DOI: 10.1002/anie.200803211

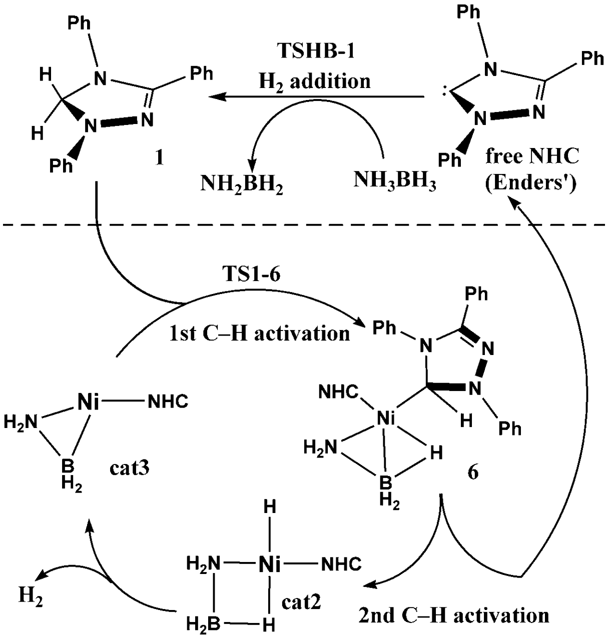
Hydrogen Storage

The Role of Free N-Heterocyclic Carbene (NHC) in the Catalytic Dehydrogenation of Ammonia–Borane in the Nickel NHC System

Paul M. Zimmerman, Ankan Paul, Zhiyong Zhang, and Charles B. Musgrave*

Ammonia–borane (AB) has attracted significant interest as a potential hydrogen storage material because it contains 19.6 wt % hydrogen.[1] However, to exploit AB for hydrogen storage, catalytic dehydrogenation is required. Several studies have investigated various catalytic dehydrogenation schemes,[2–7] including theoretical studies that reveal a diverse chemistry for iridium pincer complexes,[8] titanocene,[9] and nickel N-heterocyclic carbene (NHC) catalysts.[10,11] The Ni NHC catalyst[7] releases more than two equivalents of H_2 from AB under nonhydrolyzing conditions.[5] However, the complex chemistry of this system is not yet fully understood, especially considering that rapid decomposition of the Ni NHC catalyst releases free NHC into the reaction media.[11] Because free NHC is highly reactive,[12–16] and is released from the Ni NHC catalyst during AB dehydrogenation, its reactivity should be considered. In addition to the free NHC/Ni NHC catalytic pathway proposed herein, we have also shown that Ni NHC catalysts competitively dehydrogenate AB.[11]

Herein, we report a theoretical study of the reactivity of free NHC in the AB/Ni NHC catalytic system summarized in Scheme 1. We show that Enders' carbene (free NHC in Scheme 1) dehydrogenates AB with relatively low barrier, producing NH_2BH_2 and NHC–$(H)_2$ (**1**). Although direct elimination of H_2 from **1** is not competitive, [Ni(NHC)-(NH_2BH_2)] catalyst (cat3), formed in situ from the precursor [Ni$(NHC)_2$] (cat1) in the course of AB dehydrogenation,[11] catalyzes C–H activation of **1** to form **6**, which subsequently undergoes a second C–H activation at the active carbene to release free NHC and then H_2. The release of free NHC enables subsequent dehydrogenation of AB by the NHC. The overall catalytic cycle, which is composed of the free NHC dehydrogenation cycle coupled through cat3 to the C–H activation and H_2 release cycle, is therefore not stoichiometric in free NHC and assists Ni NHC catalysts in catalytically dehydrogenating aminoborane oligomers and AB. Scheme 1 shows an overview of the carbene chemistry in the AB/Ni NHC system, which emphasizes that NHC combined with the nickel catalyst causes catalytic AB dehydrogenation. Free NHC in the absence of the Ni catalyst can only stoichiometrically remove H_2 from AB. Our results suggest that the catalytic cycle in which free NHC plays a central role operates in parallel to the direct catalytic AB dehydrogenation using Ni NHC.[11]



Scheme 1. Catalytic dehydrogenation of AB by a Ni NHC catalyst and free NHC that operates parallel to the AB dehydrogenation by the Ni NHC catalyst.[11] The cycle involves an upper loop (above the broken line) in which free NHC stoichiometrically dehydrogenates AB to produce **1**, and a lower C–H activation loop (below the broken line) in which the Ni catalysts dehydrogenate **1** and release H_2. Intramolecular elimination of H_2 by **1** is uncompetitive. Instead, **1** undergoes C–H activation at cat3 to form **6** and then the active carbene in **6** undergoes a second C–H activation, regenerating free NHC and forming cat2. Cat2 releases H_2 to reform cat3. Both cat3 and free NHC are rapidly generated from the reaction of AB with cat1.[11] This mechanism contains both N–H and B–H kinetic isotope effects and can account for the removal of the second equivalent of H_2 from AB, in accordance with the experiment.[7] For TSHB-1 see Figure 1, for TS1-6 see Figure 5. The broken line is a guide for the eye to aid distinguishing the two parts of the catalytic cycle.

