Birch-Type Reduction of Arenes in 2-Propanol Catalyzed by Zero-Valent Iron and Platinum on Carbon

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1. INTRODUCTION

Arene reduction is a useful method of preparing cyclohexane derivatives, which are utilized as functional materials, liquid organic hydrogen carriers in the energy field, etc. However, the reduction (hydrogenation) of resonance-stabilized arenes generally requires the use of excess H₂ gas, the industrial production of which from fossil fuels such as CH₄ is accompanied by CO₂ emission. Moreover, the transportation, storage, and usage of H₂ gas are strictly regulated by law. Therefore, reduction not involving the utilization of H₂ is obviously advantageous from the viewpoint of safety, ease of handling, and avoidance of special equipment usage. Therefore, catalytic transfer hydrogenation using biomass bearing a large amount of alcohol moiety and its analogue-like partial structure within the molecule has been eagerly investigated, and bimetallic Fe- and Pd-catalyzed reductions have also been reported. We have continuously developed methods of heterogeneously catalyzed dehydrogenation of organic substrates (e.g., alcohols and cyclohexane derivatives) and investigated ways of mechanochemical H₂ generation from water, alkanes, and ether to avoid CO₂ emission. Furthermore, we demonstrated that in situ generated H₂ can be directly utilized for reduction, as exemplified by Pt on carbon (Pt/C)-catalyzed arene reduction in 2-propanol (2-ProOH) as a solvent and hydrogen source (Scheme 1, A). Unexpectedly, although this reduction proceeded smoothly in a sealed stainless steel tube, it could not be realized in a sealed glass tube. Our recent screening of metallic additives revealed that zero-valent Fe is an essential co-catalyst for arene reduction (Scheme 1, B). Although a bimetallic system containing Pt and Fe was previously utilized to control the catalyst activity in the hydrogenation of ethylene, cinnamaldehyde, and other aldehydes, all of these reductions could be realized in the presence of Pt alone. Hydrogenations promoted by bimetallic catalysts comprising Fe and Pt group metals other than Pt (Rh, Pd, and Ru) were also reported, and the performances of these catalysts were heavily reliant on the reaction conditions. For example, Pt–Fe catalysts inhibited the hydrogenation of furan and benzene rings. Herein, we demonstrate that Pt/C-catalyzed arene reduction can be switched on/off by the presence/absence of Fe and perform X-ray absorption near edge spectroscopy (XANES) analysis to suggest a mechanistic explanation. The metal-containing reaction apparatus, such as a sealed stainless steel tube, etc., is generally utilized in the reactions under high-pressure and high-temperature conditions, whereas our new approach can be utilized for more mild reactions. It is also noted that the molecular Fe species generated in situ can be switchable on/off several times without a significant loss of activity due to the stability of Pt/C, which is important for industrial applications. Therefore, we here describe the Pt/C–Fe-catalyzed arene reduction in 2-propanol and further discuss the effect of Fe on the reaction by XANES analysis in detail. In the present study, we employed 2-propanol as a hydrogen source, obviating the need for flammable (and hence, dangerous and hard-to-handle) hydrogen gas, while metallic Fe acted as an essential co-catalyst to promote reduction. The chemical states of Pt and Fe in the reaction mixture were determined by X-ray absorption near-edge structure analysis, and the obtained results were used to suggest a plausible reaction mechanism, implying that catalytic reduction involved Pt- and Fe-mediated single-electron transfer and the dehydrogenation of 2-propanol.
high-temperature conditions. In contrast with the Pt/C- and Fe-catalyzed arene reduction, H–D exchange reaction of arenes could proceed without the reduction of arene moieties in the glass flask under the similar reaction conditions using Pt/C in 2-PrOH and D₂O instead of H₂O. Therefore, the present phenomenon is valuable to alert the chemists about the effect of reaction apparatus.

