

# Arene Reduction by Rh/Pd or Rh/Pt under 1 atm Hydrogen Gas and Room Temperature

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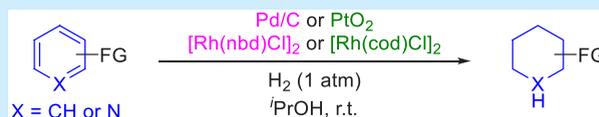


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Supporting Information

**ABSTRACT:** Current methods for arene hydrogenation generally need either harsh reaction conditions or complex catalyst preparation. Here we describe a mild and convenient protocol that only utilizes commercially available catalysts. Using  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  and Pd/C together as catalysts, arenes bearing various functional groups can be hydrogenated under 1 atm of  $\text{H}_2$  at room temperature. This arene hydrogenation can also be achieved using catalysts of  $[\text{Rh}(\text{cod})\text{Cl}]_2$  and  $\text{PtO}_2$ , thus avoiding glovebox manipulations and simplifying the reaction procedure.



The cyclohexane moiety is a ubiquitous structural motif that is widely found in drugs, agrochemicals, and natural products. As the direct functionalization of cyclohexane is much more difficult than that on arenes, reduction of arenes has become one of the most important methods to access substituted cyclohexanes.<sup>1,2</sup> However, due to the resonance stabilization of benzene rings, such transformations generally require harsh conditions, such as metal hydrides,<sup>3</sup> alkyl metal reagents,<sup>3</sup> or alkali metals (Birch reduction).<sup>4,5</sup> These methods arouse concerns both in safety and in atom economy. Recently several transfer hydrogenation reactions based on relatively stable boranes have also been developed.<sup>6,7</sup> These reactions are much safer but still produce stoichiometric amounts of solid waste.

Another method to obtain cyclohexane rings from their corresponding arenes is direct reduction with  $\text{H}_2$  in the presence of metal catalysts, especially heterogeneous metal catalysts. These reactions, featuring low price of the reductant, excellent atom economy, and easy separation of products, are therefore intensively used in industrial processes. To name a few, the Institut Français du Pétrole (IFP) process hydrogenates benzene in liquid phase using a Raney Ni catalyst under 50 atm at 200–225 °C, and the Dutch State Mines (DSM) gas-phase benzene hydrogenation uses a noble metal catalyst which operates at 400 °C under 30 atm.<sup>8</sup> However, the high pressure of  $\text{H}_2$  and the formidably high temperature make it difficult to implement these processes in ordinary laboratories.

Therefore, many groups have made great efforts to develop milder protocols for arene hydrogenation. In 2009 Sajiki's group examined the catalytic activities of Pt/C, Ru/C, and Rh/C in arene hydrogenation.<sup>9</sup> For alkylbenzenes, the reaction proceeded smoothly at 80 °C under 1 atm of  $\text{H}_2$ . However, when the substituent on the aromatic ring was not an alkyl group, the reaction became sluggish and both heating and pressurized  $\text{H}_2$  (3–5 atm) were required. In the same year, Zhou's group also reported the hydrogenation of phenols,

anisoles, and alkylbenzenes catalyzed by  $[\text{Rh}(\text{cod})\text{Cl}]_2$ , which could be realized at room temperature but required 50 atm of  $\text{H}_2$ .<sup>10</sup> In the past decade, the groups of Zeng and Glorius have independently and systematically studied Rh complexes bearing cyclic (amino)(alkyl)carbene (CAAC) ligands.<sup>11</sup> With these catalysts, hydrogenation of aromatic ketones,<sup>12</sup> fluoroarenes,<sup>13</sup> borylarenes,<sup>14</sup> silylarenes,<sup>15</sup> difluoro- and trifluoromethylated arenes<sup>16</sup> have been achieved at or slightly above room temperature. These findings greatly expanded the scope of arene hydrogenation; however, the issue of pressurized  $\text{H}_2$  (5–50 atm depending on the substrate) was still present.

