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Generation of Hydrogen from Water: A Pd-Catalyzed Reduction of Water Using Diboron Reagent at Ambient Conditions

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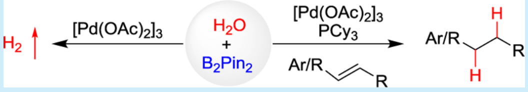
Supporting Information

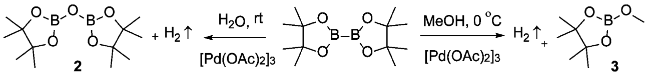


ABSTRACT: Production of hydrogen from renewable sources, particularly from water, is an intensive area of research, which has far-reaching relevance in hydrogen economy. A homogeneous catalytic method is presented for producing clean hydrogen gas from water, in a reaction of water with a diboron compound as the reductant, under ambient reaction conditions. The Pd-catalytic system is stable in water and displays excellent recyclability. Hydroxy analogues such as alcohols are compatible with the Pd/B_2Pin_2 system and generate hydrogen gas efficiently. The B_2Pin_2−H_2O system, in the presence of palladium, is an excellent catalytic system for selective hydrogenation of olefins.

The quest for developing renewable energy production and their storage feed stocks has become one of the major scientific goals in recent years. In this direction, production of hydrogen from water has direct impact on hydrogen economy and its feasibility.[1] However, these expeditions are challenging, particularly for the discovery of efficient and cost-effective catalytic processes. A vast majority of research on the generation of hydrogen gas has been focused on the transition metal driven catalytic processes by harnessing a photochemical or electrochemical method.[2] Generally, transition metal catalyzed dehydrocoupling reactions, involving p-block elements, are effective methods for the generation of hydrogen gas.[3] In this regard, considerable efforts have been devoted to designing ammonia−borane complexes and related compounds as hydrogen storage materials via dehydrocoupling reactions.[4] Beller et al. have reported a methanol dehydrogenation process using Ru-catalysts and dehydrogenation of formic acid using iron catalysts.[5] Effective utility of a variety of hydroxy systems such as sorbitol, glycerol, ethylene glycol, and methanol with Pt/Al_2O_3 at 500 K has also been explored by Dumesic.[6]

Most of the methods, which use transition metal catalyzed strategies, efficiently convert water into hydrogen gas via hydrogen evolution reaction (HER). Generally, these methods employ a variety of metal hydrides such as AlH_3, R_3SiH, BH_3, etc., which are potentially unstable and moisture sensitive.[3i] One of the main features of transition metal salts is their ability to activate nonpolar bimetallic bonds via an oxidative addition process.[7] For example, the activation of B−B, B−X, and Si−B bonds, assisted by transition metals, has led to several useful polymetallic organic compounds.[8] However, to the best of our knowledge, the metal catalyzed hydrolytic cleavage of the B−B bond using water is unknown and these reagents have never been employed in metal catalyzed transformations for producing hydrogen gas (Scheme 1). Palladium catalysts in combination with other metal systems are well-known for their reaction with HCO_2H to form hydrogen gas.[9] The utility of the homogeneous monometallic transition metal catalysts for the generation of hydrogen gas using formic acid is limited due to poisoning of metals by CO.[10] Nevertheless, there are few reports using methane (with Pd−Ag membrane), and cyclohexane (with Pt or Pd clusters) dehydrogenation strategies for generating pure hydrogen gas using heterogeneous catalysts.[11] In continuation of our work on Pd-catalyzed reactions, herein, we present a homogeneous catalytic method for producing clean hydrogen gas using water as a hydrogen source and a diboron compound as the reductant at ambient reaction conditions. The present homogeneous catalytic method for producing hydrogen gas under ambient reaction conditions involves three key reaction parameters: (i) the catalytic amount of $Pd(OAc)_2$ trimer, (ii) B_2Pin_2, and (iii) water. The salient feature of this method is that it leads to an evolution of hydrogen gas, and oxygen evolution (OER) was not observed at all. This process is very rapid and generates an accurate amount of gas on demand at ambient temperature. Besides, this method is also compatible with alcohols such as MeOH, *tert*-BuOH, and trifulroethanol and leads to efficient generation of hydrogen gas exclusively. The only limitation of this process is the use of a stoichiometric amount of *bis*-(pinacolato)diboron, which helps in trapping the oxygen. Besides, the mild and unreactive nature of these *bis*-boron reagents makes the process more attractive.

