OL Organic Letters

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Mild and Selective Rhodium-Catalyzed Transfer Hydrogenation of Functionalized Arenes

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Cite This: *Org. Lett.* 2021, 23, 1910–1914 Read Online

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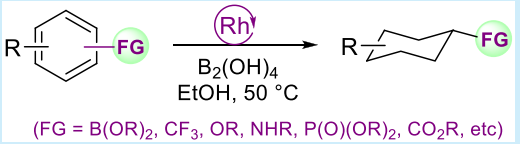
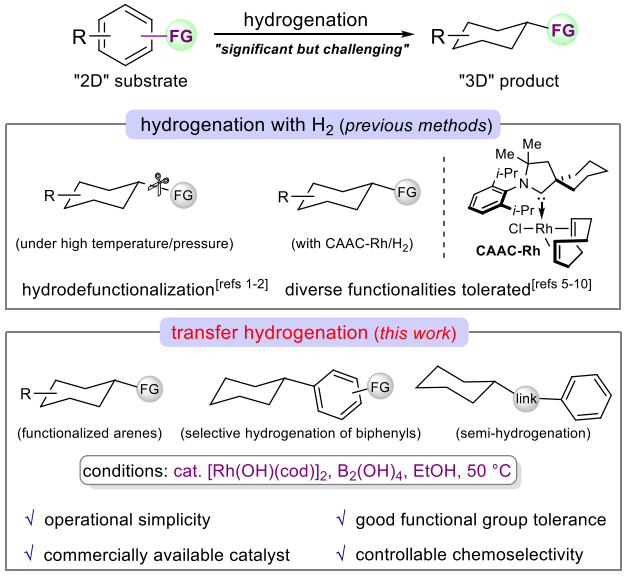
ABSTRACT: Diboron-mediated rhodium-catalyzed transfer hydrogenation of functionalized arenes is reported. In addition to good functional group tolerance, the reaction features operational simplicity and controllable chemoselectivity. The general applicability of this procedure is demonstrated by the selective hydrogenation of a range of arenes, including functionalized benzenes, biphenyls, and polyaromatics.



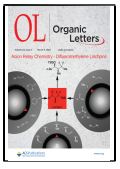
Hydrogenation of unsaturated compounds is arguably one of the most useful transformations in organic synthesis.[1] In particular, hydrogenation of arenes provides a convenient approach to access saturated carbo- and heterocycles.[2] Nevertheless, because of the inherent resonance stabilization energy, hydrogenation of arenes is far more challenging than those nonaromatic substrates.[3] Harsh reaction conditions such as high reaction temperature and highly pressurized H_2 gas were traditionally employed to overcome the higher kinetic barrier, which inevitably resulted in poor functional group (FG) tolerance.[1,2] As a result, in contrast to the remarkable advances of hydrogenation of simple arenes, the selective hydrogenation of functionalized arenes remained an unsolved problem.[4] Recently, with the use of cyclic (alkyl)(aminol)-carbene/rhodium catalyst (CAAC-Rh, Scheme 1), selective hydrogenation of diversely functionalized arenes, including aromatic ketones,[5] fluoroarenes,[6] silylated arenes,[7] di/trifluoromethylated arenes,[8] borylated arenes,[9] and phenol derivatives[10] were successfully achieved, mainly by the groups of Zeng and Glorius. These breakthroughs greatly improve the chemoselectivity and scope of arene hydrogenation. However, mild and selective arene hydrogenation methods that avoid the use of pressurized H_2 gas and elaborate setups, which is highly desirable for laboratory synthesis, are still underdeveloped.

Scheme 1. Hydrogenation of Functionalized Arenes



Transfer hydrogenation represents a practically useful hydrogenation strategy. It uses easy to handle hydrogen source other than hazardous H_2 gas and avoids the elaborate experimental setups, thus featuring operational simplicity and safety. Despite the extensive studies on transfer hydrogenation of various unsaturated substrates,[11] progress on transfer hydrogenation of arenes largely lags behind. Not surprisingly, the known reports mainly focus on the reactive azaarenes,[12] but the transfer hydrogenation of challenging benzene derivatives, especially the functionalized benzenes, remains scarce.[13] To realize the operationally simple and selective transfer hydrogenation of functionalized arenes, there are several prerequisites to be considered. First, the reducing reagent is supposed to be nontoxic, bench stable, and easy to handle; second, the catalyst should be reactive enough for hydrogenation under mild conditions while inert to labile functional groups. Diborons have been recently explored as effective and user-friendly mediators for transition-metal-catalyzed transfer hydrogenation reactions.[14] At the same time, rhodium-based catalysts have shown high reactivity and good functional group tolerance in hydrogenation reactions.[1]

