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# A metal-free approach for the hydrogenolysis of unactivated C(aryl)–C(alkyl) bonds

Huadong Wang ( huadongwang@fudan.edu.cn )

Fudan University https://orcid.org/0000-0001-9129-0004

### Yuliang Xu

Fudan University

Yizhou Yang

Fudan University

#### Yizhen Liu

Fudan University

#### Zhen Li

Fudan University

#### Article

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# Abstract

The hydrogenolysis of C–C bonds is among one of the most important processes in the petroleum industry which has been considered as a viable way to recycle waste polyolefins. These transformations typically rely on heterogeneous catalysts and take place at high temperature and high pressure with limited selectivity. Employing homogenous transition metal catalysts, while allowing the hydrogenolysis of C–C bonds to proceed under much milder conditions, is only suitable for substrates containing strained C–C bonds or directing groups. Here we report that a borenium complex can catalyze the selective hydrogenolysis of unstrained C(aryl)–C(alkyl) bonds of alkylarenes at ambient temperature, affording the corresponding alkanes and arenes. This method does not require the assistance of directing groups, and tolerates a range of functional groups. Mechanistic studies suggest a reaction pathway that involves a synergistic activation of dihydrogen by the borenium complex and alkylarenes, followed by retro-Friedel-Crafts reaction to cleave the C(aryl)–C(alkyl) bonds. The synthetic utility of this protocol was demonstrated by the conversion of post-consumer polystyrene into valuable benzene and phenylalkanes with mass recovery above 90%, thus opening up new avenues for the recycling of aromatic chemicals from waste plastics.

# Main Text

The catalytic hydrogenolysis of C–C bonds, a process involving rupture of C–C bonds via reaction with dihydrogen, plays a central role in the petroleum industry, upgrading low-value feedstocks to high-value fuels or commodity chemicals.<sup>1-3</sup> Recently, the hydrogenolysis of C–C bonds also attracted attention as a viable way for the chemical recycling of polyolefin plastic waste.<sup>4, 5</sup> Due to the large bond dissociation energy and non-polar nature of C–C bonds, industrial hydrogenolysis of C–C bonds typically takes place at temperatures above 300°C with high-pressure hydrogen (40 to 200 bar). The substantial energy requirements of this process provide a strong incentive to develop catalytic systems which can operate at ambient conditions. A number of homogenous hydrogenolysis of C–C bonds have been reported using transition metal catalysts.<sup>6</sup> The key step in these transformations is the cleavage of C–C bonds via oxidative addition, which takes place prior to the activation of H<sub>2</sub>. However, to ensure that the oxidative addition of steric shielded C–C bonds can outcompete more accessible C–H bonds, specifically designed substrates, such as those incorporated with strained C–C bonds <sup>7-9</sup> or pre-installed directing groups,<sup>10-13</sup> are required, thereby limiting the scope of this approach.