Scheme 1. Pd-Catalyzed Cleavage of B−B Bond Using H_2O and MeOH



We began our studies with serendipitous formation of the H_2 gas in a reaction designed to reduce an olefin in a reaction of 4-allyl-1,2-dimethoxybenzene (**4a**) with $[Pd(OAc)_2]_3$, B_2Pin_2, PCy_3, water, and toluene (Scheme 2). Besides, the preliminary investigation revealed that the similar reaction of $[Pd(OAc)_2]_3$, B_2Pin_2 (**1**), and water, in the absence of olefin, can lead to the

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Scheme 2. Transfer Hydrogenation of Olefins

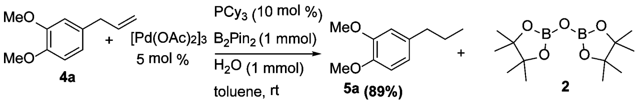
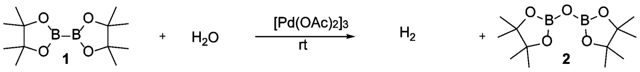


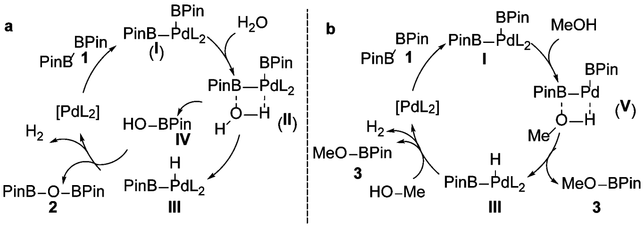
Table 1. Optimization Studies[a,b]



entry	H_2 source	B_2Pin_2 (mmol)	time (min)	H_2 (mL)	$(BPin)_2O$ (%)[b]	H_2 (%)[b]
1	H_2O (1.5 mmol)	3	60	28	44	39
2	**H_2O (3 mmol)**	**3**	**60**	**61**	**92**	**84**
3	H_2O (1 mL)	3	30	60	92	83
4	MeOH (6 mmol)	3	30	66	84	91[c]
5	MeOH (1 mL)	3	15	65	85	91[c]
6	^{t}BuOH (6 mmol)	3	30	66	96	91[c]
7	^{t}BuOH (1 mL)	3	15	63	91	85[c]
8	TFE (6 mmol)	3	30	61	92	84[c]
9	TFE (1 mL)	3	15	60	89	83[c]

[a] Reaction conditions: B_2Pin_2 (3 mmol), [Pd] (1 mol %), H_2-source, rt, 1 h. [b] Isolated yields [c] Reactions were performed at 0 °C.

Scheme 3. Working Hypothesis[a]



[a] Catalytic cycle for oxidative cleavage of B_2Pin_2 with (a) H_2O or (b) MeOH.

