atm), 100 °C, 20 h. <sup>*l*</sup>Isolated with 4% yield of the regioisomer impurity. <sup>*m*</sup>Using 4.0 mmol of 1 and 1 mL of CPME. <sup>*n*</sup>Using 2.0 mmol of 1 and 1 mL of CPME. <sup>*o*</sup>Experimental details are described in SI. Isolated yields are shown here.

HBpin and H<sub>2</sub>. Moreover, when the reaction of 1a was performed under H<sub>2</sub> atmosphere, the 2a production was suppressed (37% yield, Table S4, entry 2), suggesting that a H<sub>2</sub> elimination step from Ni–H species was involved in the borylation. In addition, when 1a- $d_2$  was treated with Ni(OH)<sub>x</sub>/ CeO<sub>2</sub>–HBpin even in the absence of HBpin, rapid H–D exchange between the benzylic C–D and homobenzylic C–H bonds was confirmed by GC–MS and NMR (Figure S10), suggesting that the Ni species catalyzed the benzylic C–H activation. According to previous reports,<sup>15</sup> the hydrogen migration likely occurs via oxidative addition of 1a to Ni(0) species followed by  $\beta$ -hydride elimination and migratory insertion on Ni(II) species. It seems reasonable to conclude that the aforementioned homobenzylic borylation with HBpin and deuteration with  $D_2$  proceeds via a similar mechanism. In addition, when HBpin was stirred under a  $D_2$  atmosphere in the presence of Ni(OH)<sub>x</sub>/CeO<sub>2</sub>-HBpin, DBpin was obtained (Figure S11), suggesting that the Ni species catalyzed the B-H cleavage independently of the benzylic C-H activation.

Finally, a plausible reaction mechanism may be proposed as follows (Scheme S3):<sup>3b,10</sup> The oxidative addition of benzylic C–H bonds occurs over the Ni species to give Ni benzyl intermediates and Ni–H species. At the same time, the reaction of the Ni species and HBpin produces Ni–H and Ni–Bpin species. Then, the desired borylated products and H<sub>2</sub> are produced by successive reductive eliminations, and the catalytically active Ni species are regenerated. Meanwhile, it

cannot be ruled out that the C–H borylation proceeds via radical intermediates.  $^{16}$ 

The present results show that the catalyst possesses high activity for the benzylic  $C(sp^3)$ -H cleavage, which proceeds preferentially over  $C(sp^2)$ -H bond cleavage, possibly as a result of the formation of highly dispersed ultrasmall Ni species as the active catalytic species. However, further studies are needed to gain more insight into the origin of the observed interesting selectivity.

# ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c00185.

Experimental details, additional experimental results, characterization data, and NMR spectra (PDF)

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#### Notes

The authors declare no competing financial interest.

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#### REFERENCES

(1) Selected reviews: (a) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. C-H Activation for the Construction of C-B Bonds. *Chem. Rev.* 2010, *110*, 890-931. (b) Hartwig, J. F. Borylation and Silylation of C-H Bonds: A Platform for Diverse C-H Bond Functionalizations. *Acc. Chem. Res.* 2012, *45*, 864-873. (c) Xu, L.; Wang, G.; Zhang, S.; Wang, H.; Wang, L.; Liu, L.; Jiao, J.; Li, P. Recent advances in catalytic C-H borylation reactions.

Tetrahedron 2017, 73, 7123-7157. (d) Ros, A.; Fernández, R.; Lassaletta, J. M. Functional group directed C-H borylation. Chem. Soc. Rev. 2014, 43, 3229-3243.

