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Letter

Nickel-Catalyzed Hydroarylation of in Situ Generated 1,3-Dienes with Arylboronic Acids Using a Secondary Homoallyl Carbonate as a Surrogate for the 1,3-Diene and Hydride Source

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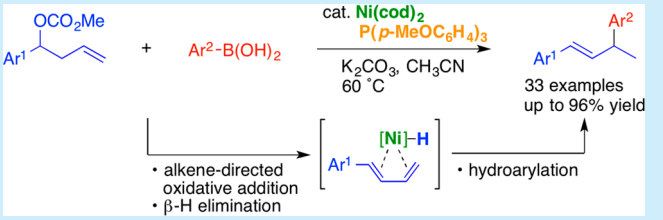
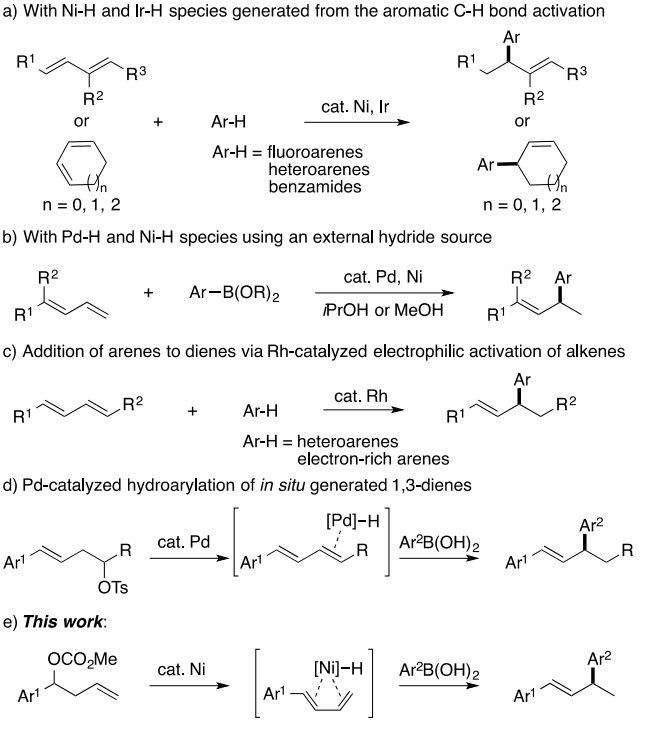
ABSTRACT: The nickel-catalyzed hydroarylation of 1,3-dienes with arylboronic acids using a secondary homoallyl carbonate as a surrogate for the 1,3-diene and hydride source has been developed. The synthetic strategy allowed an efficient access to a wide array of hydroarylation products in high yields with high functional group compatibility without the use of an external hydride source. Mechanistic experiments indicated that the alkene-directed oxidative addition and subsequent β-hydride elimination would be a critical process in this transformation.



The transition-metal-catalyzed hydrofunctionalization of carbon−carbon multiple bonds represents an attractive strategy for the formation of carbon−carbon and carbon−heteroatom bonds in organic synthesis.[1] The catalytic hydrofunctionalization of 1,3-dienes is among the most significant transformations due to its high utility in the construction of complex organic molecules.[2−9] In particular, catalytic hydroarylation of 1,3-dienes offers efficient and straightforward access to the alkenyl arenes and has received significant attention from organic chemists. The hydroarylation has been achieved by the transition-metal-catalyzed reactions involving a metal hydride species generated by the aromatic C−H bond activation (Scheme 1a)[10] and the reaction with alcohols as an external hydride source (Scheme 1b).[11,12] A carbodicarbene−Rh(I) pincer complex is also known to be an active π-acidic catalyst in the hydroarylation of conjugated dienes (Scheme 1c).[13] However, these reported methods rely on the use of special arenes (e.g., electron-rich arenes, heteroarenes, and benzamides) and the external hydride source. Therefore, developing a novel approach for realizing the highly efficient catalytic hydroarylation of 1,3-dienes with a broad scope of substrates is highly desirable.