formation of hydrogen gas and 2,2′-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2**) as a byproduct (Table 1). As can be seen from the initial experiments, we found that the Pd-catalyst is essential for this reaction (see Supporting Information (SI) Table 1). Hence, the efficacy of this reaction has been tested with variable amounts of both a boron source and water. In a reaction of bis(pinacolato)diboron (**1**, 1 equiv) and water (1 equiv), it was found that the formation of hydrogen gas depends upon the stoichiometry of both the boron source and water, and there was no formation of hydrogen in the absence of either the Pd-catalyst or B_2Pin_2 (see SI Table 1). As can be seen in Table 1 (entries 1–3), 1 equiv of B_2Pin_2 is needed for effective generation of hydrogen gas (see SI for more details). Indeed, the reaction was exothermic and reached 27 °C → 38 °C in 15 min. Under similar conditions, alcohols such as MeOH, *tert*-BuOH, or CF_3CH_2OH were also found to be useful hydrogen sources and successfully led to the efficient generation of hydrogen gas (entries 4–9, Table 1). We believe that the oxidative insertion of Pd(0) with B_2Pin_2 led to the formation of metal species **I**.[8] Further, an aquo-complex can be formed due to interaction of water with [Pd–B] to the form **II**.[12] Species **II** then can decompose to form PinB-Pd(H)L_2 (**III**). The OH-BPin (**IV**) generated from the above process eventually was trapped by intermediate **III** to form PinB-O-BPin (**2**) producing dihydrogen and regenerating the Pd-catalyst for further catalytic cycling (Scheme 3a; SI Figure 1).[13] A similar explanation can be conceived using alcohols as shown in Scheme 3b. The volume of the hydrogen gas generated has been quantified by measuring the amount of water displaced in a reverse buret apparatus. The hydrogen gas generated was passed through $CDCl_3$, and the ^1H NMR was recorded for the qualitative analysis (SI Figure 1). This has been further confirmed by gas chromatographic analysis, which showed the good purity of hydrogen gas generated in the reaction (97%; see SI for more details). The formation of PinB-O-BPin (**2**) and OH-BPin (**IV**) was confirmed by boron NMR studies (SI Figure 3). Further, all the measurements were correlated with the starting material (B_2Pin_2) used. As seen in entry 1 of Table 1, using 1 equiv of B_2Pin_2 (762 mg, 3 mmol) and 0.5 equiv of water (27 mg, 1.5 mmol) resulted in the formation of hydrogen gas in 39% yield (28 mL). A remarkable result was obtained by increasing the amount of water to 3 mmol, which resulted in the generation of hydrogen gas in 84% yield (1 equiv of H_2 per 1 equiv of B_2Pin_2; entry 2, Table 1). The experiment with 1 mL of H_2O has also shown efficient generation of H_2 gas in good yield (83%, entry 3). Based on these results, we envisioned the necessity of a hydroxy functional group, which can possibly facilitate the hydrogen generation process. Hence, the subsequent experiments with alcohols, instead of water, led to efficient generation of hydrogen gas. Thus, the reaction of MeOH (2 equiv) with B_2Pin_2 in the presence of a catalytic amount of a Pd-reagent ($[Pd(OAc)_2]_3$) produced hydrogen gas in excellent yield (91%, entry 4, Table 1). The reaction with higher stoichiometry of methanol (1 mL) has also generated a good amount of hydrogen gas (90%, entry 5). *tert*-Butanol (2 equiv) as a H_2-source displayed a remarkable result by producing hydrogen gas in 91% yield (entry 6), whereas 85% of hydrogen gas was obtained using 1 mL of *tert*-butanol (entry 7, Table 1). The reaction with MeOH was exothermic, and the gas collected showed the presence of methanol vapors (^1H NMR). This problem was circumvented by performing the reaction at 0 °C, which showed only the presence of hydrogen gas (MeOH vapors were not detected in ^1H NMR; see SI Figure 4). Similarly, trifluoroethanol (CF_3CH_2OH) also effectively produced 84% of hydrogen gas (entry 8, Table 1). A similar reaction using 1 mL of trifluoroethanol generated hydrogen gas in 83% yield (entry 9, Table 1).

In successive studies, recycling experiments of the catalyst led to interesting results. Thus, the Pd-catalyst can be effectively reused several times for generation of hydrogen gas. As observed, the reaction mixture produced 90% of hydrogen gas in the second run, but required addition of a stoichiometric amount of B_2Pin_2 and H_2O. With this interesting outcome, we performed five consecutive reactions, wherein the yields were consistent for the next 5 times with variable metal catalyst loadings. In the first set of experiments, the reaction with 5 mol % palladium acetate generated hydrogen gas in 90%, 85%, 85%, 80%, and 70% yield, respectively (Figure 1). Similarly, experiments using 2.5 mol % of the Pd-catalyst under optimal conditions for five consecutive runs generated hydrogen gas in 95%, 90%, 90%, 80%, and 80% yields, respectively (Figure 1). Interestingly, loading a lower amount of metal catalyst (1.5 mol % of $[Pd(OAc)_2]_3$ was also effective and produced yields of 95%, 90%, 85%, 85%, and 75%, respectively in consecutive runs. Similar sets of reactions were

