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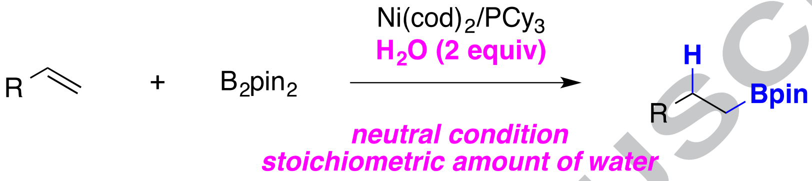

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Ni-Catalyzed hydroboration and hydrosilylation of olefins with diboron and silylborane

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ABSTRACT

Herein we report a Ni-catalyzed formal hydroboration of olefins, which afforded *anti*-Markovnikov-type alkylboranes with B_2pin_2 and a stoichiometric amount of water. Formal hydrosilylation using air- and moisture-sensitive silylboranes also proceeded under optimized conditions. The reaction with *trans*-stilbene and D_2O resulted in 1,2-H migration, which suggested that the reaction proceeded via β-hydride elimination and reinsertion mechanisms.

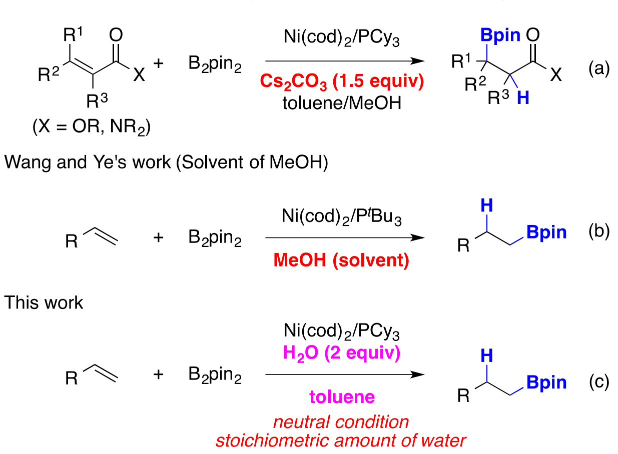
Alkene hydroboration is one of the powerful synthetic tools to synthesize alkylboranes, which can serve as valuable reagents in various transformations.[1] For example, Suzuki-Miyaura coupling, a powerful tool to construct carbon-carbon bonds, has been applied to the synthesis of materials and biologically active compounds.[2]

In general, hydroboranes $HB(OR)_2$, such as catechol borane and pinacol borane, have been adopted for catalytic hydroboration, since the first catalytic hydroboration was reported using Wilkinson's catalyst.[3] On the other hand, $B_2(pin)_2$[4] has emerged as a useful borylating reagent for metal-catalyzed formal hydroboration with the aid of a Brønsted acid proton source.[5-10] Formal hydroboration should be performed under basic conditions, although the reaction has been promoted by many metal catalysts, including those based on Rh,[5] Cu,[6] Pd,[7] Pt,[8] and Fe.[9] The basic conditions sometimes restricts the substrate scope of the reaction.

A few examples of Ni-catalyzed hydroboration have been reported in the past decade. The first example of Ni-catalyzed hydroboration across activated olefins under basic conditions was reported by Yorimitsu and Oshima (Scheme 1a).[11,12] Recently, Wang and Ye have reported a base-free hydroboration protocol using $Ni(cod)_2/P(t\text{-}Bu)_3$ catalyst in methanol (Scheme 1b).[13,14] In their reaction, a large amount of methanol was required to accelerate the protonation of the alkylnickel intermediate, which made the reaction unsuitable for proton-sensitive substrates. To expand the substrate scope of the reaction, the amount of Brønsted acid used should be reduced. In this study, we have achieved Ni-catalyzed formal hydroboration across simple olefins using stoichiometric amount of water as Brønsted acid under neutral conditions (Scheme 1c).