The substrate-directed chemical reaction, especially using metal catalysts, has been recognized as a powerful tool in the field of synthetic organic chemistry.[14] Among these reactions, the transition-metal-catalyzed alkene-directed transformations have received much attention, and several attractive reactions have been established.[15] Sigman and co-workers reported that the palladium-catalyzed reaction of homoallyl tosylates with arylboronic acids afforded the hydroarylation products (Scheme 1d).[16] In this reaction, the alkene-directed oxidative addition of a C−O bond to Pd(0) followed by β-hydride elimination produces 1,3-dienes that subsequently react with

Scheme 1. Transition-Metal-Catalyzed Hydroarylation of 1,3-Dienes



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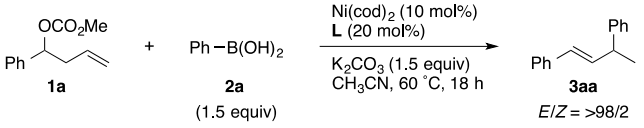
arylboronic acids in the presence of a palladium hydride species, providing the hydroarylation products. Although this reaction would provide a new path for the hydroarylation of 1,3-dienes, the catalyst system seems to be immature with respect to the substrate scope and reaction yield. This research precedent stimulated us to develop a new catalyst system for the hydroarylation of 1,3-dienes, which covers a broad scope of arenes without the use of an external hydride source. We now report the nickel-catalyzed hydroarylation of 1,3-dienes with arylboronic acids using secondary homoallyl carbonates as a surrogate for the 1,3-diene and hydride source (Scheme 1e).

We began our investigation with the optimization of the reaction conditions (Table 1). Recently, Krische and co-workers reported an intriguing result in which a homoallyl carbonate was converted into the hydroarylation product in the presence of a nickel catalyst via in situ formation of a 1,3-diene (single example).[17] Based on this result, we chose secondary homoallyl carbonate **1a**, which is readily prepared by the reaction of benzaldehyde with allylorganometallic reagents,[18] and $Ni(cod)_2$ as a catalyst. The reaction of homoallyl carbonate **1a** with phenylboronic acid (**2a**) was carried out in the presence of 10 mol % $Ni(cod)_2$, 20 mol % PPh_3, and 1.5 equiv of K_2CO_3 in CH_3CN at 60 °C for 18 h. We confirmed that hydroarylation product **3aa** was formed in 53% yield (Table 1, entry 1). Motivated by this initial result, we examined the screening of monophoshine ligands (Table 1, entries 2–9). The use of P(*p*-tol)$_3$ as the ligand improved the yield of **3aa** to 81% (Table 1, entry 2). A combination of $Ni(cod)_2$ and P(*p*-$MeOC_6H_4$)$_3$ was found to be effective for the transformation, giving the desired hydroarylation product **3aa** in 89% yield (Table 1, entry 3). In sharp contrast, the reaction with P(*p*-$CF_3C_6H_4$)$_3$ failed to give the desired product **3aa** (Table 1, entry 4). In addition, the use of sterically congested monophosphine ligands such as P(*o*-tol)$_3$, P(*o*-$MeOC_6H_4$)$_3$, PCy_3, P*t*-Bu_3, and XPhos retarded the reaction (Table 1, entries 5–9). We also evaluated the effect of the bisphosphine ligands in the nickel catalyst system. DPPPent and DPEphos were not effective for the reaction, yielding **3aa** in low yields (Table 1, entries 10 and 11). The reaction in the presence of Xantphos led to a decrease in the yield of **3aa** (Table 1, entry 12). When bipyridine- and phenanthroline-derived ligands were employed in the reaction as the ligands, the desired product **3aa** was formed in low yields (Table 1, entries 13 and 14). The ligand screening indicated that the use of a triarylphosphine bearing an electron-donating group at the *para* position on the phenyl ring is essential to proceed the transformation. To improve the yield of **3aa**, the reaction of **1a** with **2a** was performed using the $Ni(cod)_2$/P(*p*-$MeOC_6H_4$)$_3$ system for 36 h. Fortunately, the reaction proceeded quantitatively to give the desired product **3aa** in 94% isolated yield (Table 1, entry 15).

Table 1. Optimization of Reaction Conditions[a]



entry	L	conv[b] (%)	yield[b] (%)
1	PPh_3	72	53
2	P(*p*-tol)$_3$	90	81[c]
3	P(*p*-$MeOC_6H_4$)$_3$	94	89[c]
4	P(*p*-$CF_3C_6H_4$)$_3$	<1	<1
5	P(*o*-tol)$_3$	<1	<1
6	P(*o*-$MeOC_6H_4$)$_3$	25	13
7	PCy_3	32	19
8	P-*t*-Bu_3	16	2
9	XPhos	<1	<1
10	DPPPent	26	5
11	DPEphos	56	20
12	Xantphos	73	57
13	4,4′-di-*t*-Bu-2,2′-bpy	59	15
14	1,10-phenanthroline	36	6
15[d]	P(*p*-$MeOC_6H_4$)$_3$	>99	>99[e] (94)[f]

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.375 mmol), $Ni(cod)_2$ (0.025 mmol), **L** (0.05 mmol), K_2CO_3 (0.375 mmol) in CH_3CN (0.2 M) at 60 °C for 18 h. *E*/*Z* ratios were determined by ^{1}H NMR analyses of crude mixture. [b]The conversions and yields were determined by ^{1}H NMR analysis using phenanthrene as an internal standard. [c]A trace amount of the 1,4-hydroarylation product was observed by the ^{1}H NMR analysis of the crude mixture. [d]The reaction time was prolonged to 36 h. [e]The yield was determined by ^{1}H NMR analysis using CH_2Br_2 as an internal standard. [f]Isolated yield as a mixture with a trace amount of *Z* isomer.