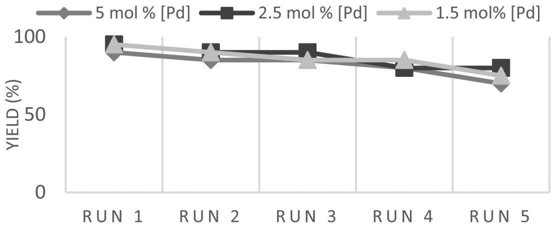


Figure 1. Recyclability of the catalyst; reactions were performed with Pd-catalyst, B_2Pin_2, and H_2O (1 mL) up to 5 consecutive runs.

carried out to examine the recyclability of MeOH under the reaction conditions. Using MeOH (1 mL) with a low catalyst loading ($[Pd(OAc)_2]_3$, 1.5 mol %) with a stoichiometric amount of B_2Pin_2 (1 equiv) in successive experiments, we were delighted to obtain 91%, 83%, and 76% yields for the consecutive runs (see SI Table 5). Subsequent experiments revealed significant activity by the catalyst. As shown in Figure 2, the catalyst exhibited a turnover number (TON) of 31.3 per 0.03 mmol of catalyst after 15 min. The catalyst also exhibited a turnover frequency (TOF) of 6.26 per min per 0.03 mmol of catalyst after 15 min. This value corresponds to 1.04 × 106 TON per mole of catalyst used (more details in SI).

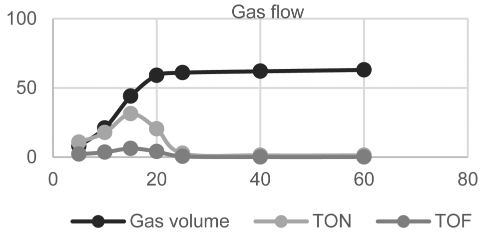
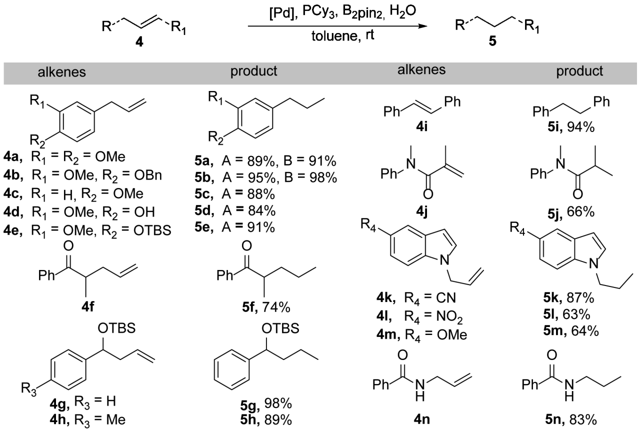


Figure 2. Efficacy of Pd-catalytic system; V_{gas} = volume of the gas; the TON (turnover number) and TOF (turnover frequency) of the catalytic process were calculated using the volume of the gas formed in 5 min intervals of the reaction.

Transition metal catalyzed homogeneous transfer hydrogenation reactions are highly exploited synthetic strategies for reducing C−C multiple bonds, which also exhibit excellent chemo-, regio-, and stereoselectivity.[14] Therefore, the reduction of a variety of functional groups, especially alkenes, has been reported using various hydrogen transfer sources such as HCO_2H, N_2H_4, $NH_3{-}BH_3$, etc.[15] On the basis of current study, optimization studies for the hydrogenation of alkenes were performed (SI Table 6, Supporting Information). Based on this study, it was found that the catalytic amount of Pd-catalyst, 2 equiv of boron source, 2 equiv of water, and 10 mol % of ligand (PCy_3) were necessary for the reduction to complete.