One solution to the aforementioned problem is to exploit the high activity of nanoscaled transition metal catalysts. Several groups have achieved arene hydrogenation under ambient pressure and temperature using various transition metal nanostructures, which include Pt nanowires,<sup>17</sup> Rh nanoparticles,<sup>18–23</sup> and Ru–Pt,<sup>24</sup> Rh–Pd,<sup>18</sup> Rh–Ir,<sup>24</sup> Rh–Pt,<sup>24,25</sup> and Ir–Pt<sup>24</sup> bimetallic nanoparticles. However, preparation of these catalysts usually involves tedious steps and is inconvenient for organic chemists. In addition, reproducing experiments could be an issue, as the preparation of catalysts cannot be easily standardized. Overall, a mild and convenient method of arene hydrogenation using commercially available catalysts is still highly desired.

During our recent investigation on Rh-catalyzed [4 + 1] cycloaddition of cyclopropyl-capped dienes,<sup>26</sup> we originally planned to reduce the alkene moiety of the cycloadduct by catalytic hydrogenation. Intriguingly, when the phenyl-

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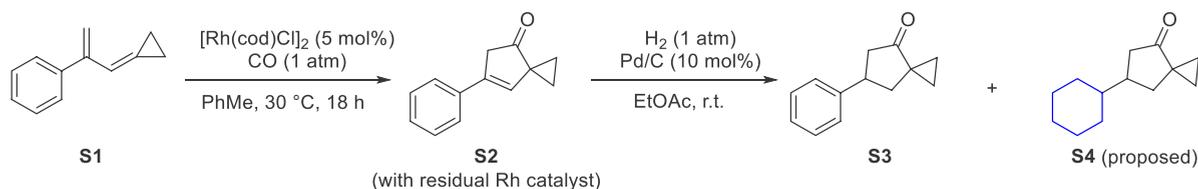
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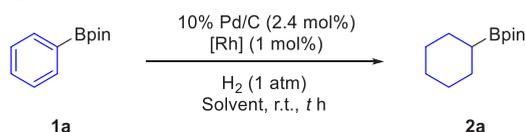


## Scheme 1. Serendipitous Discovery of Rh/Pd-Catalyzed Arene Hydrogenation



substituted [4 + 1] product was treated with Pd/C under an atmosphere of H<sub>2</sub>, a small amount of overhydrogenation product with the phenyl group reduced to a cyclohexyl group was observed (Scheme 1, see Supporting Information for details). Considering the possible influence of residual Rh catalyst, we then purified the cycloadduct carefully by preparative TLC. The Rh-free [4 + 1] cycloadduct, in contrast, was cleanly reduced under the same conditions, with the phenyl group kept intact. Importantly, we found that the phenyl group could not be reduced using [Rh(cod)Cl]<sub>2</sub> alone as a catalyst either: It was the combination of Rh and Pd catalysts that enabled this arene hydrogenation. Realizing that this may provide a novel and convenient method of arene hydrogenation under mild conditions, we decided to further optimize this reaction (Table 1).