All calculations are performed using the B3LYP hybrid–exchange density functional and a double–zeta basis with diffuse functions on all reactive atoms within the Gaussian 03 suite.[17] Intrinsic reaction coordinate (IRC) calculations and vibrational mode analysis are performed on all transition states (TSs) to confirm that they connect reported structures. Energies are reported as zero-point corrected, zero-Kelvin B3LYP CPCM solvation energies[18] in THF with energies in benzene shown in parenthesis. Additional computational

---

[*] P. M. Zimmerman, Dr. A. Paul,[+] Dr. Z. Zhang, Prof. C. B. Musgrave
Department of Chemical Engineering
Stanford University Stanford, CA-94305 (USA)

[+] Current address: Indian Association for Cultivation of Science
Kolkata, 700032 (India)
E-mail: rcap@iacs.res.in

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200803211.

© 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

details are available in the Supporting Information, including the results of additional ab initio methods. The TSs are numbered to show the compounds at the start and end of the reaction pathway, thus, for example, TS1-6 is the TS in the conversion of **1** into **6**, TSHB-1 is the TS in the conversion of the hydrogen-bonded complex (**HB**) into **1**.

We first examine the reactivity of free NHC. AB has both acidic and hydridic hydrogen atoms and an N–B bond that is weaker than the N–H and B–H bonds. Free NHC has a unique electronic structure with a lone pair and an empty p orbital each localized on a single carbon atom.[19] These factors create several possible pathways for reaction of AB with free NHC, including N–H activation, B–H activation, S_N2 nucleophilic attack to yield an NHC–BH_3 adduct, and concerted addition of a proton and hydride from AB. Figure 1 shows the TS structures for these reactions and Figure 2 illustrates the corresponding energetics for three of them.

Reactions of AB with NHC through the three pathways shown in Figure 2 each proceed through the formation of a hydrogen-bonded complex (**HB**) that lies 8.8 kcal mol^{-1} (10.9 kcal mol^{-1}) below separated NHC and AB (Figure 2). The stability of this complex arises from the strong hydrogen bond that results from the protonic character of the AB/N–H hydrogen atom and the strong Lewis base character of the carbene lone pair.

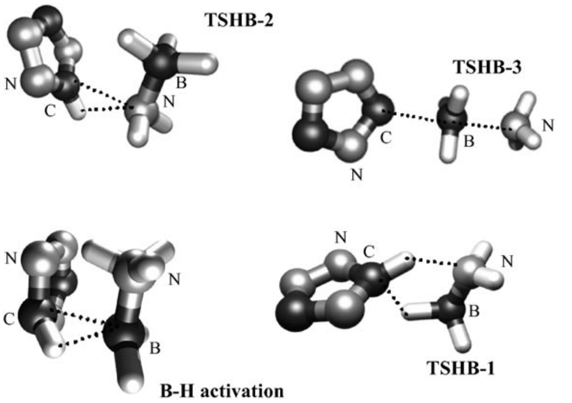


Figure 1. Reactions of free NHC with AB: N–H activation via TSHB-2 (top left), B–H activation (bottom left), S_N2 attack via TSHB-3 (top right), and concerted hydrogen addition via TSHB-1 (bottom right, upper loop of Scheme 1). Phenyl groups are not shown for clarity. Dotted lines indicate atom trajectories in the TSs.

N–H activation involves addition of a proton and NH_2BH_3 to the carbene carbon and proceeds through a TS (TSHB-2) that lies 15.4 kcal mol^{-1} (17.9 kcal mol^{-1}) above **HB** and yields NHC–(H)(NH_2BH_3) (**2**). However, because **2** is 5.7 kcal mol^{-1} (6.1 kcal mol^{-1}) above **HB**, the barrier of the reverse reaction of **2** to yield **HB** via TSHB-2 is only 9.7 kcal mol^{-1} (11.8 kcal mol^{-1}) making N–H activation easily reversible. In contrast, the B–H activation barrier (omitted from Figure 2) lies 53.5 kcal mol^{-1} (52.7 kcal mol^{-1}) above **HB**, rendering it uncompetitive.