2. RESULTS AND DISCUSSION

n-Heptylbenzene (1a, 0.5 mmol) could not be catalytically reduced by 3 h of heating at 100 °C in a sealed glass tube containing Pt/C, 2-PrOH (4 mL), and H₂O (2 mL) (Table 1, entry 1). On the other hand, this reduction proceeded in the presence of the zero-valent Fe (5 mol %) as a main component of stainless steel to produce the corresponding cyclohexane derivative (2a) in excellent isolated yield (98%). The above reduction also proceeded in the presence of Zn and Co as co-catalysts, although lower conversions were obtained (entries 3 and 4). The use of Ni and Cr as other major stainless steel components was ineffective, as was the case for Cu, Al, and Mg (entry 5). Although 2a could be obtained in the presence of iron oxides (FeO and Fe₂O₃) in moderate yields (entries 6 and 7, respectively), these reductions were incomplete within 3 h. Heterogeneous platinum-group metal catalysts other than Pt/C (e.g., Pd/C and Rh/C) were ineffective for the above reduction even in the presence of Fe (entries 8 and 9), and no conversion was observed when Fe was used as the only catalyst (entry 10). The deference of reactivity of Pt/C, Pd/C, or Rh/C cannot be explained. Furthermore, the reduction efficiency decreased with decreasing reaction temperature (entry 11, 80 °C), and no reduction was observed at 50 °C (entry 12). Notably, gram-scale reduction of 1a (1.3 g, 7.4 mmol) afforded 2a in 97% isolated yield (entry 13).

The above reduction could be carried out in a 2-PrOH (4 mL)–H₂O mixture (entry 1, Table 1; Table 2, entry 3), which allowed one to decrease the risk posed by the pyrophoric nature of Pt/C. While the arene reduction was completely performed using 3 mL of 2-PrOH, further decrease of 2-PrOH usage to 2 mL caused the incomplete reduction within 3 h (see the Supporting Information). On the other hand, the reduction was completely inhibited by the use of 1-PrOH or t-BuOH as co-solvents (Table 2, entries 2 and 3). Furthermore, pure H₂O could not be employed as a hydrogen source (entry 4). Importantly, reduction in the 2-PrOH–H₂O mixture was more effective than reduction in pure H₂O under H₂ atmosphere (entry 5).

The arene nuclei of cyclohexylbenzene (1b), t-butylbenzene (1c), and acetanilide (1d) effectively underwent Pt/C–Fe-catalyzed reduction in 2-PrOH/H₂O to produce the corresponding cyclohexane derivatives (2b–2d, Scheme 2).

| Table 1. Effect of Metal Co-catalyst on the Reduction of n-Heptylbenzene |
|---|
| entry | catalyst | additive | 1a/2a<sup>b</sup> (mol/mol) |
| 1 | 10% Pt/C |  | no reaction |
| 2 | 10% Pt/C | Fe | 0/100 (98)<sup>b</sup> |
| 3 | 10% Pt/C | Zn | 76/24 |
| 4 | 10% Pt/C | Co | 89/11 |
| 5 | 10% Pt/C | Ni, Cr, Cu, Al, or Mg | no reaction |
| 6 | 10% Pt/C | FeO | 33/67 |
| 7 | 10% Pt/C | Fe₂O₃ | 25/75 |
| 8 | 10% Pd/C | Fe | no reaction |
| 9 | 10% Rh/C | Fe | no reaction |
| 10 |  | Fe | no reaction |
| 11<sup>c</sup> | 10% Pt/C | Fe | 47/53 |
| 12<sup>d</sup> | 10% Pt/C | Fe | no reaction |
| 13<sup>e</sup> | 10% Pt/C | Fe | 0/100 (97)<sup>b</sup> |

<sup>a</sup>Ratio was determined by 1H NMR. <sup>b</sup>Isolated yield. <sup>c</sup>At 80 °C. <sup>d</sup>At 50 °C. <sup>e</sup>7.4 mmol of 1a (1.3 g) was used as a substrate.

| Table 2. Effect of Solvent on Arene Reduction Efficiency |
|---|
| entry | solvent | 10% Pt/C (5 mol%) | Fe (5 mol%) |
| 1 | 2-PrOH (4 mL)/H₂O (2 mL) | 0/100 (98)<sup>b</sup> |
| 2 | 1-PrOH (4 mL)/H₂O (2 mL) | no reaction |
| 3 | t-BuOH (4 mL)/H₂O (2 mL) | no reaction |
| 4 | H₂O (6 mL) | no reaction |
| 5 | H₂O (6 mL) | 11/89 |

<sup>a</sup>Ratio was determined by 1H NMR. <sup>b</sup>Isolated yield. <sup>c</sup>Under H₂ atmosphere.

