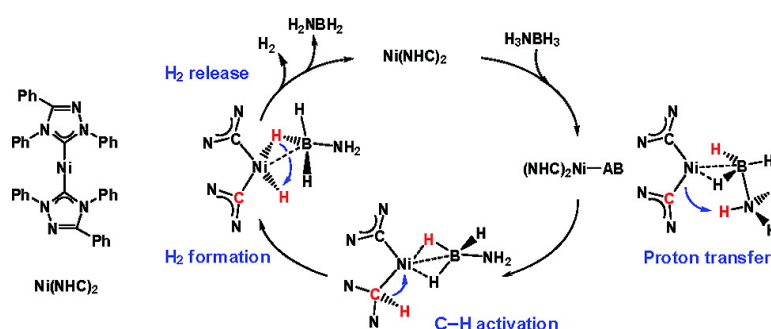


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The Catalytic Dehydrogenation of Ammonia-Borane Involving an Unexpected Hydrogen Transfer to Ligated Carbene and Subsequent Carbon–Hydrogen Activation

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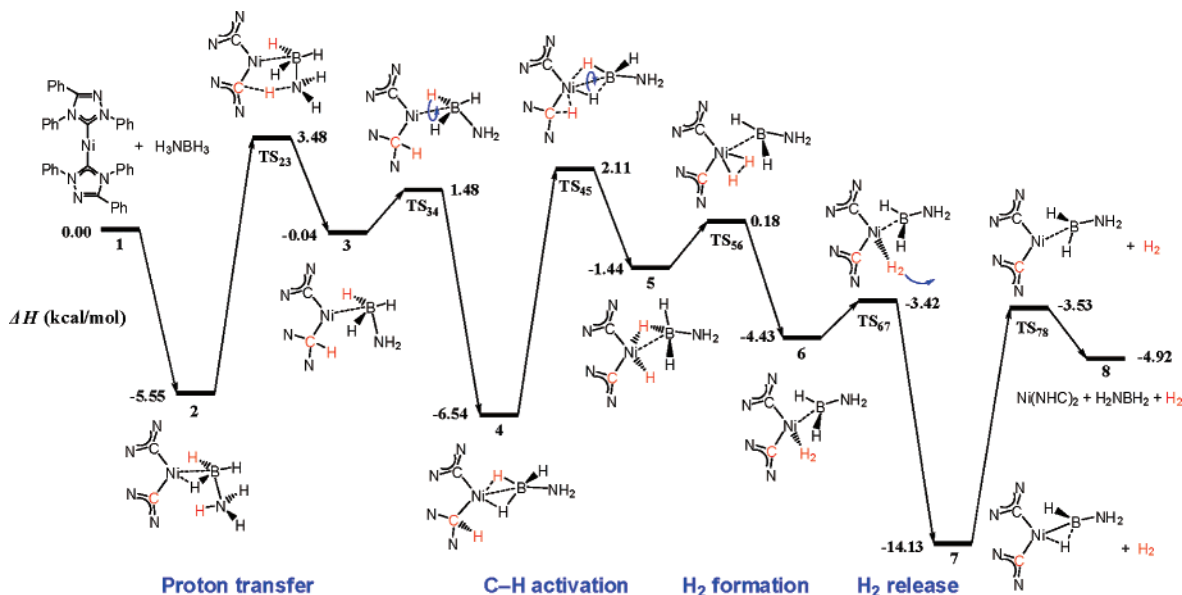
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As a very promising chemical hydrogen storage material both in its commercial availability and physical and chemical properties, ammonia-borane (AB = H₃N–BH₃) has attracted increasing attention.^{1–5} It is a solid at room temperature, stable in air and water, and contains 19.6 wt % H₂. Enhancing the release rate of hydrogen from AB is one of the foremost challenges in its practical use. Transition metal-catalyzed dehydrogenation reactions have been examined recently in this regard.² In their study of AB dehydrogenation, Baker's group³ reported a series of new catalysts based on N-heterocyclic carbene (NHC) nickel complexes, which are the best of only few examples of active first-transition-row metal catalysts for the dehydrogenation of AB reported to date. These catalysts extend the hydrogen release from AB to an unprecedented 18 wt %. Lacking a detailed catalytic mechanism for the dehydrogenation of AB on Ni(NHC)₂, these workers hypothesized a requisite mechanism, beginning with B–H bond activation and then β-H elimination from a N–H bond, for the steps in the first cycle of AB dehydrogenation (H₃N–BH₃ → H₂N–BH₂ + H₂).

