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Palladium Catalysts for Dehydrogenation of Ammonia Borane with Preferential B−H Activation

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Abstract: Cationic Pd(II) complexes catalyzed the dehydrogenation of ammonia borane in the most efficient manner with the release of 2.0 equiv of H_2 in less than 60 s at 25 °C. Most of the hydrogen atoms were obtained from the boron atom of the ammonia borane. The first step of the dehydrogenation reaction was elaborated using density functional theory calculations.

The catalytic dehydrogenation of ammonia borane (AB; NH_3BH_3) has attracted attention because of its relatively high hydrogen storage capacity (19.6 wt % H_2).[1] To develop efficient on-board hydrogen storage materials, a high-performance dehydrogenation catalyst for AB to facilitate fast hydrogen release of maximum amounts of H_2 at low temperatures is needed.[2] In this respect, several efficient dehydrogenation catalysts have been developed using a pincer-type Ir complex,[3] a PNP pincer ligand-supported Ru complex,[4] and Ru and Ir alcohol oxidation/reduction catalysts.[5] Recently, Baker suggested that the most efficient catalyst was Ni(N-heterocyclic carbene)$_2$,[6] which released 2.5 equiv of H_2 in 4 h at 60 °C. However, most other tested catalysts lack such efficiency and produce less than 2 equiv of H_2.[7−11]

This study focused on the development of high-performance catalysts for the dehydrogenation of AB. Cationic Pd(II) complexes were the most efficient catalysts, releasing 2.0 equiv of H_2 at room temperature within 60 s. Each catalyst comprised a Pd(II) complex and a charge-balancing weakly coordinating counteranion, BF_4^-.[12] The catalyst activities were fine-tuned with allyl, 2,4-hexadiene, and acetonitrile ancillary ligands.

Figure 1 shows that all three catalysts, [Pd(allyl)][BF_4] (**1**), [Pd(allyl)(2,4-hexadiene)][BF_4] (**2**), and [Pd(MeCN)$_4$][BF_4]$_2$ (**3**), exhibit excellent dehydrogenation kinetics. Within that series, **1** exhibited the best performance, completing a release of 2.0 equiv of H_2 in 20 s. Because of its relative ease of preparation, however, complex **3** was subsequently used to optimize H_2 release from AB and alkylated ABs. In a typical experiment, 3 mol % **3** dissolved in 0.5 mL of nitromethane ($MeNO_2$) was added to a stirred 2 mL tetraglyme solution containing 0.045 g (1.46 mmol) of AB at 25 °C. During dehydrogenation, a marked exothermic process and immediate palladium precipitation were noted. The dehydrogenation product completely coprecipitated with Pd from tetraglyme and was found to be insoluble in most organic solvents [STable 1 in the Supporting Information (SI)]. The homogeneous nature of the dehydrogenation reaction was suggested on the basis of the fact that the precipitated Pd did not catalyze dehydrogenation of a second charge of AB. Mercury-poisoning experiments[8c] performed on this catalytic system also supported the presence of homogeneous catalysis. The H_2 purity and quantity were determined using quadrupole mass spectroscopy (QMS) and a mass-flow meter (MFM), respectively (see SFig-2 in the SI for details). Hydrogen and trace amounts of NH_3 were identified as the main volatiles, and ~2.0 equiv of H_2 were obtained (SFig-3 in the SI). As shown in Figure 2, clean AB dehydrogenation was confirmed by monitoring the disappearance of the AB and **3** signals and the appearance of a free BF_4^- signal at δ −24.0, −1.6, and +1.3, respectively, in the ^{11}B NMR spectra. After dehydrogenation, BF_4^- and NO_2^- were the only chemical substances identified in the LC−MS spectra of the tetraglyme solution (SFig-4 in the SI). Unlike previously reported catalytic dehydrogenations, neither borazine nor polyiminoborane was detected,[4−6] implying that the mechanism in our approach was different.

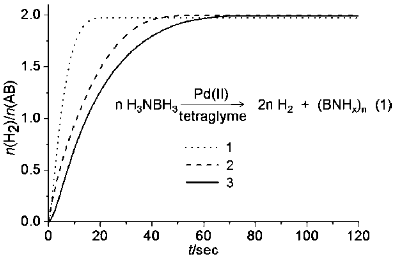

Figure 1. Kinetic profiles of AB dehydrogenation for Pd complex catalysts **1**−**3**.

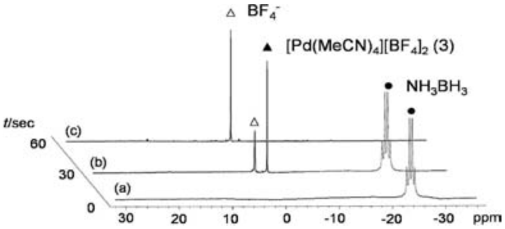

Figure 2. In situ 96.3 MHz ^{11}B NMR spectra of (a) AB, (b) AB immediately after the addition of catalyst **3** [Pd(MeCN)$_4$][BF_4]$_2$, and (c) product remaining after completion of the dehydrogenation.