In recent decades, main-group-element-based systems have drawn a surging interest as a result of their potential to mimic or even transcend the reactivities of their transition metal counterparts in catalysis.<sup>14-</sup> <sup>16</sup> Aiming to circumvent the inherent limitation associated with transition metal catalysts in C–C bond hydrogenolysis, we set out to explore the possibility of main-group-element based catalysts for the hydrogenolysis of unstrained C–C bonds in the absence of directing groups. We chose the hydrogenolysis of the C(aryl)–C(alkyl) bonds of alkylarenes as our target. This transformation, known as hydrodealkylation, plays an important role in the production of arenes in the petroleum industry (Figure 1A).<sup>2,3,17</sup> The presence of unsaturated arene moieties in this transformation, however, represents an extra challenge because of competing arene hydrogenation reactions.<sup>18</sup> The sole example of homogenous hydrogenolysis of unactivated C(aryl) - C(alkyl) bonds was reported by Milstein et al.,<sup>10</sup> in which methylarenes with two pendant phosphine arms can be converted to the corresponding arenes and methane in the presence of Rh catalysts under H<sub>2</sub> at 150°C (Figure 1B). The two phosphine moieties, which cannot be readily removed, are indispensable for the observed reactivity, as the formation of stable metallacycle intermediates provides the driving force for the oxidative addition of the C(aryl)-C(alkyl) bond.<sup>19</sup> Our hydrodealkylation approach was inspired by frustrated Lewis pair chemistry pioneered by Stephan and Erker.<sup>20-22</sup> One of the most important discoveries in this field is that  $H_2$  can be heterolytically cleaved when simultaneously interacting with an electron donor and an electron acceptor.<sup>23,24</sup> We questioned if an alkylarene, as a  $\pi$ -electron donor, is capable of activating H<sub>2</sub> in the presence of a Lewis acid, which would lead to the formation of a hydride species and a Wheland complex (Figure 1C). A retro-Friedel-Crafts reaction of the Wheland complex would yield the arene and a carbenium intermediate.<sup>25,26</sup> Subsequent hydride abstraction from the generated hydride species by the carbenium intermediate would afford the alkane and the Lewis acid catalyst, thus completing the catalytic cycle. Given that alkylarenes are much weaker electron-donors than Lewis bases typically applied in frustrated Lewis pair chemistry (such as amines and phosphines), we reasoned that an exceptionally strong Lewis acid with high hydride affinity would be needed for smooth H<sub>2</sub> activation under mild conditions.<sup>23,24</sup> Furthermore, steric protection around the Lewis acid center will be necessary to hinder the hydride transfer from the Lewis acid center to the Wheland complex, a side reaction which would lead to the hydrogenation of aromatic rings.<sup>27</sup> Recently, we reported the synthesis of an Nheterocyclic carbene (1,3-bis(2,3,4,5,6-pentafluorobenzyl)imidazol-2-ylidene, IBn<sup>F</sup>) stabilized o-carboranylsubstituted borenium complex 1a, which is Lewis acidic enough to activate methane under relatively mild conditions.<sup>28</sup> This prompted us to explore the catalytic activity of **1a** in the hydrodealkylation of unfunctionalized alkylarenes.

We began our study by choosing (1,1-dimethylpropyl)benzene (**2**) as the model substrate. Combining **2** with 10 mole percent (mol%) of **1a** under 1 bar of H<sub>2</sub> in bromobenzene resulted in the formation of benzene and isopentane with 97% and 91% yields respectively as determined by gas-chromatographymass spectrometry (GC-MS) after 24 hours at 25°C (Table S1). Increasing the pressure of H<sub>2</sub> to 20 bar allows the reaction to reach full conversion with a much lower catalyst loading (1 mol%). No arene hydrogenation products were formed under this reaction condition as indicated by the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the crude reaction mixture (Figure S2). Other haloarenes, such as C<sub>6</sub>H<sub>5</sub>Cl, C<sub>6</sub>H<sub>5</sub>F or o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>, are also suitable solvents for the hydrodealkylation reaction. In the absence of H<sub>2</sub>, both **2** and **1a** remained unchanged in C<sub>6</sub>D<sub>5</sub>Br after 24 hours at 25°C. Replacing **1a** with less electrophilic [IMe<sub>4</sub>B(H)Cb] [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (IMe<sub>4</sub> = 1,3,4,5-tetramethylimidazol-2-ylidene, Cb = o-carboran-1-yl, **1b**)<sup>29</sup> resulted in lower yields (23% and 5% for benzene and isopentane respectively) even at 50°C (Table S1). Neutral organoborane B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and strong Brønsted acid CF<sub>3</sub>SO<sub>3</sub>H are completely ineffective as catalysts.

With our optimized conditions in hand, we explored the scope of this transformation, starting with the alkyl moieties of the alkylarenes (Figure 2). Tertiary-alkyl substituted benzenes, such as *t*-butylbenzene (**3**) and 1-phenyl-adamantane (**4**), were efficiently converted to benzene and the corresponding alkanes. Secondary-alkyl substituted benzenes (**5-10**) are also suitable substrates. Interestingly, for 1-(4-chlorophenyl)-1-phenylethane (**8**), the formation of benzene is favored over electron-poor chlorobenzene, in agreement with the proposed role of arenes as  $\pi$ -bases in the H<sub>2</sub> activation process. For 1-phenyletralin (**9**), selective hydrogenolysis of the exo-ring C(aryl)–C(alkyl) bond was observed. Cumene (**11**) suffers competing transalkylation, which affords alkylated bromobenzene as a byproduct due to the reaction between 2-propyl cation intermediate and solvent bromobenzene. Similarly, diphenylmethane (**12**) also undergoes transalkylation to yield benzene and alkylated bromobenzene. When the phenyl groups of diphenylmethane were replaced with bulkier mesityl groups, the reaction proceeded smoothly to yield mesitylene and 1,2,3,5-tetramethylbenzene in o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>. Toluene and ethylbenzene failed to undergo hydrogenolysis even with 20 mol% of **1a** at 50°C under 20 bar of H<sub>2</sub> (Figure S32).