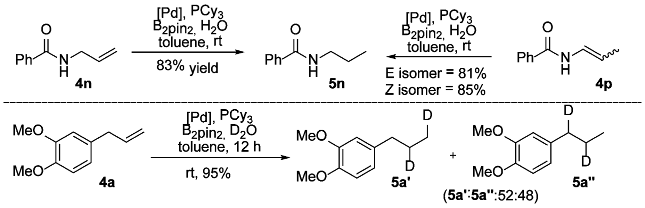
The hydrogenation reaction to obtain a saturated carbon chain was studied under these homogeneous catalytic conditions for a variety of olefins (Table 2). Olefins such as aryl allyl benzene derivatives (**4a**−**4e**) were reduced to furnish corresponding saturated products **5a**−**5e** in excellent yields (84−95%) at ambient temperature. As can be seen, the reduction of **4f** led to a chemoselective reduction of olefin in the presence of a keto group furnishing the reduced product **5f** in 74% yield. Further, O-silyl protected homoallylic alcohols (**4g** and **4h**) were effectively converted to their saturated forms (**5g** and **5h**) in excellent yields (98% and 89%, respectively). Unlike unactivated olefins, the reduction of stilbene was smooth and afforded the reduced product **5i** in excellent yield (94%). The catalytic system was also efficient in reducing *N*-methyl-*N*-phenylmethacrylamide to its corresponding hydrogenated product *N*-methyl-*N*-phenylisobutyramide (**5j**) in good yield (66%). In this example, the reduction of conjugated olefin proceeded well under the present catalytic palladium system. Next, we employed a variety of *N*-allyl derivatives such as 1-allyl-1*H*-indole-5-carbonitrile and 5-nitro-1-(prop-1-en-1-yl)-1*H*-indole, which were chemoselectively reduced into 1-propyl-1*H*-indole-5-carbonitrile (**5k**) and 5-nitro-1-propyl-1*H*-indole (**5l**) in good yields (87% and 63%, respectively), wherein sensitive nitrile and nitro groups were intact during the reaction conditions. Similarly, 1-allyl-5-methoxy-1*H*-indole underwent a smooth reduction to **5m** (64%) and a *N*-allyl derivative of benzamide furnished *N*-propylbenzamide (**5n**) in excellent yield (83%).

Table 2. Scope of the Reaction[a,b]



[a]Reaction conditions: **4a** (0.5 mmol), B_2Pin_2 (1 mmol), [Pd] (1.5 mol %), ligand (10 mol %), condition A (H_2O, 1 mmol), condition B (MeOH, 1 mmol), toluene (1.5 mL), rt, 12 h. [b]Isolated yields.

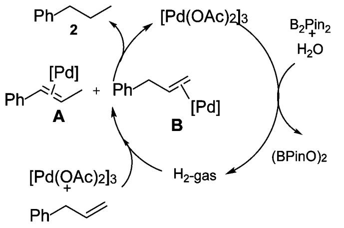
Scheme 4. Deuterium Labeling Studies[a,b]



[a]Reaction conditions: **4a** (0.5 mmol), B_2Pin_2 (1 mmol), [Pd] (1.5 mol %), ligand (10 mol %), D_2O (1 mmol), toluene (1.5 mL), rt, 12 h. [b]Isolated yields.

To gain insight into the mechanism, we designed a few controlled experiments (Scheme 4). Reaction of *N*-allyl benzamide (**4n**), under optimal conditions, formed the expected product **5n** in 83% yield. Interestingly, the reaction of *N*-(prop-1-en-1-yl)benzamide (**4p**), an isomer of **4n**, constituting a *N*-vinyl internal double bond furnished the product **5n** in good yield. Extension of the study, for comparing the reactions of *E*- and *Z*-isomers of **4p**, furnished reduced product **5n** in 81% and 85%, respectively. As can be noted from this experiment, the reaction of **4a** with $[Pd(OAc)_2]_3$, B_2Pin_2, PCy_3, and D_2O in toluene furnished a mixture of deuterated compounds **5a′** and **5a″** in 95% yield, in almost equal ratio (52:48, Scheme 4; for NMR studies, see SI). This observation clearly indicates the formation of intermediates **A** and **B** during the reaction, which is shown in Scheme 5. Further, these intermediates were hydrogenated by the hydrogen gas produced during the reaction to form the corresponding reduced products.

Scheme 5. Proposed Mechanism



In summary, we have shown for the first time that $[Pd(OAc)_2]_3$ (1 mol %) can be efficiently employed to generate hydrogen gas using water as the hydrogen source and B_2Pin_2 as the scavenger of oxygen. The major advantage of the protocol is oxygen evolution is not observed in the reaction and pure hydrogen gas is evolved in the process under ambient reaction conditions. Additionally, alcohols such as MeOH, *tert*-butanol, and CF_3CH_2OH can also be utilized under the reaction conditions. The only limitation of the process is that it requires a stoichiometric amount of the boron source. This protocol has been successfully demonstrated for the reduction of a variety of olefins. Further work is underway in our laboratory for improvement of this catalytic method.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02508.