Table 1. Optimization of Rh/Pd-Catalyzed Arene Hydrogenation<sup>a</sup>



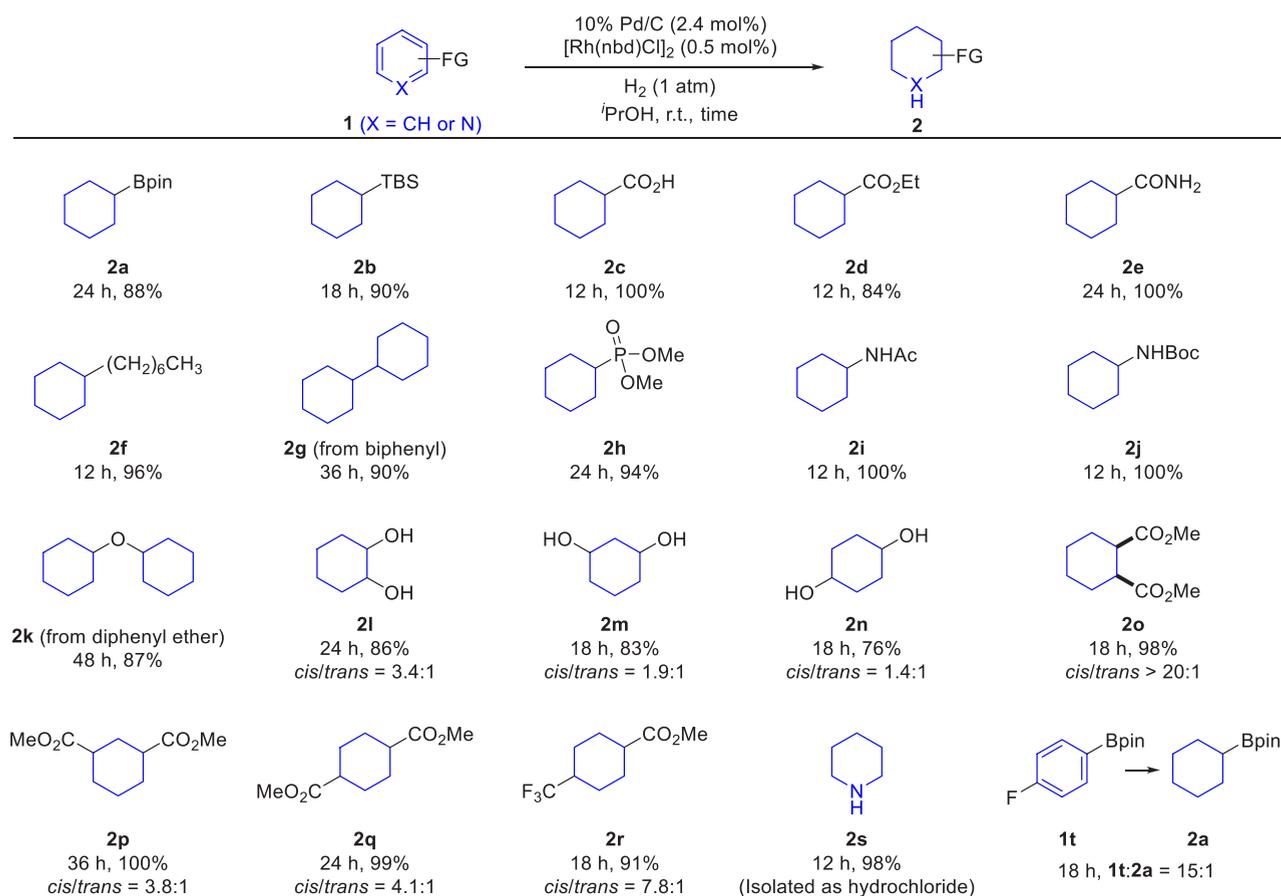
Entry	Rh catalyst	Solvent	t/h	1a Recovery <sup>b</sup>	Yield <sup>b</sup>
1	[Rh(cod)Cl] <sub>2</sub>	MeOH	12	64%	34%
2	[Rh(CO) <sub>2</sub> Cl] <sub>2</sub>	MeOH	12	90%	10%
3	[Rh(cod)(OH)] <sub>2</sub>	MeOH	12	61%	33%
4	[Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> Cl] <sub>2</sub>	MeOH	12	70%	27%
5	[Rh(nbd)Cl] <sub>2</sub>	MeOH	12	29%	70%
6	[Rh(cod) <sub>2</sub> ]BF <sub>4</sub>	MeOH	12	41%	54%
7	RhCl <sub>3</sub> ·3H <sub>2</sub> O	MeOH	12	40%	41%
8	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl	MeOH	12	–	0%
9	Rh(PPh <sub>3</sub> ) <sub>3</sub> (CO)H	MeOH	12	–	0%
10	[Rh(cod)Cl] <sub>2</sub>	EtOH	12	74%	28%
11	[Rh(cod)Cl] <sub>2</sub>	<sup>i</sup> PrOH	12	50%	41%
12	[Rh(cod)Cl] <sub>2</sub>	HFIP	12	79%	19%
13	[Rh(nbd)Cl] <sub>2</sub>	<sup>i</sup> PrOH	24	0	92% (88%) <sup>c</sup>
14 <sup>d</sup>	–	<sup>i</sup> PrOH	24	–	0%
15 <sup>e</sup>	[Rh(nbd)Cl] <sub>2</sub>	<sup>i</sup> PrOH	24	–	0%