Subsequently, the scope of the arene moiety was investigated (Figure 2). Functional groups, such as primary alkyl (**14-18**), fluoro, chloro and bromo groups (**20-22**) are tolerated, although the substrates with electron-withdrawing groups require higher catalyst loading. While weakly coordinating methoxy group (**19**) is tolerated, albeit at slightly elevated temperatures and increased catalyst loading, the presence of stronger coordinating functional groups, such as amino and ester, however, completely inhibited the hydrogenolysis reaction (Figure S32). For the substrates containing C(aryl)–C(aryl) bonds (**23**, **24** and **28**), only the C(aryl)–C(alkyl) bonds were selectively cleaved. Hydrogenolysis of 1-(4-chlorophenyl)-1-(2-naphthyl)ethane (**25**) led to partial reduction of naphthalene to give tetralin. Dialkyl-substituted arenes (**26-29**) undergo double C–C bond hydrogenolysis, affording the corresponding arenes and alkanes. Heteroarenes, such as alkyl-substituted dibenzofuran (**30**) and xanthene (**31**), are compatible with the reaction conditions. This catalytic system can also be applied to a gram scale reaction, where 1.33 g of **28** undergoes hydrogenolysis to yield biphenyl in 93% isolation yield.

To understand the mechanism of this hydrodealkylation reaction, we conducted kinetic experiments to determine the order of the reaction in each reactant by monitoring the hydrogenolysis of **6** in  $C_6D_5Br$  by <sup>1</sup>H NMR analysis. Throughout the reaction, **1a** remained the only observable IBn<sup>F</sup>-coordinated complex as indicated by <sup>1</sup>H and <sup>19</sup>F NMR spectra, revealing **1a** as the resting state with respect to the catalytic boron component. The reaction displayed first-order dependence on catalyst **1a**, **6** and the pressure of H<sub>2</sub> (Figure S33, S36, S41). This is consistent with our proposed reaction pathway entailing synergistic activation of H<sub>2</sub> with **1a** and **6**. The involvement of H<sub>2</sub> in the rate law also indicates that the activation of H<sub>2</sub> takes place either prior to or during the turnover-determining step. Replacing H<sub>2</sub> with D<sub>2</sub> resulted in the formation of C<sub>6</sub>H<sub>5</sub>D and (CH<sub>3</sub>)C(D)(H)(C<sub>6</sub>H<sub>5</sub>), as determined by the <sup>2</sup>H NMR spectrum (Figure S48). 1111111sssMeasuring the rate constants in the presence of H<sub>2</sub> or D<sub>2</sub> led to the determination of a kinetic isotope effect (KIE) of 1.17 (Figure 3A). Furthermore, Eyring analysis over a 40°C range (50 to

90°C, Figure S47) revealed the enthalpy and entropy barriers ( $\Delta H^{\neq} = 18.4 \pm 1.7$  kcal mol<sup>-1</sup>,  $\Delta S^{\neq} = -23.9 \pm 4.9$  e.u.) for the catalytic reaction. The small KIE value, combined with the moderately negative  $\Delta S^{\neq}$  value,<sup>30</sup> effectively rules out the involvement of the cleavage of H–H bond in the turnoverdetermining step. To gauge the impact of electron density of the aryl ring on the rate of the hydrogenolysis reaction, we examined the initial rates of a series of *para*-substituted (1,2,3,4-tetrahydronaphthalen-1-yl)benzene, and created a Hammett plot by plotting log( $k_X / k_H$ ) against substituent parameters  $\sigma_p$  (Figure 3B). A negative Hammett parameter p of -2.46 was observed, indicative of increased reactivity for electron rich arenes, consistent with the proposed role of the arenes as  $\pi$  base in the activation of H<sub>2</sub>.