Experimental procedures, characterization data, and spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Turner, J. A. *Science* **2004**, *305*, 972. (b) Schlapbach, L.; Züttel, A. *Nature* **2001**, *414*, 353. (c) Armstrong, F. A.; Fontecilla-Camps, J. C. *Science* **2008**, *321*, 498.

(2) (a) Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 15729. (b) Khaselev, O.; Turner, J. A. *Science* **1998**, *280*, 425. (c) Wentorf, R. H., Jr.; Hanneman, R. E. *Science* **1974**, *185*, 311. (d) Karunadasa, H. I.; Montalvo, E.; Sun, Y.; Majda, M.; Long, J. R.; Chang, C. J. *Science* **2012**, *335*, 698. (e) Heyduk, A. F.; Nocera, D. G. *Science* **2001**, *293*, 1639. (f) Vyas, V. S.; Lotsch, B. V. *Nature* **2015**, *521*, 41. (g) Wagner, F. T.; Somorjai, G. A. *Nature* **1980**, *285*, 559. (h) Dawson, J. K. *Nature* **1974**, *249*, 724. (i) Esswein, A. J.; Nocera, D. G. *Chem. Rev.* **2007**, *107*, 4022.

(3) (a) Ison, E. A.; Corbin, R. A.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 11938. (b) Kim, B.-H.; Woo, H.-G. *Adv. Organomet. Chem.* **2004**, *52*, 143. (c) Clark, T. J.; Lee, K.; Manners, I. *Chem. - Eur. J.* **2006**, *12*, 8634. (d) Less, R. J.; Melen, R. L.; Naseri, V.; Wright, D. S. *Chem. Commun.* **2009**, 4929. (e) Less, R. J.; Melen, R. L.; Wright, D. S. *RSC Adv.* **2012**, *2*, 2191. (f) Stubbs, N. E.; Robertson, A. P. M.; Leitao, E. M.; Manners, I. *J. Organomet. Chem.* **2013**, *730*, 84. (g) Waterman, R. *Chem. Soc. Rev.* **2013**, *42*, 5629. (h) Leitao, E. M.; Jurca, T.; Manners, I. *Nat. Chem.* **2013**, *5*, 817. (i) Sakintuna, B.; Lamari-Darkrim, F.; Hirscher, M. *Int. J. Hydrogen Energy* **2007**, *32*, 1121.

(4) (a) Hamilton, C. W.; Baker, R. T.; Staubitz, A.; Manners, I. *Chem. Soc. Rev.* **2009**, *38*, 279−293. (b) Staubitz, A.; Robertson, A. P. M.; Manners, I. *Chem. Rev.* **2010**, *110*, 4079−4124. (c) Staubitz, A.; Robertson, A. P. M.; Sloan, M. E.; Manners, I. *Chem. Rev.* **2010**, *110*, 4023−4078. (d) Waterman, R. *Chem. Soc. Rev.* **2013**, *42*, 5629−5641.

(5) (a) Boddien, A.; Mellmann, D.; Gärtner, F.; Jackstell, R.; Junge, H.; Dyson, P. J.; Laurenczy, G.; Ludwig, R.; Beller, M. *Science* **2011**, *333*, 1733. (b) Nielsen, M.; Alberico, E.; Baumann, W.; Drexler, H.; Junge, H.; Gladiali, S.; Beller, M. *Nature* **2013**, *495*, 85. (c) Boddien, A.; Loges, B.; Gärtner, F.; Torborg, C.; Fumino, K.; Junge, H.; Ludwig, R.; Beller, M. *J. Am. Chem. Soc.* **2010**, *132*, 8924. (d) Jiang, K.; Xu, K.; Zou, S.; Cai, W. *J. Am. Chem. Soc.* **2014**, *136*, 4861. (e) Yu, W.; Mullen, G. M.; Flaherty, D. W.; Mullins, C. B. *J. Am. Chem. Soc.* **2014**, *136*, 11070. (f) Mori, K.; Dojo, M.; Yamashita, H. *ACS Catal.* **2013**, *3*, 1114. (g) Bulushev, D. A.; Bulusheva, L. G.; Beloshapkin, S.; O'Connor, T.; Okotrub, A. V.; Ryan, K. M. *ACS Appl. Mater. Interfaces* **2015**, *7*, 8719.