<sup>a</sup>Reaction conditions: 0.50 mmol of **1a**, 1 mol % [Rh], 2.4 mol % Pd/C in 5 mL of solvent, stirred under H<sub>2</sub> (1 atm) at room temperature for *t* h. cod = 1,5-cyclooctadiene, nbd = norbornadiene, HFIP = 1,1,1,3,3,3-hexafluoroisopropanol. <sup>b</sup>Determined by <sup>1</sup>H NMR, 1,3,5-trimethoxybenzene as internal standard. <sup>c</sup>Isolated yield. <sup>d</sup>No Rh catalyst was added. <sup>e</sup>No Pd/C was added.

We used phenylboronic acid pinacol ester (**1a**) as the model substrate for reaction optimization, considering that hydrogenation of borylarenes is usually more challenging than ordinary arenes.<sup>1,14</sup> First, we examined the activity of the different Rh catalysts. For the ease of analysis and comparison, we chose a Pd loading of 2.4 mol %, a Rh loading of 1 mol %, and a reaction time of 12 h (the hydrogenation proceeded

within this time significantly but not fully). When the reaction was performed in MeOH, [Rh(cod)Cl]<sub>2</sub> gave 34% of **2a** together with 64% of **1a** recovered (entry 1). Another commonly used air-stable Rh catalyst, [Rh(CO)<sub>2</sub>Cl]<sub>2</sub>, proved much less effective than [Rh(cod)Cl]<sub>2</sub>, and only 10% of the substrate was consumed in 12 h (entry 2). The catalytic activities of [Rh(cod)(OH)]<sub>2</sub> and [Rh(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>Cl]<sub>2</sub> (entries 3–4) were close to that of [Rh(cod)Cl]<sub>2</sub>, while [Rh(nbd)Cl]<sub>2</sub> gave an exceptionally high conversion of 70% (entry 5). [Rh(cod)<sub>2</sub>]BF<sub>4</sub> and RhCl<sub>3</sub>·3H<sub>2</sub>O (entries 6–7) outperformed [Rh(cod)Cl]<sub>2</sub>, but were still less effective than [Rh(nbd)Cl]<sub>2</sub>. In addition, Rh complexes bearing phosphine ligands were completely inactive in this reaction (entries 8–9). Next, we screened several commonly used alcohol solvents using [Rh(cod)Cl]<sub>2</sub> as the Rh catalyst, which is air-stable and can be weighed outside a glovebox. EtOH and HFIP proved inferior to MeOH, while <sup>i</sup>PrOH resulted in the highest conversion of **1a** among all alcohols investigated (entries 10–12). <sup>i</sup>PrOH has another advantage over MeOH: It does not dissolve silica gel, which provides a convenience for product separation. Considering this and the outstanding performance of [Rh(nbd)Cl]<sub>2</sub>, we finally decided to use [Rh(nbd)Cl]<sub>2</sub> and Pd/C together as catalysts, and <sup>i</sup>PrOH as solvent (entry 13). Under these standard conditions, **1a** can be completely consumed within 24 h, and **2a** was isolated in 88% yield. Importantly, no **2a** was formed either without Pd/C or without the Rh catalyst (entries 14–15), suggesting that both catalysts were indispensable in this hydrogenation reaction.