With the optimized reaction conditions in hand, we examined the reaction of various homoallyl carbonates **1** with phenylboronic acid (**2a**) (Scheme 2). The reaction could be conducted on a 3 mmol scale to give the desired hydroarylation product **3aa** in 93% yield. The reaction of homoallyl carbonates **1b**–**e** bearing electron-donating (Me, MeO) and -withdrawing (CF_3, CO_2Me) substituents at the *para* position on the phenyl rings smoothly proceeded to provide the corresponding hydroarylation products **3ba**–**ea** in 83–93% yields. Homoallyl carbonates **1f** and **1g** having 4-fluorophenyl and biphenyl groups underwent the reaction to give the desired products **3fa** and **3ga** in 87% and 89% yield, respectively. Both electron-donating and -withdrawing substituents at the *meta* and *ortho* positions on their phenyl rings were compatible with the reaction, giving the corresponding hydroarylation products **3ha**–**ma** in 71–91% yields. The other substituents, such as piperonyl (**1n**), 2-naphthyl (**1o**), and 6-methoxy-2-naphthyl (**1p**) groups, were well tolerated during the nickel catalysis. Our nickel catalyst system can be also applicable to the transformation of homoally carbonates **1q** and **1r** having pyridine rings, affording the hydroarylation product **3qa** and **3ra** in 65% and 93% yield, respectively. Unfortunately, other heterocyclic rings such as furan and thiophene were not tolerated during the reaction, resulting in the complex mixture of unassigned products. In addition, although the reaction of homoally carbonates bearing aliphatic substituents (R = cyclohexyl) proceeded under the reaction conditions, we could not isolate the desired products as a pure form (89% conv, 42% NMR yield). We confirmed that the reaction of homoally carbonates **1s** and **1t** did not take place under the optimized reaction conditions. In the reactions with **1e**, **1i**, **1o**, and **1q**, we confirmed the formation of a trace amount of the corresponding 1,4-hydroarylation products by ^{1}H NMR analyses of the crude mixture.

We next investigated the scope of arylboronic acids **2** in the reaction of homoallyl carbonate **1a** (Scheme 3). Both electron-rich and -poor phenylboronic acids **2b**–**f** underwent the reaction to afford the hydroarylation products **3ab**–**af** in high yields. Functionalized phenylboronic acids bearing acetyl and terminal alkene groups also participated in the reaction, providing the desired hydroarylation products **3ag** and **3ah** in

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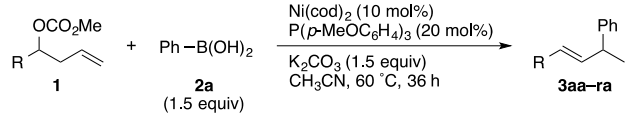
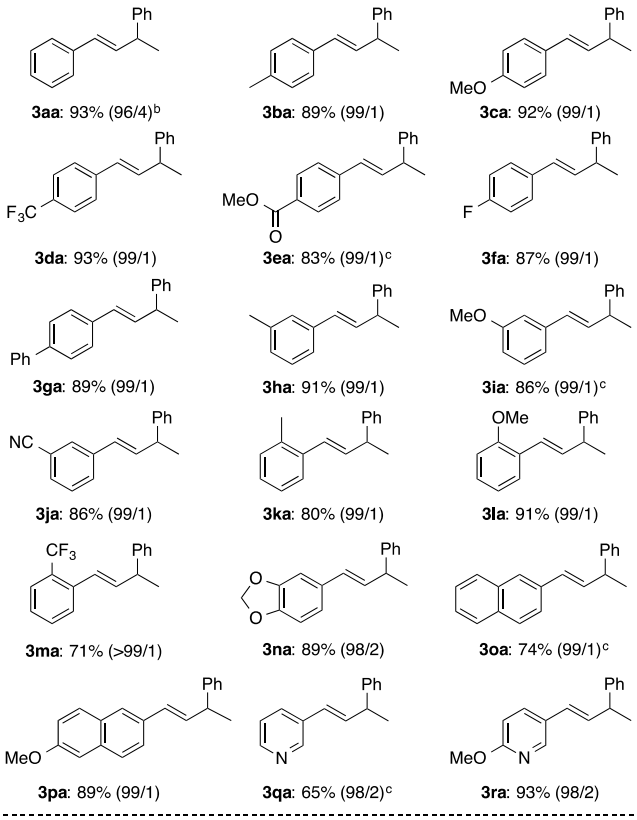
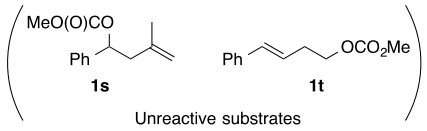
Scheme 2. Scope of Secondary Homoallyl Carbonates[a]