To provide further insight into the mechanism, we investigated the hydrogenolysis of **6** with the density functional theory (DFT (M06-2X)) calculations (Figure 3C).<sup>31</sup> Catalyst **1a** (the [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> anion was omitted during the calculation, details see supplementary information) first forms a high energy H<sub>2</sub>-adduct **1a-H<sub>2</sub>** with H<sub>2</sub>, which in turn reacts with **6** to afford Wheland complex **6-H<sup>+</sup>** and neutral borane **1a- H** via transition state **TS1**. At **TS1**, the H–H distance is elongated to 1.17 Å with one hydrogen atom (H1) interacting with the borenium center (B–H1 = 1.26 Å) and the other hydrogen atom (H2) interacting with the *ipso*-carbon atom of one of the phenyl rings of **6** (C–H2 = 1.37 Å). A similar transition state was also proposed by Grimme and Stephan for a B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> mediated hydrogenation of anilines.<sup>27</sup> The Mulliken charge analysis revealed that the H1 atom bears a negative charge of -0.16 e and the H2 atom bears a positive charge of +0.22 e, indicating the heterolytic nature of the H–H bond activation. In agreement with experimental observation, the formation of 1-phenylethylium and benzene from the Wheland complex **6-**H<sup>+</sup> is the turnover-determining step which needs to overcome an overall free energy barrier of 28.1 kcal mol<sup>-1</sup>, comparable to the experimental value of 25.5 ± 2.2 kcal mol<sup>-1</sup> (298 K). The subsequent barrier for the generation of ethylbenzene and catalyst **1a** is very small (6.1 kcal mol<sup>-1</sup>). The overall reaction is exergonic with  $\Delta G$  = -10.5 kcal mol<sup>-1</sup> at 298 K.

Besides small organic molecules, we also examined the possibility of applying this hydrogenolysis system to recycle aromatic chemicals from polystyrene (PS), the most widely used aromatic plastics.<sup>32,33</sup> Stirring a solution of laboratory-grade polystyrene (**PS1**, 106 mg;  $M_W = 3.10 \times 10^5$  g mol<sup>-1</sup>; polydispersity index (PDI) = 2.01) and 51 µmol of **1a** (5 mol% per styrene unit) in 10 mL of o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> under 5 bar of H<sub>2</sub> at 60°C for 16 hours resulted in the formation of 52 mg of benzene (49 wt%) as determined by GC analysis (Figure 4). This corresponds to 65% of yield based on the phenyl moieties, comparable to the state-of-art heterogeneous polystyrene hydrogenolysis catalyst Ru/Nb<sub>2</sub>O<sub>5</sub> (65% yield of benzene at 300°C).<sup>34</sup> Significantly, benzene is the only low boiling point (<200°C) product which can be detected by GC analysis (Figure S52). This unprecedented selectivity is in stark contrast to the complex monoarene products obtained from pyrolysis or hydrocracking of PS. <sup>34-36</sup> In addition to benzene, long-chain phenylalkanes were obtained as 47 mg of colorless oil (44 wt%) after the removal of the catalyst by flash column chromatography. Gel permeation chromatography analyses showed that the  $M_W$  of this oil is 674

g mol<sup>-1</sup> with a PDI of 1.64, indicating that the main-chain of PS is also cleaved during the hydrogenolysis process. We tentatively assume that the main-chain C-C bonds could be cleaved via β-scission of the carbenium intermediates,<sup>37</sup> releasing terminal alkenes which could subsequently be hydrogenated in the presence of **1a** (the proposed reaction pathway see Figure S74).<sup>38</sup> The <sup>1</sup>H NMR analyses confirmed the absence of olefins in the phenylalkane product, as no signals were observed in the region between 3.5 to 6.5 ppm. The integration ratio of the aromatic and aliphatic proton signals is 1: 3.95, which led to estimation that ca. 81% of phenyl moieties of polystyrene were replaced with hydrogen atoms (deduction details see supplementary information), correlating relatively well with the yield of benzene determined by GC analysis. The low percentage of CH<sub>3</sub> resonances (0.8 to 1.0 ppm) among the total integration of the aliphatic protons (ca. 6%) indicates that the phenylalkane product is mainly composed of phenylsubstituted linear alkanes, which are valuable precursors for the production of biodegradable surfactants.<sup>3,39</sup> To the best of our knowledge, no precedented synthesis of linear long chain phenylalkanes from PS has been reported. Taken together, ca. 93% of the weight of PS was successfully converted to valuable aromatic chemicals. To test if this catalytic system could be utilized to upcycle waste PS, we carried out the hydrogenolysis reaction with post-consumer PS from a single-use plastic cup (**PS2**,  $M_W$  = 1.76 × 10<sup>5</sup> g mol<sup>-1</sup>; PDI = 2.12) and expanded PS foam (**PS3**,  $M_W$  = 2.86 × 10<sup>5</sup> g mol<sup>-1</sup>; PDI = 2.21). Comparable yields of benzene (49 and 47 wt% for PS2 and PS3, respectively) and phenylalkanes (42 wt%,  $M_W$  = 600 g mol<sup>-1</sup>, PDI = 1.45 for **PS2**; 44 wt%,  $M_W$  = 671 g mol<sup>-1</sup>, PDI = 1.54 for **PS3**) from these post-consumer PS plastics were obtained, revealing remarkable tolerance of the catalytic system to common processing impurities.