Using the optimal conditions above, we examined the performance of this Rh/Pd-catalyzed hydrogenation reaction for a variety of arenes bearing different functional groups (FGs, see Figure 1). We carried out all reactions for 12 h, and then monitored them every 6 h until full conversion. Silylarene **1b** cleanly afforded the hydrogenation product **2b** in 90% yield within 18 h. Benzoic acid (**1c**) and its derivatives, including ester (**1d**) and amide (**1e**), can all be hydrogenated efficiently in 12–24 h. Product **2d** was obtained in a slightly lower yield due to its volatile nature. Alkyl substituted arene **1f** was smoothly reduced to **2f** in 12 h, and biphenyl was fully hydrogenated in 36 h to afford **2g** in 90% yield. Phosphonate **1h** was also successfully reduced in 24 h, giving **2h** in 94% yield. For nitrogen-substituted arenes, we examined acetyl- and Boc-protected anilines **1i** and **1j**, both of which afforded the hydrogenation products quantitatively in 12 h. We did not investigate unprotected aniline and *N*-alkyl anilines, because these substrates can be reduced by 1 atm of H<sub>2</sub> at room temperature using Pd/C alone.<sup>27</sup> Oxygen-substituted arenes **1k–1n** showed a slight tendency to undergo hydrodefunctionalization, all giving cyclohexanol as a side product. Fortunately, this side product could be removed simply by rotary evaporation, leading to pure hydrogenation products **2k–2n** in high yields. For cyclohexanediols **2l–2n**, *cis* isomers were found to be the major products, with *dr* values ranging from 1.4:1 to 3.4:1. We also investigated the hydrogenation of three