Received: January 28, 2021
Published: February 18, 2021



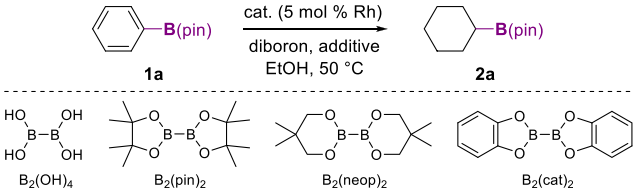
https://dx.doi.org/10.1021/acs.orglett.1c00341
Org. Lett. 2021, 23, 1910–1914

We recently studied the rhodium-catalyzed diboron-mediated transfer hydrogenation reaction of alkenes and carbonyls, and high reactivity of the catalytic system was observed.[15] Given the unique reactivity and selectivity of rhodium in hydrogenation, we envisioned the rhodium/diboron system might work for the selective transfer hydrogenation of functionalized arenes. During the course of our study, the Glorius group reported the transfer hydrogenation of arenes and heteroarenes with ammonia borane/TFE (2,2,2,-trifluoroethanol) as the hydrogen donor, and several types of functionalized arenes were efficiently hydrogenated.[16] Herein, we report the transfer hydrogenation of functionalized arenes using $B_2(OH)_4$/EtOH as the hydrogen donor. This new protocol shows good functional group tolerance, operational simplicity, and controllable chemoselectivity (Scheme 1).

We commenced the investigation with phenylboronic acid pinacol ester **1a** (Table 1). With cyclooctodiene (cod)-coordinated rhodium(I) chloride as the catalyst, the desired cyclohexylboronic acid pinacol ester **2a** was obtained using tetrahydroxydiboron as the reducing reagent in ethanol, and the conversion was higher by using the hydroxorhodium catalyst (Table 1, entries 1 and 2). In contrast to the high conversion of **1a** in these two reactions, the yield of **2a** was low. Given that other arylboronic esters undergo transmetalation with rhodium catalyst much easier than the corresponding pinacol ester[17] and no side product was detected by ^{1}H NMR analysis of the crude reaction mixture, we reasoned that solvolysis of **1a**/**2a** with EtOH followed by rhodium-catalyzed protodeboronation can be the possible side reaction to give volatile side products. Additional pinacol was then added to minimize the possible solvolysis of substrate/product, and gratifyingly the isolated yield of **2a** was improved to 74% (entry 3). Rhodium phosphine complexes, including the Wilkinson's catalyst, were not active (entries 4–6). The commercial Rh/C was found to be active for the transfer hydrogenation but showed a lower efficiency (entry 7). Different diborons were next investigated with $[Rh(OH)(cod)]_2$ as the catalyst, and bis(catecholate) diboron $B_2(cat)_2$ was found to be ineffective while both bis(pinacolate) diboron $B_2(pin)_2$ and bis(neopentylglycolate) diboron $B_2(neop)_2$ gave low yield of the desired product (entries 8–10). Thus, $[Rh(OH)(cod)]_2$ was chosen as the catalyst and $B_2(OH)_4$ was chosen as the diboron reagent for further studies.

With the established conditions for transfer hydrogenation of arylboronic acid pinacol ester in hand (Table 1, entry 3), the substrate scope was then studied. As shown in Scheme 2, a range of arylboronic acid pinacol esters bearing diverse substitutions (**2b**–**2g**) and substitutions at different positions (**2h**–**2i**) were all tolerated, giving the cis products as the major isomer. When the naphthyl substrates were employed, the unsubstituted ring was preferentially hydrogenated (semi:full >20:1) to give the tetrahydro-naphthylboronic acid pinacol esters (**2j**–**2k**) in high yields, and no fully hydrogenated product was observed. Note that the lower isolated yields of some products than NMR yields were mainly due to their instability on the silica gel column.