S_N2 attack of carbene at AB to form NHC–BH_3 (**3**) and NH_3 involves a TS (TSHB-3) that lies 25.4 kcal mol^{-1} (24.5 kcal mol^{-1}) above **HB** and is exothermic by 12.1 kcal mol^{-1} (10.9 kcal mol^{-1}) relative to **HB**. The exothermicity of S_N2 attack results in a large reverse barrier, which combined with release of NH_3 make the reverse reaction uncompetitive. Although carbene–BH_3 adducts (**3**) are possibly formed by reactions other than S_N2, the S_N2 reaction via TSHB-3 may account for the carbene–BH_3 adducts present in experimental ^{11}B NMR spectra.[7] The circa 25 kcal mol^{-1} energy barrier for the formation of the NHC–BH_3 adduct (**3**) is similar to the

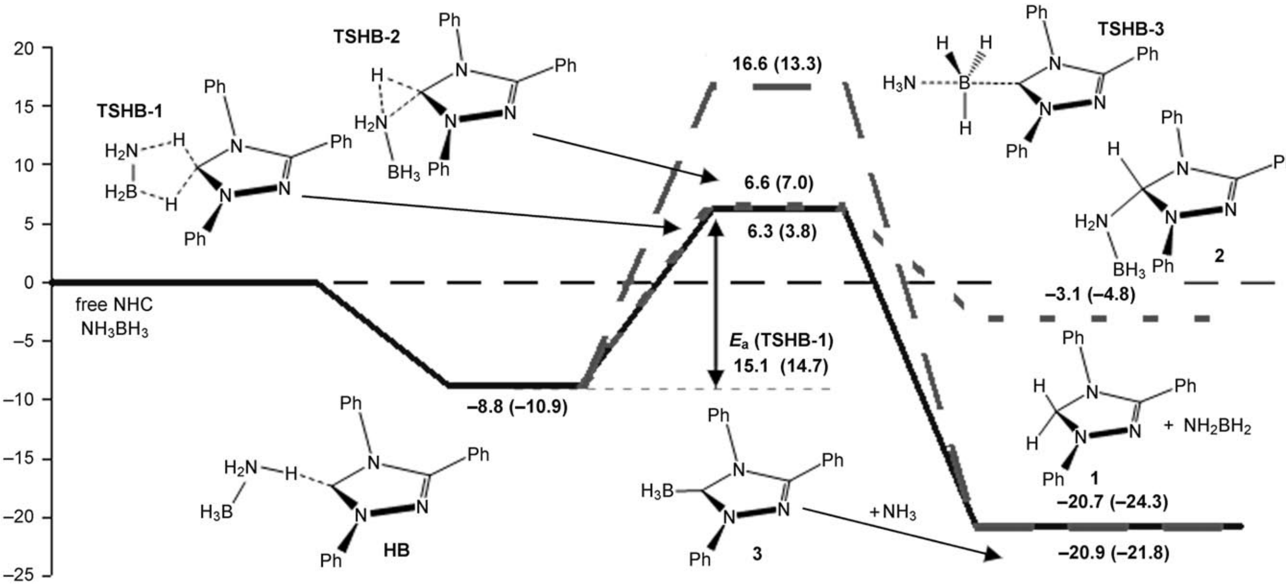


Figure 2. Energetic profile for three low-energy pathways for NHC reaction with AB (upper loop of Scheme 1). Shown are N–H activation (TSHB-2), S_N2 attack (TSHB-3), and concerted addition of hydrogen to free NHC (TSHB-1). B–H activation involves a barrier of 53.5 kcal mol^{-1} above **HB** and is not shown. TSHB-2 has a similar energy barrier as TSHB-1, but the reaction is easily reversible because its product (**2**) is thermodynamically uphill from **HB**. Energies are reported as zero-point corrected, zero-Kelvin B3LYP CPCM solvation energies[18] in THF with energies in benzene shown in parenthesis.

© 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

barrier for transformation of cat2 (see Scheme 1) to cat3 and suggests that although TSHB-3 is feasible at 60 °C, it is uncompetitive with concerted addition of H_2 to NHC (TSHB-1), so that carbene–BH_3 production (and NHC consumption) is limited by TSHB-3.