Anthracene (1e) was partially reduced to 1,2,3,4,5,6,7,8-octahydroanthracene (2e) in good yield. Toluene (1f) could be smoothly transformed to methylcyclohexane (2f) if the substrate was treated for 4 h under H₂ atmosphere. In all cases, substrates (1b–1f) were completely reduced without any byproduct formation.

Although the Pt/C–Fe-catalyzed reduction of stilbene (3) hardly proceeded in 2-PrOH/H₂O at 25 or 40 °C (Table 3, entries 1 and 2, respectively), the olefin functionality of 3 was selectively reduced at 60 °C without the reduction of arene nuclei to produce 1,2-diphenylethane (4) in 98% isolated yield (entry 3). However, olefin reduction was hardly catalyzed at 60 °C by Pt/C in the absence of Fe (entry 4). On the other hand, both olefin and arene functionalities of 3 were reduced in the presence of Pt/C and Fe (5 mol % each) at 100 °C (12 h) to afford 1,2-dicyclohexylethane (5) in quantitative yield (entry 5). 7-Tetradecene (6), bearing no aromatic nucleus within the molecule, also efficiently underwent Pt/C–Fe-catalyzed reduction also completely performed using 3 mL of 2-PrOH, further decrease of 2-PrOH usage to 2 mL caused the incomplete reduction within 3 h (see the Supporting Information).
reduction of the olefin functionality at 60 °C to give tetradecane (7) in 88% yield, while 11% of 6 was recovered (Scheme 3). Complete reduction was observed at 100 °C, furnishing 7 in 97% isolated yield. Meanwhile, in the absence of Fe powder, 6 was completely recovered at 60 and 100 °C.

Scheme 3. Reduction of 7-Tetradecene under Different Conditions

Subsequently, we compared the hydrogenation activities of Pt/C−Fe, Pt/C, and Fe in 1-PrOH (poor hydrogen source; Table 2, entry 2) and H2O at 100 °C under H2 (1 atm, 1 h; Scheme 4). In the case of Pt/C−Fe (5 mol % Pt and Fe each), 11% of 1a was reduced, and 89% of 1a was recovered, whereas 2a was obtained in 17% yield when Pt/C was used on its own, and no hydrogenation was observed when Fe was employed on its own. These results indicated that under the conditions of the Pt/C−Fe-catalyzed reaction, Fe does not facilitate Pt/C-catalyzed hydrogenation, with H2 gas generated in situ by the Pt/C-catalyzed dehydrogenation of 2-PrOH (Table 1, entry 2). Thus, as has previously been reported,11 the accelerating effect of combining Pt and Fe on hydrogenation was not observed in the present arene reduction.

Figure 1 shows the time profiles of the internal pressure in a 50 mL sealed glass tube filled with different reaction mixtures.

Table 3. Reduction of Stilbene under Different Conditions

Table 4. Gaseous Products Produced under the Conditions of Figure 1 after 6 h

thermal conductivity detection (GC−TCD). The reduction of 1a (0.5 mmol) in 2-PrOH (4 mL)−H2O (2 mL) in the presence of 10% Pt/C (5 mol %: 0.025 mmol) and Fe (5 mol %: 0.025 mmol) at 100 °C was complete within 3 h (Table 1, entry 2). The internal pressure after 3 h reached ~2 atm, and no further increase was observed after the completion of arene reduction (Figure 1, conditions A), with the yield of H2 after 6 h equaling only 0.33 mmol (Table 4, entry 1). Heating of the 2-PrOH−H2O mixture only resulted in a slight increase of the internal pressure up to ~2 atm due to simple vaporization and thermal expansion of the fluid and gas (air) (conditions B).

These results indicated that the developed arene reduction could safely proceed without the generation of excessive amounts of high-pressure flammable H2 gas. Since Fe did not catalyze H2 generation in 2-PrOH/H2O (conditions C, H2 generation by corrosion (oxidation) of Fe in the aqueous solution was ruled out.14 The simple use of Pt/C in 2-PrOH/H2O resulted in the generation of a massive amount of propane (116.2 mmol) by Pt/C-catalyzed hydrodeoxygenation,15 while only traces of H2 were concomitantly produced (conditions D). On the other hand, the generation of propane...
could be suppressed by the use of Fe powder along with Pt/C (conditions E). Furthermore, the addition of 1a to the solvent mixture containing Pt/C but no Fe powder suppressed the generation of C₆H₆ and H₂, while no reduction of the aromatic nucleus was observed (conditions F). Probably, Pt metal was strongly coordinated by arene nuclei, which inhibited the Pt/C-catalyzed dehydrogenation and hydrodeoxygenation of 2-PrOH.