Kinetic isotope effect (KIE) values of 2.5, 8.2, and 9.5 were measured for ND_3BH_3, NH_3BD_3, and ND_3BD_3, respectively, indicating that the B−H and B−D bonds weakened considerably (SFig-5 in the SI). To further consolidate the facile B−H activation, a series of alkyl and aryl ABs (Table 1) was examined in order to show that the H_2 release amount was dependent on the number of hydrogen atoms at the boron atom and that the reaction kinetics slowed in accordance with the bulkiness of the substituents at both the boron and nitrogen atoms. Most of the AB and *N*-alkyl and -aryl AB samples (Table 1, entries 1−5) discharged 2.0 equiv of

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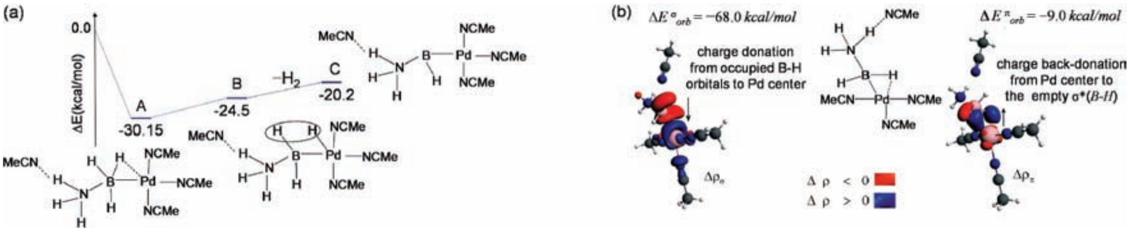

Figure 3. (a) DFT energy profile for the first AB dehydrogenation step using catalyst **3**, $[Pd(MeCN)_4][BF_4]_2$. (b) Donation and back-donation channels obtained using the ETS-NOCV method for the B−H bond between AB and the rest of the catalyst complex for the most stable intermediate product, **A**.

Table 1. Dehydrogenation of N- or B-Alkylated/Arylated ABs with Catalyst **3**

entry	alkyl/aryl AB	equiv of H_2	time (s)	spent fuel[a]
1	NH_3BH_3	2.0	60	BNH_x
2	$MeNH_2BH_3$	2.0	10	$BNMeH_x$
3	$EtNH_2BH_3$	2.0	10	$BNEtH_x$
4	$^iPrNH_2BH_3$	2.0	40	BN^iPrH_x
5	$PhNH_2BH_3$	2.0	50	$BNPhH_x$
6	Et_2NHBH_3	1.5	1500	$BNEt_2H_x$
7	$NH_3BH_2{}^iPr$	1.0	90	$^iPrBNH_x$
8	NH_3BH_2Ph	1.0	90	$PhBNH_x$

[a] Insoluble in organic solvents and no B−H signals in the IR spectra (see SFig-6 in the SI).

H_2 in <60 s, whereas *B*-alkyl and -aryl ABs (entries 7 and 8) released only 1 equiv H_2 after 90 s. The data for entry 6 (a sample with three H atoms located on the boron atom and one H atom on the nitrogen atom) indicate that H_2 release was hindered by the two ethyl substituents. Again, B−H activation[13] dictated the rate of AB dehydrogenation kinetics and produced only 1.5 equiv of H_2 over an extended period (1500 s).

These results are consistent with the reaction $H_3NBH_3 \rightarrow [H_2NB]_n + 2H_2$, which produces only spent fuels containing no B−H bonds. Preferential activation of B−H bonds suggests the formation of two B−B bonds and one B−N bond for every two H_2 molecules lost. Similar metal-catalyzed dehydrocoupling of B−H bonds leading to the formation of a B−B bond was first developed by Sneddon[14] and provided new synthetic pathways to materials with higher boron content.[15] Manners recently reported metal-catalyzed dehydropolymerization of *N*-*n*-butylamine borane to give the B−N linear polymer,[16] but in our case, the dehydropolymerization forms mostly B−B bonds in a less regular process, as evidenced by the multiple environments in the ^{11}B magic-angle-spinning (MAS) NMR spectra. One- and two-dimensional solid-state ^{11}B NMR spectra of the AB spent fuel sorted out all of the nonequivalent boron sites and classified them into B^3 and B^4 borons (SFig-7 in the SI). Two broad signals at δ +21.6 and 18.4 compare favorably with the sp² boron (B^3) framework in cross-linked polyborazylene-type structures.[17] Major peaks at δ +6 to −6 are a distinctive feature of AB spent fuel that is attributed to the presence of four-coordinate sp³ boron (B^4). Structural elucidation of each peak remains a challenge, but this distinctive feature is general for other alkylated AB spent fuels, including BN^iPrH_x and $BNEt_2H_x$ (SFig-8 in the SI).

Density functional theory (DFT) calculations indicated that the most stable complex of AB with the Pd(II) catalyst is structure **A** (Figure 3a). In that structure's geometry, the AB molecule is bound to Pd via the boron atom through an α-agostic B−H···Pd interaction. Also, the AB in **A** replaces one of the MeCN ligands, which forms a hydrogen bond with a hydrogen atom on NH_3. The AB complexation energy in **A** is relatively high, −30.15 kcal/mol. In **A**, the B−H bond that forms an α-agostic interaction is ~0.2 Å longer than that in free AB. Figure 3b presents the results of the extended transition state−natural orbitals for chemical valence (ETS-NOCV) analysis of the bond between AB and the metal-containing fragment. There are two major components of the B−H bond: an electron density transfer from the B−H bonding orbital (AB → metal donation; −68 kcal/mol) and a charge transfer from the metal to the antibonding B−H σ^* orbital (back-bonding; −9 kcal/mol). Thus, both of the NOCV charge-transfer channels result in a marked weakening of the B−H bond. Such weakening facilitates proton transfer to the Pd center to form base-stabilized boryl complex **B** followed by further intramolecular H_2 loss to give base-stabilized borylene complex **C**. This process, $\mathbf{A} \rightarrow \mathbf{B} \rightarrow \mathbf{C} + H_2$, requires ~10 kcal/mol and proceeds without any practical activation barrier. We are currently undertaking a detailed DFT analysis of the mechanism of the second dehydrogenation step.

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Supporting Information Available: Experimental details on dehydrogenation conditions, kinetic data, spectroscopic data for the spent fuels, ^{11}B NMR spectra of the spent fuels, and details of the DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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