In this Communication, the detailed catalytic mechanism of the first H₂ release from AB on the experimental catalyst, 2,2'-bis-(1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)-Ni, is predicted by using density functional theory⁶ with the ab initio TPSS⁷ functional and the all-electron cc-pVDZ⁸ basis set. (Computational details are provided in Supporting Information.) Several other functionals were tested for key barriers and give similar relative energies.

Our predictions for the complete catalytic cycle of the first H₂ release from AB, including relative gas-phase enthalpies, are displayed in Scheme 1. Corresponding structures are drawn in Figure 1. Free energies and solvent effects were calculated and are provided in the Supporting Information. At first, AB and the catalyst Ni(NHC)₂ bind directly to form a relatively stable intermediate **2**, in which AB links to Ni through the electrons in B–H bonds with one B–H–Ni interaction dominating. Our structure **2** does not involve a κ³-H₃B–NH₃ interaction but has a geometry more typical of a H–X σ-complex.⁹ From **2**, a hydrogen atom bound to the nitrogen of AB moves toward one NHC ligand, and in particular the carbon atom bonding with Ni, and forms a C–H bond through transition state **TS**₂₃ with an enthalpic barrier of only 9.03 kcal/mol (Δ*G*[‡]_{solv} = 11.94 kcal/mol). In **TS**₂₃, the H is migrating as a proton to the “sp²” electron pair on the carbene, which rotates to donate this pair to the H⁺ and to accept a pair of electron from Ni formally oxidizing it to Ni^{II}, or alternatively a Ni⁰ with a “reverse” metal-to-ligand dative bond.¹⁰ The N lone pair created in this H⁺ transfer begins the formation of the B–N multiple bond: shortening the B–N distance, lengthening a B–H bond, and shortening the corresponding Ni–H distance. Intermediate **3** is not very stable, and H₂N–BH₃ rotates about the Ni–B line through a rather low transition state **TS**₃₄ (Δ*H*[‡] = 1.44 kcal/mol) to form a more stable intermediate **4**. These movements convert the tetrahedral structure at Ni in **3** to the square-planar structure in **4**, shorten the B–N and

Scheme 1. Predicted Reaction Mechanism and Relative Enthalpies of Ammonia-Borane Dehydrogenation Catalyzed by Ni(NHC)₂ Showing Four Main Steps: Transfer of H⁺ from N to C(Carbene), Transfer of H from C to Ni, Transfer of H from B to Ni, and Release of H₂ and H₂B–NH₂



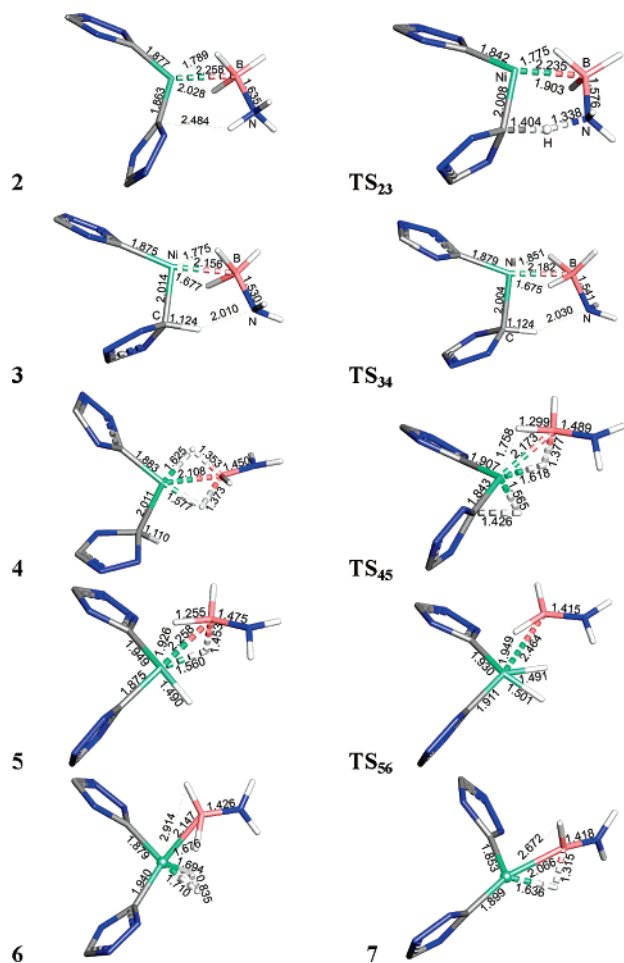


Figure 1. Optimized geometry of complexes **2**, **3**, **4**, **5**, **6**, and **7** and the transition states **TS₂₃** (1193.11 cm⁻¹), **TS₃₄** (85.31 cm⁻¹), **TS₄₅** (389.91 cm⁻¹) and **TS₅₆** (511.01 cm⁻¹). Bond lengths are in Ångström. The phenyl groups are not shown for clarity. The C–Ni–B–N dihedral angles of **3**, **TS₃₄**, and **4** are –16.17°, 12.37°, and 87.80°.