To elucidate the mechanism of arene reduction, the mean valence of Fe in reaction mixtures was analyzed by XANES. As noted in the Introduction section, the Pt/C-catalyzed reduction of 1a proceeded only in a stainless steel vessel, while the addition of Fe (5 mol%) allowed this reduction to be performed in a glass tube. Figure 2 shows the X-ray fluorescence profiles of the reaction mixtures A and B (see Scheme 1) after 3 h of heating, revealing that these mixtures contained 4.4 and 5.0 mmol Fe, respectively, as determined from the peak integral values. These findings clearly confirmed the leaching of Fe from stainless steel during the reaction.

The valences of Fe and Pt in the mixtures A and B after reduction were determined from Fe K-edge (Figure 3) and Pt LIII-edge (Figure 4) XANES spectra of these mixtures using Fe⁰ powder, Pt⁰ foil, FeCl₃, and PtCl₄ as standards (detailed descriptions are provided in the Supporting Information). Compared with each energy based on the absorption edge energy shift (normalized absorbance = 0.5 in Figure 3a), the Fe K-edge absorptions of the samples A and B were shifted to higher energies than that of the zero-valent Fe,¹⁶ and the mean valence of Fe in these samples was estimated as 1.57 and 1.50, respectively (Figure 3b).

X-ray absorption fine structure (XAFS) and polarized neutron reflectivity (PNR) analyses also strongly supported the generation of oxidized Fe ions during the reduction (see the Supporting Information). Similarly, the analysis of Pt LIII-edge XANES spectra (Figure 4a) in comparison with the absorption peak energy (absorbance = 0.5)¹⁷ revealed that the absorption peaks of the samples A and B shifted to higher energies (i.e., to higher oxidation states) than that of zero-valent Pt metal (Figure 4b).¹⁸ As a result, the valence of Pt in both A and B samples after reduction was determined to be 1.51 and 1.32, respectively, which indicated that both A and B reactions were triggered by electron transfer from Pt and Fe metals to the aromatic ring to form partially oxidized Pt and Fe ions.

Two reaction mechanisms were proposed based on these findings (Scheme 5). First, the Pt/C-catalyzed dehydrogenation of 2-PrOH produces H₂, which can be consumed in the traditional Pt/C-catalyzed arene (1) hydrogenation¹⁷ and acetone (route a). In situ generated H₂ rapidly reacts with acetone to afford 2-PrOH, which suppresses the accumulation of excess H₂ in the vessel. Although the role of Fe is unclear, its addition promotes the dehydrogenation of 2-PrOH (Table 4, conditions A vs F) and suppresses the hydrodeoxygenation of 2-PrOH to propane, precluding the consumption of H₂ required for arene hydrogenation (Table 4, conditions D vs E). As shown in Table 2, entries 2 and 3, arene reduction cannot be achieved when 2-PrOH is substituted for 1-PrOH or t-BuOH. This behavior is ascribed to the fact that Pt-group metal/C-catalyzed dehydrogenation of primary alcohols is accompanied by several side reactions such as decarbonylation of intermediate aldehyde derivatives,⁷b which can retard arene reduction, while tertiary alcohols without α-protons cannot act as H₂ sources. Therefore, Pt/C–Fe-catalyzed arene reduction effectively proceeds only in 2-PrOH.

Alternatively, arene reduction can take place via single electron transfer (SET) analogously to the Birch reduction (route b). SET from zero-valent Pt metal¹⁸ to the arene nucleus of the charge transfer complex (A) formed from I, and Pt/C gives a radical anion intermediate (B) that is immediately protonated by 2-PrOH or H₂O to form C. The subsequent second SET and protonation afford a 1,3-cyclohexadiene intermediate (E) complexed by Pt¹Ⅰ. Pt¹Ⅰ smoothly accepts electrons from Fe⁰ to regenerate Pt⁰ (F) and produce Fe¹Ⅰ, which is immediately reduced to Fe⁰ by H₂ generated via Pt/C-catalyzed dehydrogenation of 2-PrOH (route a). Repetition of SET and protonation processes afford cyclohexane product 2 and regenerated Pt⁰ (catalytic cycle 1). The Pt¹ intermediate C can also be reduced to Pt⁰ by Fe⁰ to produce intermediate G and Fe¹. Subsequent SET within G and the protonation of anion intermediate H furnishes a diene–Pt¹ complex (I). Pt¹ can then be reduced by Fe¹ to generate a diene–Pt⁰ complex J.