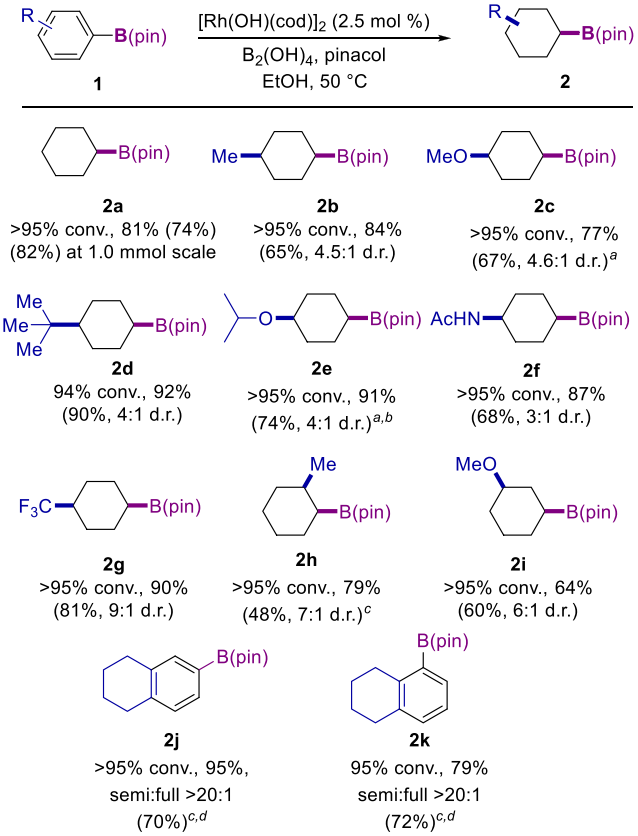
Table 1. Study on the Transfer Hydrogenation of Phenyl Boronate Ester 1a[a]



entry	catalyst and additive	diboron	conv (%)[b]	yield (%)[c]
1	$[RhCl(cod)]_2$	$B_2(OH)_4$	80	24 (23)
2	$[Rh(OH)(cod)]_2$	$B_2(OH)_4$	>95	44 (41)
3	$[Rh(OH)(cod)]_2$, pinacol	$B_2(OH)_4$	>95	81 (74)
4	$[Rh(OH)(binap)]_2$, pinacol	$B_2(OH)_4$	<5	<5
5	$[Rh(OH)(dppe)]_2$, pinacol	$B_2(OH)_4$	7	<5
6	$RhCl(PPh_3)_3$, pinacol	$B_2(OH)_4$	<5	<5
7	Rh/C, pinacol	$B_2(OH)_4$	55	55 (53)
8	$[Rh(OH)(cod)]_2$, pinacol	$B_2(cat)_2$	<5	<5
9	$[Rh(OH)(cod)]_2$, pinacol	$B_2(pin)_2$	27	<5
10	$[Rh(OH)(cod)]_2$, pinacol	$B_2(neop)_2$	28	17

[a]Reaction conditions: **1a** (0.20 mmol), diboron (0.90 mmol), catalyst (5 mol % Rh), pinacol (1.0 mmol, if added), EtOH (1.0 mL), 50 °C, 18 h. [b]Conversion of **1a**, determined by ^{1}H NMR analysis of the crude reaction mixture with 1,1,2,2-tetrachloroethane (0.20 mmol) as the internal standard. [c]Yield of **2a** based on the crude ^{1}H NMR with 1,1,2,2-tetrachloroethane (0.20 mmol) as the internal standard. Isolated yield is shown in parentheses.

Scheme 2. Transfer Hydrogenation of Aryl Boronate Esters[e]



[a]*i*PrOH instead of EtOH. [b]Et_3N (0.30 mmol) was added. [c]$[Rh(OH)(cod)]_2$ (10.0 μmol) was used. [d]$B_2(OH)_4$ (0.80 mmol) was used. [e]General conditions: aryl boronate ester (0.20 mmol), $B_2(OH)_4$ (0.90 mmol), $[Rh(OH)(cod)]_2$ (5.0 μmol), pinacol (1.0 mmol), EtOH (1.0 mL), 50 °C, 18 h. Conversion and NMR yields are given (1,1,2,2-tetrachloroethane as the internal standard), and isolated yields are shown in parentheses.