(2) Benzylic boronate esters are important synthetic building blocks, and various synthetic methods from other abundant and renewable feedstocks have also been reported. Selected examples: (a) Friese, F. W.; Studer, A. Deoxygenative Borylation of Secondary and Tertiary Alcohols. *Angew. Chem., Int. Ed.* **2019**, *58*, 9561–9564. (b) Li, J.; Wang, H.; Qiu, Z.; Huang, C.-Y.; Li, C.-J. Metal-Free Direct Deoxygenative Borylation of Aldehydes and Ketones. *J. Am. Chem. Soc.* **2020**, *142*, 13011–13020. (c) Fawcett, A.; Pradeilles, J.; Wang, Y.; Mutsuga, T.; Myers, E. L.; Aggarwal, V. K. Photoinduced decarboxylative borylation of carboxylic acids. *Science* **2017**, *357*, 283–286. (d) Hu, J.; Wang, G.; Li, S.; Shi, Z. Selective C-N Borylation of Alkyl Amines Promoted by Lewis Base. *Angew. Chem., Int. Ed.* **2018**, *57*, 15227–15231.

(3) (a) Shimada, S.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B. Formation of Aryl- and Benzylboronate Esters by Rhodium-Catalyzed C-H Bond Functionalization with Pinacolborane. Angew. Chem., Int. Ed. 2001, 40, 2168-2171. (b) Lam, W. H.; Lam, K. C.; Lin, Z.; Shimada, S.; Perutz, R. N.; Marder, T. B. Theoretical study of reaction pathways for the rhodium phosphine-catalysed borylation of C-H bonds with pinacolborane. Dalton Trans. 2004, 1556-1562. (c) Boebel, T. A.; Hartwig, J. F. Iridium-Catalyzed Preparation of Silylboranes by Silane Borylation and Their Use in the Catalytic Borylation of Arenes. Organometallics 2008, 27, 6013-6019. (d) Cho, S. H.; Hartwig, J. F. Iridium-catalyzed diborylation of benzylic C-H bonds directed by a hydrosilyl group: synthesis of 1,1-benzyldiboronate esters. Chem. Sci. 2014, 5, 694-698. (e) Larsen, M. A.; Wilson, C. V.; Hartwig, J. F. Iridium-Catalyzed Borylation of Primary Benzylic C-H Bonds without a Directing Group: Scope, Mechanism, and Origins of Selectivity. J. Am. Chem. Soc. 2015, 137, 8633-8643. (f) Palmer, W. N.; Obligacion, J. V.; Pappas, I.; Chirik, P. J. Cobalt-Catalyzed Benzylic Borylation: Enabling Polyborylation and Functionalization of Remote, Unactivated C(sp<sup>3</sup>)-H Bonds. J. Am. Chem. Soc. 2016, 138, 766-769.

(4) (a) Cho, S. H.; Hartwig, J. F. Iridium-Catalyzed Borylation of Secondary Benzylic C-H Bonds Directed by a Hydrosilane. J. Am. Chem. Soc. 2013, 135, 8157-8160. (b) Palmer, W. N.; Zarate, C.; Chirik, P. J. Benzyltriboronates: Building Blocks for Diastereoselective Carbon-Carbon Bond Formation. J. Am. Chem. Soc. 2017, 139, 2589-2592. (c) Jayasundara, C. R. K.; Sabasovs, D.; Staples, R. J.; Oppenheimer, J.; Smith, M. R., III; Maleczka, R. E., Jr. Cobalt-Catalyzed C-H Borylation of Alkyl Arenes and Heteroarenes Including the First Selective Borylations of Secondary Benzylic C-H Bonds. Organometallics 2018, 37, 1567-1574.

(5) (a) Fine Chemicals through Heterogeneous Catalysis; Sheldon, R. A., van Bekkum, H., Eds.; Wiley-VCH: Weinheim, 2001. (b) Climent, M. J.; Corma, A.; Iborra, S. Heterogeneous Catalysts for the One-Pot Synthesis of Chemicals and Fine Chemicals. *Chem. Rev.* 2011, 111, 1072–1133.