**Figure 2.** X-ray fluorescence profiles of the mixtures A and B (see Scheme 1).

**Figure 3.** (a) Normalized Fe K-edge XANES profiles. (b) Plot of Fe K-edge absorption edge energy shift vs the valence of Fe. Reaction conditions A and B are described in Scheme 1.
(catalytic cycle-2), and the resulting FeII species are reduced to Fe0 by H2 derived from 2-PrOH. The mean valence of Pt (1.32 and 1.51) determined by XANES analysis supports the operation of catalytic cycle 1, which involves redox shuttling between Pt0 and PtII. The release of PtII from complex E in the absence of catalytic Fe powder should afford diene intermediate K. Notably, 1a was completely recovered under the conditions of Pt/C catalysis in the absence of Fe (Table 1, entry 1). On the other hand, unsaturated cyclohexane derivatives such as cyclohexadiene and cyclohexene easily undergo Pt-group metal-catalyzed dehydrogenative aromatization in H2O to form the corresponding benzene derivatives.8a Therefore, diene intermediate K might be immediately transformed to 1 via Pt-catalyzed dehydrogenation. Indeed, a mixture of toluene (8; 0.95 mmol) and 1-methyl-1,4-cyclohexadiene (9; 0.05 mmol) as a model of the corresponding diene intermediate (K) was smoothly converted to toluene (8; 0.99 mmol) as the sole product via the dehydrogenation of K under conditions of 2-PrOH-free aqueous Pt/C catalysis in both the presence and absence of Fe (Scheme 6).19 K2PtCl4 and PtO2 also catalyzed the dehydrogenation of 9, which resulted in the formation of 8. Furthermore, the use of 1-PrOH or t-BuOH instead of 2-PrOH should afford diene intermediates equivalent to K, since in these cases, Fe0 cannot be regenerated from FeII because of the poor (or absence of) H2 generation ability of these alcohols. The regeneration of 1 from K also causes the complete recovery of 1 when 1-PrOH and t-BuOH are used as solvents (Table 2, entries 2 and 3). Meanwhile, the (Pt/C (5 mol %) + 2-PrOH)-mediated reduction of the olefin functionality of stilbene (3) in the absence of Fe proceeded to an insignificant extent to produce 1,2-diphenylethane (4; 3% yield) via the SET mechanism not involving redox shuttling between PtI/PtII and Pt0 (Table 3, entry 4). This finding was ascribed to the fact that the dehydrogenation of the saturated ethylene function of 4 to 3 was not catalyzed by Pt/C in H2O (Scheme 7). The consecutive generation of appropriate quantities of H2 via Pt/C−Fe-catalyzed dehydrogenation of 2-PrOH for the regeneration of Fe0 from FeII was required to

Scheme 5. Proposed Mechanisms or Pt/C−Fe-Catalyzed Arene Reduction

Scheme 6. Pt-Catalyzed Dehydrogenative Regeneration of Toluene (8) from Cyclohexadiene Derivative 9

Scheme 7. Results of 1,2-Diphenylethane (4) Reduction under the Conditions of Pt/C Catalysis

Figure 4. (a) Normalized Pt LIII-edge XANES profiles. (b) Plot of Pt LIII-edge absorption edge energy shift vs the valence of Pt. Reaction conditions A and B are described in Scheme 1.
**Scheme 8. Reaction Using Deuterated Solvents**

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Reference 13a

(N. 25 mmol)

10% Pt/C (3 mol%) Fe (5 mol%)

2-PrOH (0.1 mL) D2O (2 mL)

/ 2-Hex (0.9 mL)

80 °C, 24 h

100 °C, 4 h

5% yield

1d-1d-

(0.25 mmol)

10% Pt/C (3 mol%)

2-PrOH (0.4 mL) D2O (2 mL)

100 °C, 4 h

61% yield

1d-

(0.5 mmol)