Concerted addition of a proton and hydride from AB to the Enders' NHC can also occur. This reaction proceeds over a barrier (TSHB-1) that lies 15.1 $kcal\,mol^{-1}$ (14.7 $kcal\,mol^{-1}$) above **HB**, making the reaction fast compared to activations of AB by [Ni(NHC)$_2$] (cat1) and [Ni(NHC)(NH_2BH_2)] (cat3)[11] which have barriers of 21.9 $kcal\,mol^{-1}$ (20.9 $kcal\,mol^{-1}$) and 21.1 $kcal\,mol^{-1}$ (19.8 $kcal\,mol^{-1}$), respectively. At TSHB-1, proton transfer to the NHC is nearly complete, indicating that the hydride addition to the empty carbon p orbital can only occur after protonation of the carbene lone pair lowers the energy of the carbene's empty p orbital. Following the reaction by an IRC calculation shows that the products of this step are **1** and free NH_2BH_2, which lie 11.9 $kcal\,mol^{-1}$ (13.4 $kcal\,mol^{-1}$) below **HB**. Calculation of the vibrational frequencies shows that TSHB-1 exhibits a kinetic isotope effect (KIE) for both N–H and B–H hydrogen in AB (ND_3BH_3: 1.7, NH_3BD_3: 1.4, ND_3BD_3: 2.4). This result agrees with the KIE observed experimentally for the combined N–H and B–H hydrogen atoms.[7]

Figure 2 shows that N–H activation via TSHB-2 competes with concerted addition of hydrogen via TSHB-1. However, because **2** rapidly reverts to **HB**, which in turn transforms to **1** and releases NH_2BH_2 the competition between TSHB-1 and TSHB-2 eventually leads to the formation of **1** and free NH_2BH_2. Furthermore, NH_2BH_2 is highly reactive and quickly oligomerizes, further reducing the rate of reverse reaction of TSHB-1 back to **HB**.[2]

Reduced N-heterocyclic carbenes similar to **1** have been experimentally identified and shown to be stable.[20] However, **1** was not observed in the Ni NHC system,[7] most likely because an exhaustive identification of intermediates was not attempted, although NHC–(H)$_2$ might have been present in the system.[7] We used a diverse set of ab initio methods to produce similar barriers for TSHB-1, supporting the prediction that this reaction readily occurs when free NHC is combined with AB (see the Supporting Information for details).

Dissociation of H_2 and NH_3 by alkyl carbenes via intermediates analogous to TSHB-1 and TSHB-2, respectively, has been observed.[19] Although N-heterocyclic carbenes are generally inert to hydrogen[20] and ammonia,[21] addition of hydrogen to NHC is exothermic and has been achieved by using a catalyst.[20]

The electronic structure for concerted addition of hydrogen from AB to the aminal carbon of NHC involves hydride acceptance by the carbene singlet lone pair (the HOMO) and proton acceptance by the empty carbene p orbital (the LUMO). Simulations predict an analogous concerted hydrogen addition from AB to an iridium pincer-complex catalyst, in which the Ir center has an available LUMO d orbital for hydride acceptance and a HOMO d orbital for proton acceptance.[8] An animation of the HOMO along the reaction coordinate through TSHB-1 (see the Supporting Information) clearly illustrates the roles of the hydrogen atoms and the NHC HOMO and LUMO, both localized on the aminal carbon atom. Thus, the unique electronic structure of AB makes the addition of two hydrogen atoms to an NHC via TSHB-1 kinetically feasible[20] and chemically reasonable, and therefore is expected to occur even in the absence of the Ni catalyst. However, free NHC is unable to catalytically dehydrogenate AB without the assistance of the Ni catalyst.

Concerted addition of two hydrogen atoms from AB to free NHC inactivates the carbene, both with respect to reaction with AB and as a potential Ni ligand. Fortunately, the shift in equilibrium towards deactivated carbene (**1**) can be circumvented if free NHC can be regenerated from **1**. Intramolecular regeneration of free NHC, however, is not feasible because the barrier to reductive elimination of H_2 from **1** is 50.5 $kcal\,mol^{-1}$ (53.9 $kcal\,mol^{-1}$). This is consistent with the experimental observation that free carbenes alone do not catalyze AB dehydrogenation.[7] We therefore investigated the possibility of C–H activation of **1** by catalytic Ni species (cat1 and cat3) identified in our investigation of Ni NHC/AB chemistry.[11]

One path for C–H activation of **1** involves the dicarbene species cat1. We find no favorable association of **1** to cat1 prior to activation. Despite the steric bulk of the phenyl groups on the carbenes and a total of three carbenes near the Ni atom, **1** can approach cat1 and oxidatively add a C–H bond via TS1-4 (Figure 3). TS1-4 lies 32.7 $kcal\,mol^{-1}$ (31.6 $kcal\,mol^{-1}$) above the separated species and produces the square planar species *cis*-[Ni(NHC)$_2$(H)NHC-(H)] (**4**, shown in the Supporting Information), which lies 18.7 $kcal\,mol^{-1}$ (18.2 $kcal\,mol^{-1}$) above and separated cat1 and **1**. Because of the relatively high barrier for TS1-4 and the high energy of **4** this pathway was not investigated further.