two Ni–H bond lengths by about 0.1 Å, and lead to an increase in stability by 6.50 kcal/mol.

Then, the hydrogen atom that has just detached from nitrogen and bonded to the carbon atom moves toward Ni through transition state **TS₄₅** with an enthalpic barrier of 8.65 kcal/mol ($\Delta G^{\ddagger}_{\text{solv}} = 7.90$ kcal/mol) and bonds to Ni forming intermediate **5**. Here, the transfer is formally H⁻ and Ni remains formally Ni^{II} in **5**. In addition to the formation of the Ni–H bond in **5**, the H₂N–BH₃ has rotated and one H has moved further from B to form a 3-center, 2-electron Ni–H–B bridging interaction. These two hydrogen atoms then move together through transition state **TS₅₆**: breaking the B–H bond, creating the H–H bond, and forming intermediate **6** over a rather low enthalpic barrier ($\Delta H^{\ddagger} = 1.62$ kcal/mol). Finally, H₂ is easily released to form intermediate **7**, which has shorter Ni–C, Ni–H, and Ni–B bonds and is more stable than **6** by about 9.7 kcal/mol. Loss of H₂N–BH₂ first is somewhat less favorable. The catalyst Ni(NHC)₂ regenerates after release of H₂N–BH₂ through transition state **TS₇₈** ($\Delta H^{\ddagger} = 10.6$ kcal/mol, $\Delta G^{\ddagger}_{\text{solv}} = 9.18$ kcal/mol).

Furthermore, the kinetic isotope effects were calculated for deuterated AB and are consistent with the experimental observations (Table S2). The effect of different NHC ligand was studied by replacing the current Enders' NHC ligand with the more electron rich ligand 1,3-diphenyl-4,5-dihydro-2-ylidene (phenyl NHC). In agreement with the experimental observations the predicted relative enthalpies show a higher barrier for this phenyl NHC ligand (Table

S3). To evaluate Baker's hypothesized mechanism, the stable structure from B–H bond activation, H–Ni(NHC)₂(H₂BNH₃), was optimized (Figure S1). Its relative gas-phase enthalpy is already 6.8 kcal/mol higher than that of **TS₂₃**. Ni activated N–H bond breaking was also examined by optimizing the transition state **TS_{N–H–Ni}** (Figure S2), which activates the N–H bond of the optimized stable structure (NHC)₂Ni–H₃NBH₃ (Figure S3) with 22.6 kcal/mol of enthalpy. These results indicate that either B–H or N–H bond activation catalyzed directly by Ni have much higher energy barriers than proton transfer (**2** → **TS₂₃**). In addition, theoretical studies of H₃N–BH₃ dehydrogenation catalyzed by Ir-pincer dihydrogen complex⁴ and of Me₂NH–BH₃ dehydrogenation catalyzed by Cp₂Ti⁵ predict rate determining energy barriers close to the carbene assisted H transfer for these Ni(NHC)₂ complexes.

In summary, our calculations demonstrate that the Ni(NHC)₂-catalyzed mechanism for ammonia-borane dehydrogenation of AB begins with proton transfer from nitrogen to the metal-bound carbene carbon, instead of B–H or N–H bond activation. This new C–H bond is then activated by the metal, transferring the H to Ni, then forming the H₂ molecule by transferring another H from B to Ni, rather than β -H transfer. This reaction pathway explains the importance of NHC ligands in this catalytic process and gives lower energy barriers than mechanisms that begin with N–H or B–H activations catalyzed by the metal atoms. The predicted reaction mechanism which features unexpected ligand participation points the way to finding new catalysts with higher efficiency, as partial unsaturation of the M–L bond may be essential for low-energy H transfers.

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Supporting Information Available: Complete ref 6, computational details, solvent effects, kinetic isotope effects, effect of different NHC ligand, and atomic coordinates of optimized stationary points and transition states. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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