10% Pt/C (5 mol%)

2-PrOH-d8 (4 mL) H2O (2 mL)

100 °C, 4 h

35% yield

1d-

(0.5 mmol)

10% Pt/C (5 mol%)

2-PrOH-d8 (4 mL) H2O (2 mL)

100 °C, 4 h

1d-
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*Italic number means the deuterium content*

3. CONCLUSIONS

Pt/C–Fe-catalyzed arene reduction with 2-PrOH as a hydrogen source under ambient-pressure conditions was developed. The Pt/C-catalyzed in situ production of H2 via the dehydrogenation of 2-PrOH was shown to play a critical role in the regeneration of the composite catalyst to promote arene reduction. Since only small amounts of H2 accumulated in the reaction vessel after reduction, the present method was concluded to be useful from the viewpoint of safety. The presence of a catalytic amount of Fe was found to be crucial for the external hydrogen-free reduction of aromatic nuclei in aqueous 2-PrOH.

4. EXPERIMENTAL SECTION

4.1. General Information. Ten percent Pt/C, Pd/C, Rh/C, and Ru/C were supplied by the N. E. Chemcat Corporation (Tokyo, Japan). 1-PrOH, 2-PrOH, t-BuOH, and water were purchased from commercial sources and used without further purification. All of the commercially available reagents were used without further purification. Reactions were carried out in 50 mL glass sealed tube (tinyclave steel (Büchiglasuster, Switzerland)) or 15 × 150 mm/tube. 1H NMR spectra were recorded on a JEOL ECZ 400 or ECA 500 spectrometer at room temperature in CDCl3 as a solvent and internal standard (1H NMR: δ = 7.26 for CDCl3) with tetramethylsilane as a further internal standard. A JMS Q1000 GC [7890A gas chromatography (Agilent Technologies, USA) equipped with a JEOL MK II mass spectrometer (JEOL Co., Ltd., Japan)] and an Inert CapS/M/sil capillary column (30 × 0.25 mm i.d., 0.25 μm film thickness; GL Science, Japan) were used for toluene and methylcyclohexane analyses. GC-3200 [gas chromatography equipped with thermal conductivity detector (GC/TCD; GL Science, Japan)] was used for gas analysis with Molecular Sieve 5 Å (60/80 mesh) packed column (3 × 2.2 mm i.d., 1/8 inch; GL Science, Japan) for H2 analysis, Porapak Q (80/100 mesh) packed column (2 × 2.2 mm i.d., 1/8 inch: GL Science, Japan) for C3H8 analysis. EXAFS measurements of solutions were performed using the fluorescence mode at the BL11S2 Hard X-ray EXAFS beamline station in the Aichi SR.
The incident X-rays were monitored by an ionization chamber (14 cm in length) filled with N₂ gas.

4.2. General Procedure for Arene Reduction (Tables 1–3; Schemes 2 and 3). 4.2.1. Reduction of n-Heptylbenzene, Cyclohexylbenzene, tert-Butylbenzene, or Anthracene. A 50 mL sealed glass tube was sequentially charged with arene (0.50 mmol), Fe⁰ (1.4 mg, 0.025 mmol, 5 mol %), 10% Pt/C (48.8 mg, 0.025 mmol, 5 mol %), H₂O (2 mL), and 2-PrOH (4 mL), and the suspension was stirred at 100 °C (Caution: the addition of 2-PrOH in the absence of H₂O causes the ignition of Pt/C). After stirring for 1 h, the mixture was cooled to room temperature and filtered through a membrane filter (Millipore, Millex-LH, 0.2 μm) to remove catalysts. The filtrate was extracted with Et₂O (3 × 10 mL) and the organic layer was further extracted with Et₂O (3 × 10 mL). The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated in vacuo to give the cyclohexane product.

4.2.2. Reduction of Toluene. A 50 mL sealed glass tube was sequentially charged with toluene (1f; 46.1 mg, 0.50 mmol), Fe⁰ (2.8 g, 0.050 mmol, 10 mol %), 10% Pt/C (97.6 g, 0.050 mmol, 10 mol %), H₂O (2 mL), and 2-PrOH (4 mL), and the suspension was stirred at 100 °C (Caution: the addition of 2-PrOH in the absence of H₂O causes the ignition of Pt/C). After stirring for 3 h, the mixture was cooled to room temperature and anisole added (50 μL) as an internal standard. The mixture was filtered through a membrane filter (Millipore, Millex-LH, 0.2 μm) to remove catalysts. The filtrate was transferred to a 50 mL volumetric flask with Et₂O. Twenty microliters of the sample solution was injected (split; 1:10). The products were identified by their GC/MS retention times in comparison to those of authentic commercial samples. Retention times (min) were 1.3 (H₂, Molecular Sieve 5 Å) and 13.7 (C₇H₈, Porapak Q).