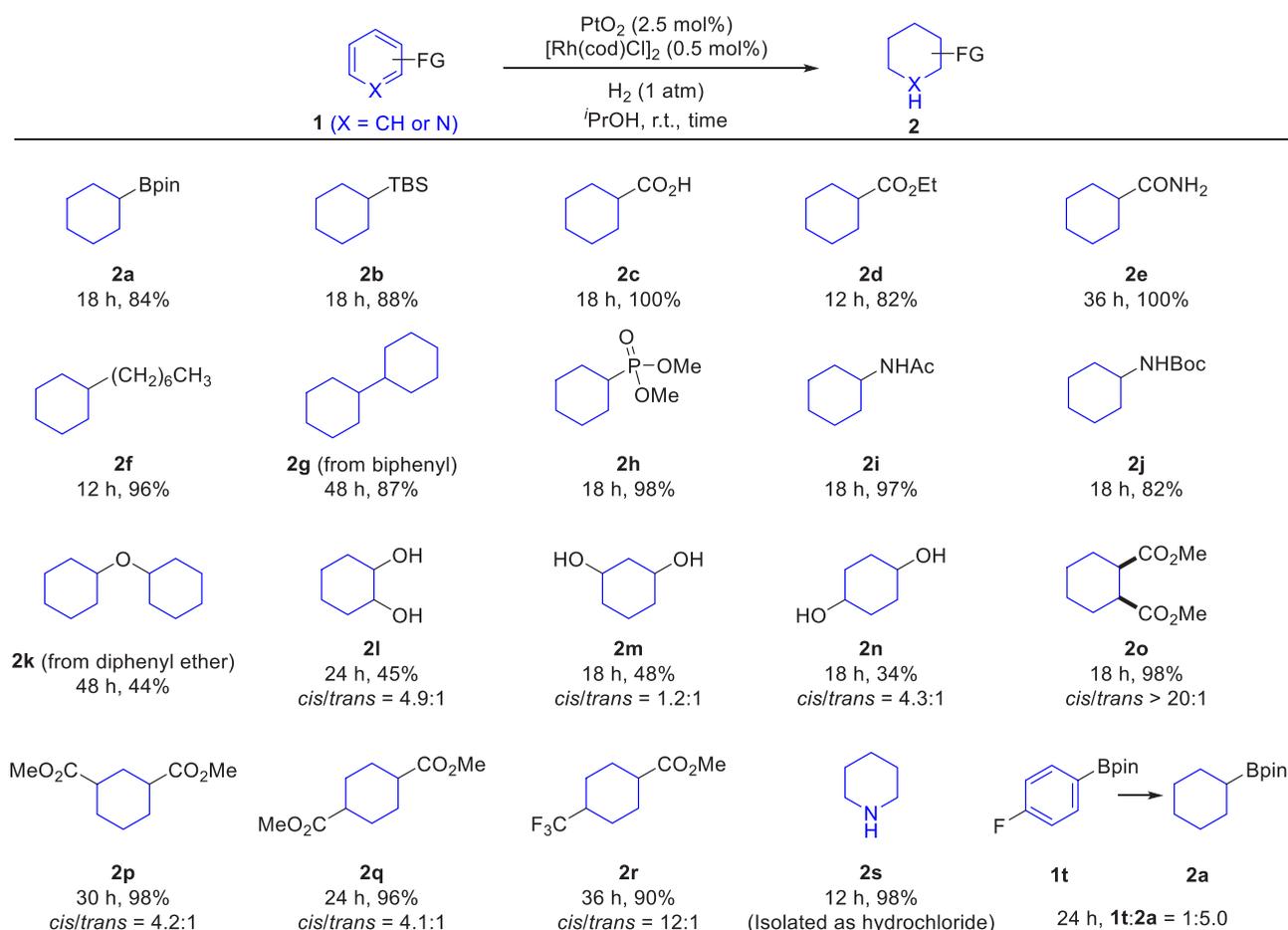
**Figure 1.** Reaction scope of Rh/Pd-catalyzed arene hydrogenation. Reaction conditions: 0.50 mmol of **1**, 2.4 mol % Pd/C, 0.5 mol % [Rh(nbd)Cl]<sub>2</sub>, 5 mL of *i*PrOH, r.t., 1 atm of H<sub>2</sub>. Every yield shown was an isolated yield, which was an average of two runs.

regioisomers of dimethylbenzenedicarboxylate, finding that all of them (**1o–1q**) can be quantitatively reduced. Compared with diols, diester substrates gave higher diastereoselectivities, especially for dimethyl phthalate, which was reduced to **2o** in an exclusive *cis* manner. Considering the wide presence of trifluoromethyl group in fine chemicals, we also tested the hydrogenation of methyl 4-trifluoromethylbenzoate (**1r**). We were delighted to find that this substrate was successfully hydrogenated in 18 h, leading to **2r** in 91% yield and 7.4:1 *dr*. We did not observe any defluorination product during this reaction. In contrast, fluorine-substituted arene **1t** underwent hydrodefluorination to give **2a**, and the desired product **2t** was not detected. In addition to arenes, pyridine can also be reduced to piperidine (**2s**) using the present method. However, as pyridines can actually be hydrogenated under ambient conditions using Pd/C alone,<sup>27</sup> we did not investigate more of these substrates.

We have also carried out the reaction under reduced catalyst loading, finding that gram-scale hydrogenation of **1o** can be accomplished quantitatively in 36 h using 1 mol % Pd/C and 0.2 mol % [Rh(nbd)Cl]<sub>2</sub>. Importantly, the “Rh–Pd/C” catalyst can be recycled and reused at least four times without significant loss of activity (see Supporting Information (SI) for details).