https://dx.doi.org/10.1021/acs.orglett.1c00341
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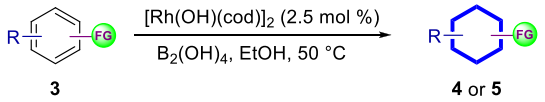
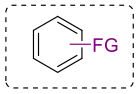
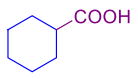
Scheme 3. Transfer Hydrogenation of Diverse Arenes[g]



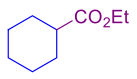
3 4 or 5

benzenes bearing different functionalities

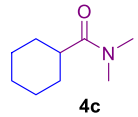




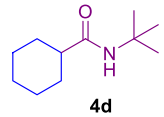
4a
>95% conv., >95%
(98%)



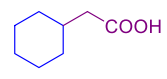
4b
>95% conv., >95%
(95%)



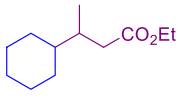
4c
94% conv., 93%
(91%)



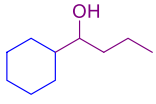
4d
>95% conv., >95%
(93%)



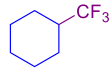
4e
>95% conv., >95%
(98%)



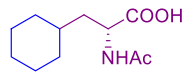
4f
>95% conv., >95%
(98%)



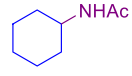
4g
91% conv., 87%
(85%)[a]



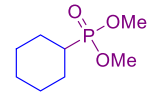
4h
>95% conv.[b]



4i
>95% conv., >95%
(98%)

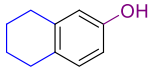


4j
>95% conv., >95%
(98%)

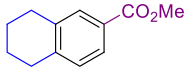


4k
>95% conv., >95%
(95%)

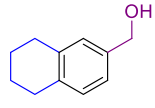
polycyclic aromatic hydrocarbons and biphenyls



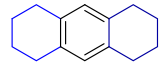
5a
87% conv., 87%
semi:full >20:1
(86%)[c]



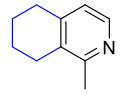
5b
82% conv., 74%
semi:full = 9.3:1
(71%)[c]



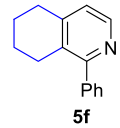
5c
77% conv., 77%
semi:full >20:1
(72%)[d]



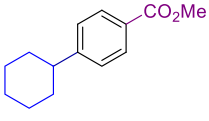
5d
>95% conv., >95%
semi:full >20:1
(97%)[e]



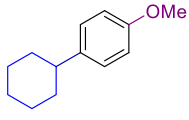
5e
93% conv.,91%
semi:full >20:1
(84%)[c]



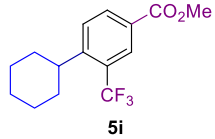
5f
76% conv., 76%
semi:full >20:1
(69%)[c,d]



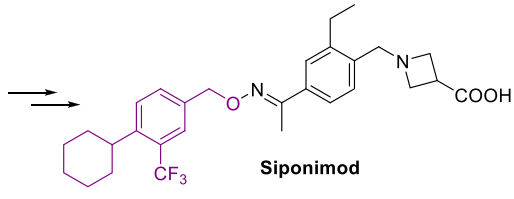
5g
85% conv., 78%
semi:full = 12.6:1
(72%)[e]



5h
83% conv., 65%
semi:full = 3.8:1
(61%)

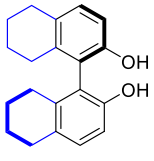


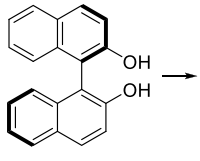
5i
84% conv., 60%
semi:full = 2.4:1
(60%)[d,e]

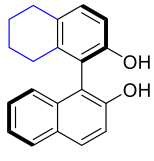


Siponimod

controllable reduction of unbiased arenes

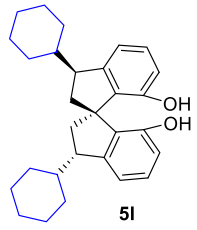


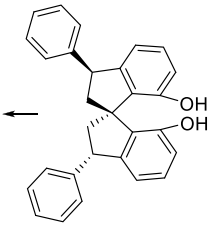




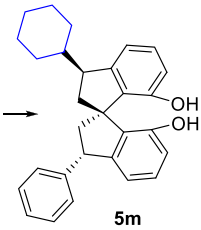
5j
>95% conv., >95%
semi:full <1:20
(98%)[d,e]