(6) Selected reviews: (a) Santoro, S.; Kozhushkov, S. I.; Ackermann, L.; Vaccaro, L. Heterogeneous catalytic approaches in C-H activation reactions. *Green Chem.* **2016**, *18*, 3471–3493. (b) Pla, D.; Gómez, M. Metal and Metal Oxide Nanoparticles: A Lever for C-H Functionalization. *ACS Catal.* **2016**, *6*, 3537–3552. (c) Reay, A. J.; Fairlamb, I. J. S. Catalytic C-H bond functionalisation chemistry: the case for quasi-heterogeneous catalysis. *Chem. Commun.* **2015**, *51*, 16289–16307.

(7) Ishiyama, T.; Ishida, K.; Takagi, J.; Miyaura, N. Palladium-Catalyzed Benzylic C–H Borylation of Alkylbenzenes with Bis-(pinacolato)diboron or Pinacolborane. *Chem. Lett.* **2001**, *30*, 1082–1083.

(8) Manna, K.; Ji, P.; Lin, Z.; Greene, F. X.; Urban, A.; Thacker, N. C.; Lin, W. Chemoselective single-site Earth-abundant metal catalysts at metal–organic framework nodes. *Nat. Commun.* **2016**, *7*, 12610.

(9) Furukawa, T.; Tobisu, M.; Chatani, N. Nickel-catalyzed borylation of arenes and indoles via C-H bond cleavage. *Chem. Commun.* 2015, *51*, 6508–6511.

(10) Das, A.; Hota, P. K.; Mandal, S. K. Nickel-Catalyzed  $C(sp^2)$ -H Borylation of Arenes. *Organometallics* **2019**, *38*, 3286–3293. (11) It was revealed by <sup>11</sup>B NMR that  $O(Bpin)_2$  and HOBpin were

(11) It was revealed by <sup>11</sup>B NMR that  $O(Bpin)_2$  and HOBpin were produced during the reduction of  $Ni(OH)_x/CeO_2$  by HBpin (Figure S12).

(12) Akri, M.; Zhao, S.; Li, X.; Zang, K.; Lee, A. F.; Isaacs, M. A.; Xi, W.; Gangarajula, Y.; Luo, J.; Ren, Y.; Cui, Y.-T.; Li, L.; Su, Y.; Pan, X.; Wen, W.; Pan, Y.; Wilson, K.; Li, L.; Qiao, B.; Ishii, H.; Liao, Y.-F.; Wang, A.; Wang, X.; Zhang, T. Atomically dispersed nickel as coke-resistant active sites for methane dry reforming. *Nat. Commun.* **2019**, *10*, 5181.

(13) Matte, L. P.; Kilian, A. S.; Luza, L.; Alves, M. C. M.; Morais, J.; Baptista, D. L.; Dupont, J.; Bernardi, F. Influence of the  $CeO_2$ Support on the Reduction Properties of  $Cu/CeO_2$  and  $Ni/CeO_2$ Nanoparticles. J. Phys. Chem. C 2015, 119, 26459–26470.

(14) Du, X.; Zhang, D.; Shi, L.; Gao, R.; Zhang, J. Morphology Dependence of Catalytic Properties of Ni/CeO<sub>2</sub> Nanostructures for Carbon Dioxide Reforming of Methane. *J. Phys. Chem. C* **2012**, *116*, 10009–10016.

(15) (a) Juliá-Hernández, F.; Moragas, T.; Cornella, J.; Martin, R. Remote carboxylation of halogenated aliphatic hydrocarbons with carbon dioxide. *Nature* **2017**, *545*, 84–88. (b) He, J.; Song, P.; Xu, X.; Zhu, S.; Wang, Y. Migratory Reductive Acylation between Alkyl Halides or Alkenes and Alkyl Carboxylic Acids by Nickel Catalysis. *ACS Catal.* **2019**, *9*, 3253–3259.

(16) The effect of the addition of a radical scavenger was investigated, and the radical clock experiment was performed (see SI).