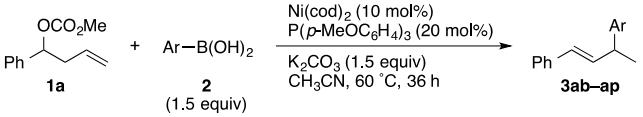


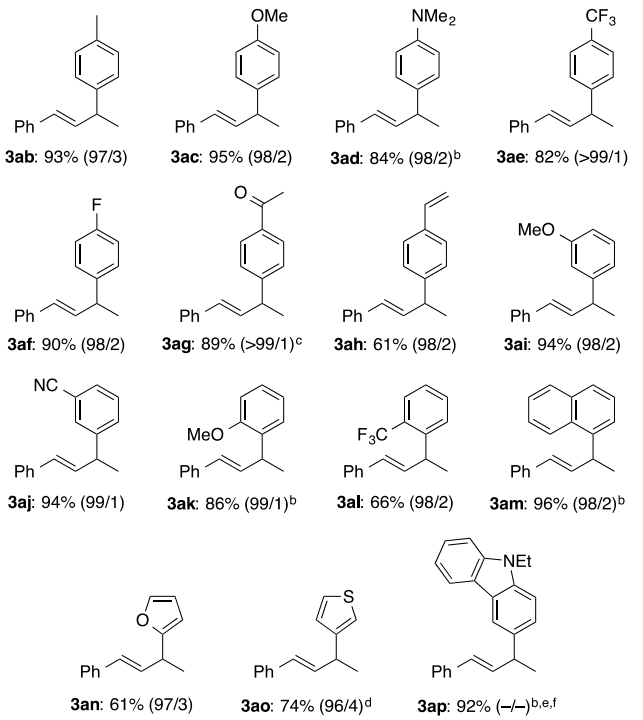
[a]Reaction conditions: **1** (0.25 mmol), **2a** (0.375 mmol), $Ni(cod)_2$ (0.025 mmol), $P(p\text{-}MeOC_6H_4)_3$ (0.05 mmol), K_2CO_3 (0.375 mmol) in CH_3CN (0.2 M) at 60 °C for 36 h. *E*/*Z* ratios were determined by ^1H NMR analyses of the crude mixture and are shown in parentheses. [b]3 mmol scale. [c]Trace amounts of the corresponding 1,4-hydroarylation products were observed by ^1H NMR analyses of the crude mixture.

89% and 61% yield, respectively. *Meta*- and *ortho*-substituted phenyl boronic acids **2i**–**k** also worked well in the reaction system, giving the desired products **3ai**–**ak** in high yields. The use of phenylboronic acid **2l** bearing a trifluoromethyl group at the *ortho* position led to a slight decrease of the reaction efficiency. When the reaction 1-naphthalenylboronic acid **2m** was subjected to the reaction conditions, the desired product **3am** was obtained in 96% yield. Heterocyclic rings such as furan, thiophene, and carbazole were compatible with the nickel catalyst system, providing the corresponding hydroarylation products **3an**–**ap** in 61–92% yields. In the reactions with **2d**, **2k**, **2m**, and **2p**, we confirmed the formation of a trace amount of the corresponding 1,4-hydroarylation products by ^1H NMR and GC–MS analyses.

To identify the role of the alkene group on the substrate, we examined several control experiments as shown in Scheme 4.