4.4. General Procedure for Arene Reduction under Hydrogen Condition (Scheme 4). A 50 mL sealed glass tube was sequentially charged with n-heptylbenzene (1a; 88.3 mg, 0.50 mmol), Fe⁰ (1.4 mg, 0.025 mmol, 5 mol %), 10% Pt/C (48.8 mg, 0.025 mmol, 5 mol %), H₂O (2 mL), and 1-PrOH (4 mL). The inside air was replaced with H₂ (balloon) in five vacuum/argon cycles, and the suspension was stirred at 100 °C. After stirring for 1 h, the mixture was cooled to room temperature and filtered through a membrane filter (Millipore, Millex-LH, 0.2 μm) to remove the catalysts. The filtrate was extracted with Et₂O (20 mL), diluted with H₂O (20 mL), and then the aqueous layer was further extracted with Et₂O (3 × 10 mL). The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated in vacuo to give the cyclohexane product.

4.5. General Procedure for the Dehydrogenation of Cyclohexadiene Derivative (9) Mixed with Small Amount of Arene (8) (Scheme 6, Equation 1). A 30 mL co-plug test tube was sequentially charged with toluene (8; 100 μL, 0.95 mmol), 1-methyl-1,4-cyclohexadiene (9; 5.6 μL, 0.05 mmol), Fe⁰ (2.8 mg, 0.050 mmol, 10% Pt/C (97.6 mg, 0.050 mmol) and H₂O (6 mL), and the suspension was stirred at 100 °C. After stirring for 1 h, the mixture was cooled to room temperature and anisole (100 μL) added as an internal standard. The mixture was filtered through a membrane filter (Millipore, Millex-LH, 0.2 μm) to remove the catalysts. The filtrate was transferred to a 100 mL volumetric flask with Et₂O. Twenty microliters of the sample was dissolve in 1.5 mL of Et₂O. Compound 9 was detected by GC/MS.

4.6. General Procedure for Dehydrogenation of 1,2-Diphenylethane (4) Mixed with Small Amount of Stilbene (3) (Scheme 6, Equation 2). A 50 mL sealed glass tube was sequentially charged with stilbene (3; 171.2 mg, 0.95 mmol), 1,2-diphenylethane (4; 9.5 mg, 0.05 mmol), Fe⁰ (2.8 mg, 0.050 mmol, 10% Pt/C (97.6 mg, 0.050 mmol), and H₂O (6 mL), and the suspension was stirred at 100 °C. After stirring for 1 h, the mixture was cooled to room temperature and filtered through a membrane filter (Millipore, Millex-LH, 0.2 μm) to remove the catalysts. The filtrate was extracted with Et₂O (20 mL), diluted with H₂O (20 mL), and then the aqueous layer was further extracted with Et₂O (3 × 10 mL). The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated in vacuo to give the products.