5k
72% conv., 68%
semi:full >20:1
(61%)[c]





5l
>95% conv., >95%
semi:full <1:20
(99%)[d,f]



5m
88% conv., 77%
semi:full = 5.9:1
(65%)[d]

[a]The corresponding ketone was used as substrate. [b]Determined by ^{19}F NMR of the reaction mixture; no side product was detected. [c]$B_2(OH)_4$ (0.60 mmol) was used. [d]$[Rh(OH)(cod)]_2$ (10.0 μmol) was used. [e]$B_2(OH)_4$ (1.60 mmol) was used. [f]$B_2(OH)_4$ (1.80 mmol) was used. [g]General conditions: **3** (0.20 mmol), $B_2(OH)_4$ (0.90 mmol), $[Rh(OH)(cod)]_2$ (5.0 μmol), EtOH (1.0 mL), 50 °C, 18 h. Conversion and NMR yields are given (1,1,2,2-tetrachloroethane as the internal standard), and isolated yields are shown in parentheses.

The general applicability of the developed method was further demonstrated by selective hydrogenation of diverse functionalized arenes (Scheme 3). Benzenes bearing different functionalities, including carboxylic acid (**4a**), ester (**4b**), amide (**4c**–**4d**), alkyl chain with functional groups (**4e**–**4g**), trifluoromethyl group (**4h**), amino acid moiety (**4i**), amino group (**4j**), and phosphonate (**4k**), were all efficiently reduced to the corresponding cyclohexanes, with functional groups unperturbed. The current method showed moderate to good selectivities for partial reduction of polyaromatic hydrocarbons and biphenyls. For example, the functionalized naphthalenes were selectively reduced on the less hindered ring (**5a**–**5c**)[18] and 1,2,3,4,5,6,7,8-octahydroanthracene was obtained by hydrogenation of anthracene (**5d**). Unusual chemoselectivity

https://dx.doi.org/10.1021/acs.orglett.1c00341
Org. Lett. 2021, 23, 1910–1914

was observed in the case of 1-substituted isoquinoline, and selective reduction of the fused benzene ring over pyridine ring was observed (**5e**−**5f**). When biphenyl substrates were employed, the phenyl ring with less substitution group was preferentially reduced (**5g**−**5i**), and this semihydrogenation provides a convenient route to prepare the key intermediate for synthesizing the FDA approved new drug siponimod.[19] One important advantage of transfer hydrogenation is the easily tunable amount of added reductant, which might be used to control the degree of reduction. In this study, we achieved the controllable hydrogenation of unbiased arenes in a substrate. Products from semi- or full reduction of the unbiased naphthalene ring in BINOL (**5j** and **5k**) and unbiased phenyl ring in 3,3′-Ph-SPINOL[20] (**5l** and **5m**) were attainable by adjusting the amount of diboron reagent.

Although further investigation is required to fully understand the reaction mechanism, successive homogeneous rhodium catalysis for hydrogen generation−heterogeneous rhodium catalysis for hydrogenation was considered as a working model on the basis of our previous study[15] and literature reports[21] (see Scheme S1 in the SI). Homogeneous rhodium catalysis led to the fast generation of hydrogen gas from diboron and ethanol (see Figure S1 in the SI), and the rhodium catalyst was then reduced to heterogeneous rhodium particles (see Figure S2 in the SI). The heterogeneous rhodium catalyst catalyzed the hydrogenation of arenes with the generated hydrogen gas.[21]

In summary, we have reported a new strategy for selective hydrogenation of functionalized arenes by diboron-mediated rhodium-catalyzed transfer hydrogenation. This protocol showed broad substrate scope, good functional group tolerance, and controllable chemoselectivity. Given the operational simplicity of the method, as well as commercial availability of the catalyst and diboron reagent, it shall provide a practically useful tool for laboratory synthesis. Further studies on the detailed mechanism of this rhodium-catalyzed transfer hydrogenation are currently ongoing 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.1c00341.

Experimental procedures, characterization data, and copies of ^{1}H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Natural Science Foundation of Jiangsu Province (BK20200080) and the "Double First-Class" University project of China Pharmaceutical University (CPU2018GY35) for financial support.

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