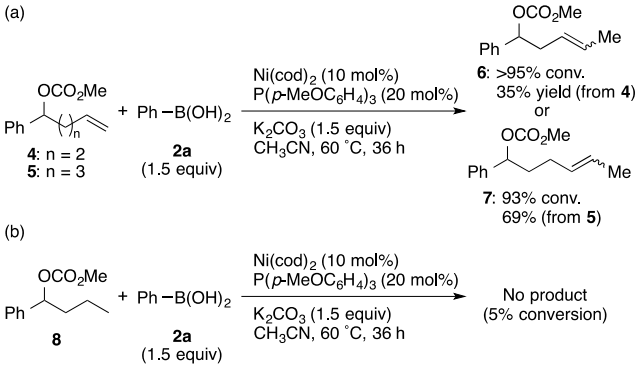
Scheme 3. Scope of Arylboronic Acids[a]





[a]Reaction conditions: **1a** (0.25 mmol), **2** (0.375 mmol), $Ni(cod)_2$ (0.025 mmol), $P(p\text{-}MeOC_6H_4)_3$ (0.05 mmol), K_2CO_3 (0.375 mmol) in CH_3CN (0.2 M) at 60 °C for 36 h. *E*/*Z* ratios were determined by ^1H NMR analyses of the crude mixture and are shown in parentheses. [b]Trace amounts of the corresponding 1,4-hydroarylation products were observed by ^1H NMR analyses of the crude mixture. [c]Yield of the corresponding alcohol. See the Supporting Information for details. [d]20 mol % of $Ni(cod)_2$ and 40 mol % of $P(p\text{-}MeOC_6H_4)_3$ were used. [e]As a mixture with a trace amount of inseparable impurity. [f]A trace amount of *Z* isomer was observed by GC–MS analysis.

Scheme 4. Control Experiments



The reaction of bishomoallyl carbonate **4** with phenylboronic acid (**2a**) was carried out under the optimized reaction conditions, giving the olefin isomerization product **6** in 35% yield. We could not observe the formation of hydroarylation products by the reaction of the isomerized product **6** with **2a** probably due to the inert nature of homoallyl carbonate

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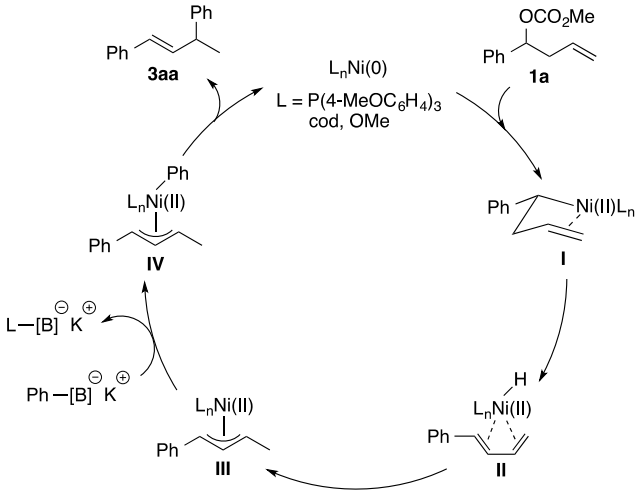
bearing a disubstituted alkene group in the nickel catalyst system (see Scheme 2, substrates **1s** and **1t**). The reaction of carbonate **5** having three methylene units also afforded the alkene-isomerized product **7** in 69% yield (Scheme 4a).[19] When the reaction of secondary alkyl carbonate **8** with **2a** was performed under the optimized reaction conditions, no products were observed by ^{1}H NMR and GC−MS analyses of the reaction mixture (Scheme 4b). These results indicated that the alkene group of the homoalyll carbonates plays a key role for the present nickel catalyzed hydroarylation as a directing group.

Based on the results of the control experiments and the reaction mechanism of the palladium-catalyzed reaction of homoallyl tosylates with arylboronic acids reported by Sigman and co-workers,[16] we proposed a plausible catalytic cycle for the present nickel catalysis (Scheme 5). Initially, the alkene-directed oxidative addition of a C−O bond of homoallyl carbonate **1a** to nickel(0) species would occur to generate secondary alkylnickel intermediate **I**. Subsequent β-hydride elimination would produce nickel hydride intermediate **II** stabilized by the coordination of the diene ligand derived from the homoallyl carbonate. Insertion of the terminal alkene moiety of the diene ligand to a Ni−H bond seems to take place due to the formation of the π-allylnickel intermediate **III**.[20] Transmetalation between the intermediate **III** and borate species followed by the reductive elimination from intermediate **IV** would produce the desired coupling product **3aa** along with the regeneration of nickel(0) species.[21]

Scheme 5. Plausible Reaction Mechanism



In conclusion, we have developed the nickel-catalyzed hydroarylation of 1,3-dienes with arylboronic acids in which secondary homoallyl carbonates would act as a surrogate for the 1,3-diene and hydride source. The nickel catalyst system enabled the straightforward access to a series of alkenyl arenes in high yields using readily accessible secondary homoallyl carbonates and arylboronic acids. The development of the hydrofunctionalization using this methodology and the detailed mechanistic study are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b04634.

Experimental details and procedures; experimental details for control experiments; NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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