4.7. Spectroscopic Data of the Products. 4.7.1. n-Heptylcyclohexane (2a) in Tables 1 and 2. n-Heptylbenzene (1a; 88.3 mg, 0.50 mmol), Fe⁰ (5 mol %), 10% Pt/C (5 mol %), H₂O (2 mL), and 2-PrOH (4 mL) were used, and the reaction was carried out according to the general procedure shown in Section 4.2.1 to give 2a (92.2 mg, 0.49 mmol) in 98% yield. Scale-up study (Table 1, entry 13): A 200 mL two-neck round-bottom flask was sequentially charged with n-heptylbenzene (1a; 130 g, 7.40 mmol), Fe powder (21.3 mg, 0.38 mmol, 5 mol %), 10% Pt/C (731.4 mg, 0.37 mmol, 5 mol %), amounts of H₂ and C₇H₈ were detected from the analysis of the headspace gas by GC/TCD. Helium was employed as a carrier gas at 220 kPa (molecular sieve 5 Å) and 140 kPa (Porapak Q). The injector and detector temperatures were 100 °C. The column temperature was programmed to 70 °C. One milliliter of sample gas was injected. The products were identified by their GC/TCD retention times in comparison to those of authentic commercial samples. Retention times (min) were 1.3 (H₂, Molecular Sieve 5 Å) and 13.7 (C₇H₈, Porapak Q).
H₂O (15 mL), and 2-PrOH (30 mL). The air inside was replaced with argon (balloon) by five vacuum/argon cycles, and the suspension was stirred at 100 °C. After stirring for 4 h, the mixture was cooled to room temperature and filtered through celite pad to remove catalysts. The filtrate was extracted with Et₂O (40 mL) and H₂O (40 mL), and then the aqueous layer was further extracted with Et₂O (3 × 20 mL). The organic layer was dried over anhydrous MgSO₄, and concentrated in vacuo to give 2a (1.32 mg, 7.21 mmol) in 97% yield. Colorless oil; 1H NMR (400 MHz, CDCl₃): δ 1.75–1.67 (m, 5H), 1.31–1.12 (m, 16H), 0.94–0.85 (m, 5H). ¹H NMR spectrum of the product was identical to that of the ref 10b.

### 4.7.4. N-Cyclohexylacetamide (2c) in Scheme 2.

Cyclohexylacetamide (1c; 67.1 mg, 0.50 mmol), Fe⁰ (1.4 mg, 10% Pt/C (5 mol %), H₂O (2 mL), and 2-PrOH (4 mL) were used, and the reaction was carried out according to the general procedure shown in Section 4.2.1 to give 2c (53.5 mg, 0.382 mmol) in 78% yield. Colorless oil; ¹H NMR (500 MHz, CDCl₃): δ 1.74–1.62 (m, 10H), 1.24–0.89 (m, 12H); ¹H NMR spectrum of the product was identical to that of the ref 10b.

### 4.7.5. 1,2,3,4,5,6,7,8-Octahydroanthracene (2e) in Scheme 2.

Anthracene (1e; 89.1 mg, 0.50 mmol), Fe⁰ (5 mol %), 10% Pt/C (5 mol %), H₂O (2 mL), and 2-PrOH (4 mL) were used, and the reaction was carried out according to the general procedure shown in Section 4.2.1 to give 2e (85.6 mg, 0.46 mmol) in 92% yield. Colorless solid; ¹H NMR spectrum of the product was identical to that of the ref 3e.

### 4.7.6. 1,2-Diphenylethane (4) in Table 3, Entry 3.

Stilbene (3; 45.1 mg, 0.25 mmol), Fe powder (5 mol %), 10% Pt/C (5 mol %), H₂O (1 mL), and 2-PrOH (2 mL) were used, and the reaction was carried out according to the general procedure shown in Section 4.2.3 to give 4 (44.7 mg, 0.25 mmol) in 98% yield. Colorless solid; ¹H NMR (400 MHz, CDCl₃): δ 7.33–7.20 (m, 10H), 2.95 (s, 4H). ¹H NMR spectrum of the product was identical to that of the ref 21.

### 4.7.7. 1,2-Dicyclopheylethane (5) in Table 3, Entry 4.

Stilbene (3; 45.1 mg, 0.25 mmol), Fe powder (5 mol %), 10% Pt/C (5 mol %), H₂O (1 mL), and 2-PrOH (2 mL) were used, and the reaction was carried out according to the general procedure shown in Section 4.2.3 to give 5 (48.1 mg, 0.25 mmol) in 99% yield. Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 1.70–1.62 (m, 10H), 1.26–1.12 (m, 12H), 0.89–0.84 (m, 4H). ¹H NMR spectrum of the product was identical to that of the ref 10b.

### 4.7.8. Tetradecane (7) in Scheme 3.

Tetradecane (6; 49.1 mg, 0.25 mmol), Fe powder (5 mol %), 10% Pt/C (5 mol %), H₂O (1 mL), and 2-PrOH (2 mL) were used, and the reaction was carried out according to the general procedure shown in Section 4.2.3 to give 7 (47.1 mg, 0.24 mmol) in 97% yield. Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 1.32–1.26 (m, 24H), 0.90–0.86 (m, 6H). ¹H NMR spectrum of the product was identical to that of the ref 22.
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