Our first attempt at Ni-catalyzed formal hydroboration was performed with *trans*-stilbene (**1a**) as the model olefin. In the presence of $Ni(cod)_2$, 1,2-dicyclohexylphosphinoethane (dcype), and trifluoroethanol (TFE), hydroboration proceeded to afford the product **2a** in 89% yield (Table 1, entry 1). The Ni catalyst could not be replaced with other Ni precursors, such as $NiCl_2$ and $NiBr_2$ (entries 2 and 3). The reaction performed with $Ni(acac)_2$ to give the product **2a** in 40% yield (entry 4) Starting materials were recovered in the absence of any Ni precursor or ligand (entries 5 and 6).

Scheme 1. Ni-Catalyzed hydroboration of olefins with B_2pin_2



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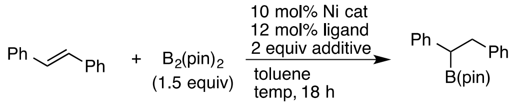
The ligands that showed good hydroboration performance were next investigated. The monodentate ligand, PCy_3, improved the yield of **2a** (entry 7). However, electron-rich and bulky carbene ligands, IMes and IPr, gave poor results (entries 8 and 9). Bidentate ligands, dppe and 2,2'-bipyridine, also reduced the efficiency of reaction (entries 10 and 11).

Addition of acetic acid as the proton source could not drive the reaction due to decomposition of the Ni catalyst under strongly acidic conditions (entry 12). Weaker proton sources, such as PhOH, HFIP, IPA, and H_2O, gave excellent results (entries 13–16). We chose H_2O as the best proton source because of its availability and cost-effectiveness. The reaction temperature could be reduced to 60 ºC to give **2a** in 95% yield (entry 17). However, the reaction did not occur at lower temperatures, and the starting materials were recovered (entry 18). The reaction could be scaled up under the optimum conditions, albeit in lower yield (76%).

Table 1. Screening of reaction conditions of hydroboration



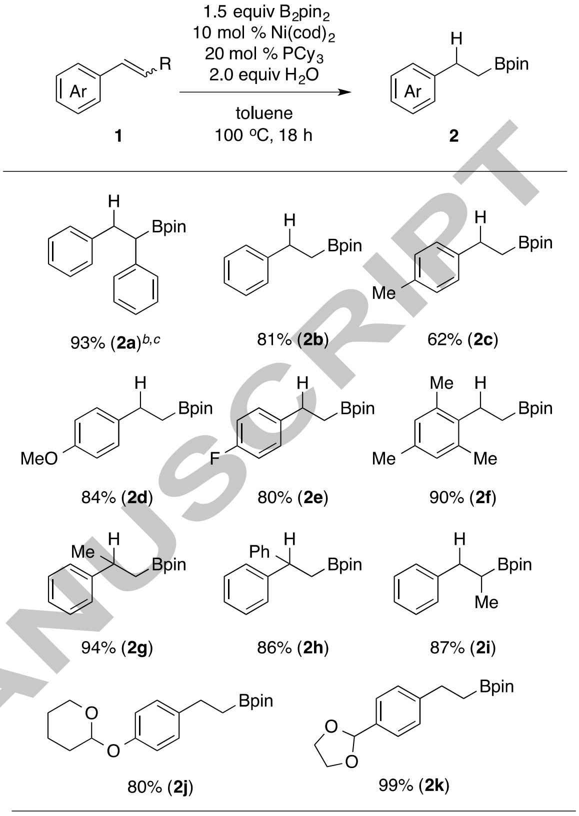
entry	Ni cat.	ligand	additive	temp (°C)	yield(%)[a]
1	$Ni(cod)_2$	dcype	TFE	80	89
2	$NiCl_2$	dcype	TFE	80	0
3	$NiBr_2$	dcype	TFE	80	0
4	$Ni(acac)_2$	dcype	TFE	80	40
5	–	dcype	TFE	80	0
6	$Ni(cod)_2$	–	TFE	80	0
7	$Ni(cod)_2$	PCy_3[b]	TFE	80	99
8	$Ni(cod)_2$	IMes[b]	TFE	80	0
9	$Ni(cod)_2$	IPr[b]	TFE	80	0
10	$Ni(cod)_2$	dppe	TFE	80	0
11	$Ni(cod)_2$	Bipy	TFE	80	5
12	$Ni(cod)_2$	PCy_3[b]	AcOH	80	0
13	$Ni(cod)_2$	PCy_3[b]	PhOH	80	99
14	$Ni(cod)_2$	PCy_3[b]	HFIP	80	99
15	$Ni(cod)_2$	PCy_3[b]	IPA	80	99
16	$Ni(cod)_2$	PCy_3[b]	H_2O	80	99
17	$Ni(cod)_2$	PCy_3[b]	H_2O	60	99 (95)[c]
18	$Ni(cod)_2$	PCy_3[b]	H_2O	40	<5