(6) (a) Cortright, R. D.; Davda, R. R.; Dumesic, J. A. *Nature* **2002**, *418*, 964. (b) Huber, G. W.; Chheda, J. N.; Barrett, C. J.; Dumesic, J. A. *Science* **2003**, *300*, 2075. (c) Huber, G. W.; Dumesic, J. A. *Catal. Today* **2006**, *111*, 119. (d) Huber, G. W.; Cortright, R. D.; Dumesic, J. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 1549. (e) Shabaker, J. W.; Huber, G. W.; Davda, R. R.; Cortright, R. D.; Dumesic, J. A. *Catal. Lett.* **2003**, *88*, 1.

(7) Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685.

(8) (a) Takaya, J.; Iwasawa, N. *ACS Catal.* **2012**, *2*, 1993. (b) Ojha, D. P.; Prabhu, K. R. *Org. Lett.* **2016**, *18*, 432. (c) Neeve, E. C.; Geier, S. J.; Mkhalid, I. A. I.; Westcott, S. A.; Marder, T. B. *Chem. Rev.* **2016**, *116*, 9091.

(9) (a) Tedsree, K.; Li, T.; Jones, S.; Chan, C. W. A.; Yu, K. M. K.; Bagot, P. A. J.; Marquis, E. A.; Smith, G. D. W.; Tsang, S. C. E. *Nat. Nanotechnol.* **2011**, *6*, 302. (b) Yu, W.-Y.; Mullen, G. M.; Flaherty, D. W.; Mullins, C. B. *J. Am. Chem. Soc.* **2014**, *136*, 11070.

(10) Crabtree, R. H. *Chem. Rev.* **2015**, *115*, 127.

(11) Wang, Y.; Shah, N.; Huffman, G. P. *Energy Fuels* **2004**, *18*, 1429.

(12) Rossin, A.; Bottari, G.; Lozano-Vila, A. M.; Paneque, M.; Peruzzini, M.; Rossi, A.; Zanobini, F. *Dalton Trans.* **2013**, *42*, 3533−3541.

(13) Couturier, M.; Tucker, J. L.; Andresen, B. M.; Dubé, P.; Negri, J. T. *Org. Lett.* **2001**, *3*, 465.

(14) (a) Wang, D.; Astruc, D. *Chem. Rev.* **2015**, *115*, 6621. (b) Korstanje, T. J.; van der Vlugt, J. I.; Elsevier, C. J.; de Bruin, B. *Science* **2015**, *350*, 298. (c) Chen, Q.-A.; Ye, Z.-S.; Duan, Y.; Zhou, Y.-G. *Chem. Soc. Rev.* **2013**, *42*, 497.

(15) (a) Shen, R.; Chen, T.; Zhao, Y.; Qiu, R.; Zhou, Y.; Yin, S.; Wang, X.; Goto, M.; Han, L.-B. *J. Am. Chem. Soc.* **2011**, *133*, 17037. (b) Tani, K.; Ono, N.; Okamoto, S.; Sato, F. *J. Chem. Soc., Chem. Commun.* **1993**, 386. (c) Uematsu, N.; Fujii, A.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 4916. (d) Sawadjoon, S.; Lundstedt, A.; Samec, J. S. M. *ACS Catal.* **2013**, *3*, 635. (e) Ito, M.; Ikariya, T. *Chem. Commun.* **2007**, 5134. For NH_2NH_2: (f) Jurcik, V.; Nolan, S. P.; Cazin, C. S. J. *Chem. - Eur. J.* **2009**, *15*, 2509−2511. While preparing this manuscript, the following papers appeared employing heterogeneous catalysis and $B_2(OH)_4$ and water for transfer hydrogenation of olefins: (g) Cummings, S. P. *J. Am. Chem. Soc.* **2016**, *138*, 6107. (h) Xuan, Q.; Song, Q. *Org. Lett.* **2016**, *18*, 4250. However, the generation of H_2 has not been reported.