In conclusion, by exploiting the synergistic activation of H–H bond with an alkylarene and a boron Lewis acid, we have achieved the hydrogenolysis of the C(aryI)-C(alkyI) bonds of unactivated alkylarenes without directing groups. The potential of this catalytic system was manifested by its application in conversion of post-consumer polystyrene into valuable benzene and long-chain phenylalkanes under near ambient temperature with unprecedented selectivity. Although the turnover numbers of the catalyst still need improvement, this metal-free approach reported herein enables a top-down strategy for the synthesis of organic molecules from complex precursors that remains a challenge for homogenous transition metal systems.

# Declarations

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## Author contributions

H.W. conceived the research and designed the project. Y.X. and Y.L. optimized the reaction conditions. Y.X. studied the substrate scope and carried out experimental mechanism investigation. Y.Y studied the hydrogenolysis of polystyrene. Z.H.L. undertook the DFT calculations. H.W. wrote the manuscript with input from all authors. All authors analyzed the results and commented on the manuscript.

#### **Competing financial interests**

The authors declare no competing financial interests.

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## **Figures**

#### (A) Industrial hydrodealkylation

(B) Directing-group assisted hydrodealkylation (Milstein, 1998)



(C) Metal- and directing-group-free hydrodealkylation (this work)



synergistic H<sub>2</sub> activation by Lewis-acid / n-base

#### Figure 1

Different approaches of hydrodealkylation. (A) Industrial hydrodealkylation. (B) Directing-group assisted hydrodealkylation. (C) Metal- and directing-group-free hydrodealkylation



## Figure 2

Substrate scope of of hydrodealkylation. Standard reaction conditions: alkylarenes (1.0 mmol) and 1a (0.010 mmol) in C6H5Br (0.5 mL) under H2 (20 bar) at room temperature; yields were determined by GC analysis and isolated yields were given in parenthesis. a not pursued; analysis of the overhead gas by GC revealed the presence of isobutane. b 5 mol% of 1a was used. c 10 mol% of 1a was used. d o-C6H4F2 was used as solvent. f transalkylation products between the substrate and solvent were observed. g 20

mol% of 1a was used and the reaction was run at 50°C. h C6H5Cl was used as solvent. i the reaction was carried out in 5 mmol scale.



#### Figure 3

Mechanism investigation of the hydrogenolysis of 6. (A) KIE study. (B) Hammett plot of ln(kX / kH) vs. op for the hydrogenolysis reaction. (C) Gibbs free energy profile at 298 K for the hydrogenolysis of 6 catalyzed by 1a and the geometry of TS1 (hydrogen atoms except H1, H2 and the one connected to the borenium center are omitted for clarity)



#### Figure 4

Hydrogenolysis of polystyrene with 1a as catalyst. PS1: laboratory-grade polystyrene; PS2: polystyrene single-use cup; PS3: expanded polystyrene foam. Reactions were run with 0.1 g of polystyrene and 0.05 mmol of 1a in o-C6H4F2 (10 mL) under 5 bar of H2 at 60°C.

## **Supplementary Files**

This is a list of supplementary files associated with this preprint. Click to download.

• supplementaryinformation.pdf