[a] NMR yield using $Me_3SiOSiMe_3$ as internal standard, [b] using 20 mol% of ligand, [c] isolated yield

With the optimum conditions of Ni-catalyzed hydroboration in hand, the scope of this reaction in terms of alkene substrates was studied (Table 2). The reaction with *cis*-stilbene (**1a'**) gave **2a** in 93% yield. The reactions with electron-rich (**1c**, **1d**), electron-deficient (**1e**), and sterically hindered (**1f**) styrene derivatives should be performed at 100 ºC for full conversion due to their low reactivities to give the corresponding *anti*-Markovnikov adducts in high yields. Other α- and β-substituted styrenes (**1g-1i**) also show high reactivity towards hydroboration to afford the corresponding products **2g-2i**. Since proton sensitive groups were tolerated under the reaction condition, styrenes **1j** and **1k** afforded the corresponding products in good yield.

Hydroboration with 1-decene (**1l**) also gave the product in good yield, albeit as a mixture of regioisomers (Scheme 2). This result show the formation of benzylnickel species after borylnickelation were the key to regioselective hydroboration.

Table 2. Ni-Catalyzed hydroboration of styrenes[a]



[a] isolated yield [b] 60 °C, [c] from *cis*-stilbene (**1a'**)

Scheme 2. Hydroboration with 1-decene

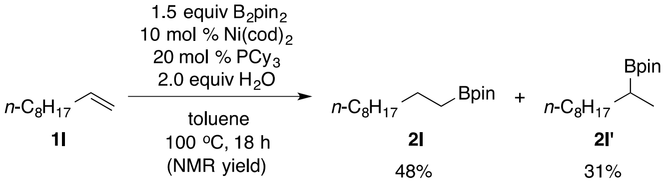
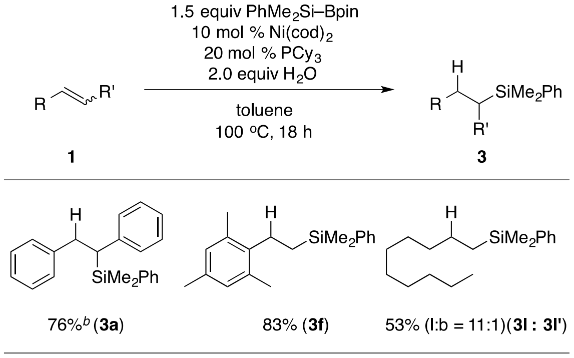


Table 3. Ni-catalyzed hydrosilylation of styrenes[a]