After establishing the protocol of arene hydrogenation using [Rh(nbd)Cl]<sub>2</sub> and Pd/C together as catalysts, we further sought a new method which utilizes [Rh(cod)Cl]<sub>2</sub> instead of [Rh(nbd)Cl]<sub>2</sub>, because the latter is less air-stable and is usually stored in a glovebox. Considering that Pt was also frequently

used in arene hydrogenation,<sup>17,25,28,29</sup> we attempted to replace Pd/C with PtO<sub>2</sub>. To our delight, a combination of catalysts [Rh(cod)Cl]<sub>2</sub> (0.5 mol %) and PtO<sub>2</sub> (2.5 mol %) can fully reduce **1a** in just 18 h—even faster than the Rh/Pd protocol above. Therefore, these reaction conditions were directly applied without further optimization. We examined the performance of this Rh/Pt-catalyzed arene hydrogenation using the same substrates as we did for the Rh/Pd protocol, and the results are shown in Figure 2. For B-, Si-, C-, P-, and N-substituted arenes and pyridine (**1a–1i**, **1o–1s**), the Rh/Pt method generally gave yields close to those from the Rh/Pd method, and the reaction times for both methods were also comparable. However, the issue of hydrodefunctionalization was more pronounced in the Rh/Pt protocol. Boc-protected aniline **1j** partially (~18%) underwent N–C bond cleavage to give BocNH<sub>2</sub> as a side product, which could only be removed by column chromatography. Oxygen-substituted arenes **1k–1n** suffered from defunctionalization more severely, and the corresponding products **2k–2n** were obtained in relatively low yields. Fluorine-substituted arene **1t** again underwent hydrodefluorination to give **2a**. Other failed substrates are listed in SI. One advantage of the Rh/Pt protocol over the Rh/Pd counterpart, however, is the higher diastereoselectivity in the former. Among the seven disubstituted arenes investigated, **1l**, **1n**, and **1r** were hydrogenated with higher *dr* values, and **1o–1q** gave *dr* values essentially the same as those obtained using the Rh/Pd method. Only in one case (**1m**) was the Rh/Pt method slightly outperformed by its Rh/Pd counterpart in terms of diastereoselectivity. We notice that the composition of



**Figure 2.** Reaction scope of Rh/Pt-catalyzed arene hydrogenation. Reaction conditions: 0.50 mmol of **1**, 2.5 mol % PtO<sub>2</sub>, 0.5 mol % [Rh(cod)Cl]<sub>2</sub>, 5 mL of *i*PrOH, r.t., 1 atm of H<sub>2</sub>. Every yield shown was an isolated yield, which was an average of two runs.

this catalytic system is actually similar to Nishimura's catalyst (rhodium–platinum oxide) which was prepared by fusion of RhCl<sub>3</sub>, H<sub>2</sub>PtCl<sub>6</sub>, and NaNO<sub>3</sub> at 460–480 °C.<sup>28,30</sup> Our method, in contrast, does not need such steps and is obviously much simpler.

In conclusion, we have developed a mild and practical method for arene hydrogenation using commercially available [Rh(nbd)Cl]<sub>2</sub> and Pd/C catalysts. This protocol operates at room temperature under 1 atm of H<sub>2</sub>, and can be performed using common laboratory glassware and a hydrogen balloon. A variety of functionalized arenes, including B-, Si-, C-, N-, P-, and O-substituted arenes can be reduced efficiently to give corresponding cyclohexanes in high yields. The combination of catalysts can also be changed into fully air-stable [Rh(cod)Cl]<sub>2</sub> and PtO<sub>2</sub>, which eliminates the need for glovebox manipulations and further simplifies the reaction implementation. We do not have expertise in studying heterogeneous reaction mechanisms and encourage other scientists to investigate the mechanism of the present reaction.

## ASSOCIATED CONTENT

### Data Availability Statement

The data underlying this study are available in the published article and its [Supporting Information](#).

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.4c01029>.

Initial discovery of arene hydrogenation, experimental procedures, characterization data, and copies of NMR spectra ([PDF](#))

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### Notes

The authors declare the following competing financial interest(s): A patent of the present research, CN2024103221423, has been applied.

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