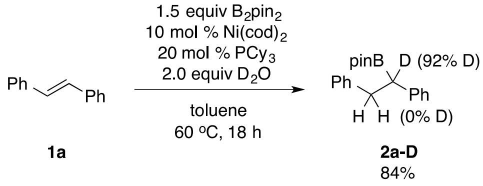


[a] isolated yield. [b] at 60 °C from *trans*-stilbene

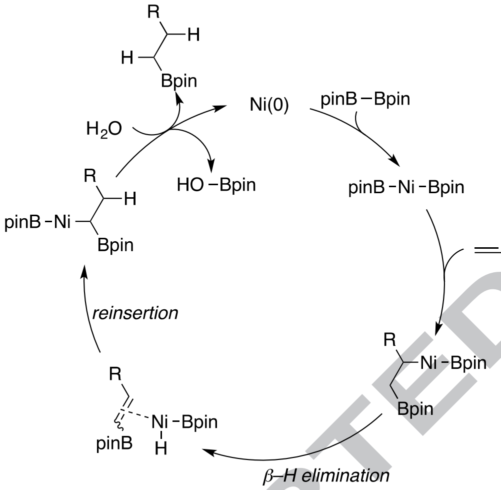
To show the advantage of the reaction described here, the scope of borane nucleophiles was expanded using phenyl(dimethyl)silyl pinacol borate,[15] which is a useful but moisture-sensitive silylating reagent, instead of B_2pin_2. Treatment of silylborane with *trans*-stilbene in the presence of $Ni(cod)_2$, PCy_3, B_2pin_2, and H_2O realized formal hydrosilylation to afford the alkylsilane **3a** in 76% yield as the sole product.[16-18] Similar to hydroboration, 2,4,6-trimethylstyrene **1f** was converted to the corresponding *anti*-Markovnikov adduct **3f**. The reaction with 1-decene **1j** resulted in highly regioselective hydrosilylation to give the **3j** and **3j'** (linear:branched=11:1). In all cases, no hydroboration product was observed.

To obtain mechanistic insights of Ni-catalyzed hydroboration, D-labeling experiment was performed on **1a** by addition of D_2O at 60 ºC to give **2a-D** in 84% yield (Scheme 3). Surprisingly, deuterium atom was introduced at the α-position of the boryl group (92%-D incorporation), and D-scrambling reactions of other hydrogen atoms were not observed. Since no other proton sources were added, the two benzylic hydrogen atoms of **2a-D** originated from **1a**, implying that 1,2-H migration proceeded via β-hydride elimination and reinsertion. Recently, Xiao and Bin observed similar 1,2-H atom migration during Ni-catalyzed 1,1-diboration of alkene derivatives.[19]

Scheme 3. D-Labeling experiment



Scheme 4. Plausible reaction pathway



Our proposed mechanisms are shown in Scheme 5, based on the experiments conducted in this study and in Xiao and Bin's study. Oxidative addition of B_2pin_2 to nickel generated a boryl nickel species, which underwent olefin insertion into the B–Ni bond, following β-hydride elimination from the alkyl nickel species. Reinsertion of alkenylborane into the H–Ni bond produced an α-boryl nickel species, which was protonated with water to afford the product.[20,21]

In conclusion, we developed a Ni-catalyzed formal hydroboration of olefins with B_2pin_2 and water. The addition of stoichiometric amount of water as the proton source under neutral conditions enabled the use of other organoborane nucleophiles. Ni-catalyzed formal hydrosilylation was achieved using air- and moisture-sensitive $PhMe_2SiBpin$ instead of B_2pin_2. D-Labeling experiment indicated that the reaction proceeded via β-hydride elimination and reinsertion pathways. Further investigation to improve the catalyst activity in terms of the regioselectivity of less-hindered olefins and application of this methodology is currently in progress.

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Supplementary Material

Detailed experimental procedures and spectral data (PDF)

Highlights

- Ni-Catalyzed formal hydroboration with B_2pin_2 in the presence of H_2O as proton source
- Ni-Catalyzed formal hydroboration with $PhMe_2SiBpin$ in the presence of H_2O as proton source
- These reactions were applicable to aryl- and alkyl olefins.
- The reaction proceeded via β-hydride elimination/reinsertion pathway determined by D-labeling experiment.