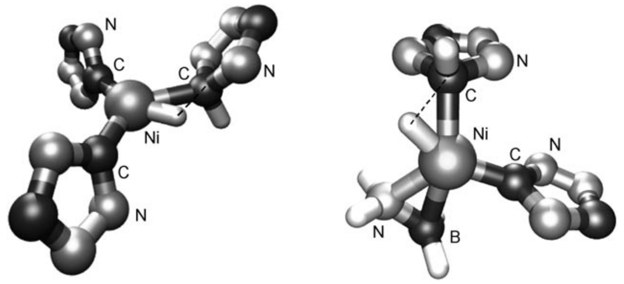


Figure 3. C–H activations of **1** at cat1 via TS1-4 (left) and at cat3 via TS1-5 (right). These two activations are not competitive with TS1-6 (Figures 4 and 5). Dotted lines indicate atom trajectories in the TSs.

We previously found that cat1 decomposes during AB dehydrogenation, releasing free NHC and forming the monocarbene species cat3.[11] Cat3 is less sterically hindered than cat1, allowing two reasonable pathways for C–H activation of **1** at cat3: activation with **1** nearest to the nitrogen of the NH_2BH_2 ligand (TS1-5 in Figure 3) and activation with **1** nearest to the boron of the NH_2BH_2 ligand (TS1-6 in Figure 4). In both cases **1** does not complex with cat3 prior to the reaction. Figure 3 shows TS1-5, which is situated 31.0 $kcal\,mol^{-1}$ (29.3 $kcal\,mol^{-1}$) above **1** and cat3. TS1-5 yields [Ni(NHC)H(NH_2BH_2)(NHC-H)] (**5**, shown in

© 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

the Supporting Information) that is 22.9 kcal mol^{-1} (21.4 kcal mol^{-1}) above **1** and cat3. Pathways through TS1-5 are not considered further because TS1-6 and **6** are significantly lower in energy than TS1-5 and **5**, respectively.

C–H activation through TS1-6 (Figure 4) results in the lowest barrier and most thermodynamically favorable C–H activation of **1** (see Figure 5). The calculated barrier for TS1-6 of 22.1 kcal mol^{-1} (20.1 kcal mol^{-1}) is low enough for this pathway to be active at reaction conditions. Furthermore, this TS exhibits C–H KIE (H from AB: 3.9) and yields **6**, which is also an intermediate in AB activation at the Ni NHC catalysts,[11] and lies in energy only 2.8 kcal mol^{-1} (1.4 kcal mol^{-1}) above **1** and cat3. The chemistry of **6** has been described in Ref. [11] and is represented by the two overall reactions [Eqs. (1) and (2)].

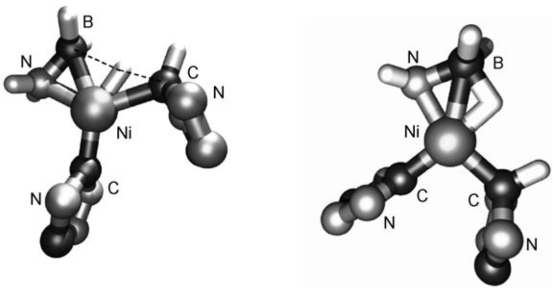


Figure 4. TS for C–H activation of **1** at cat3 via TS1-6 (left) and its product (**6**; right). The BH_2 end of NH_2BH_2 helps provide a site for acceptance of a hydride from **1**. The dotted line indicates atom trajectories in the TS.

$$6 \rightarrow \text{cat2} + \text{free NHC},\ E_a = 10.5\ \text{kcal mol}^{-1}\ (12.2\ \text{kcal mol}^{-1}) \qquad (1)$$

$$\text{cat2} \rightarrow \text{cat3} + H_2,\ E_a = 25.4\ \text{kcal mol}^{-1}\ (25.1\ \text{kcal mol}^{-1}) \qquad (2)$$

The rate of regeneration of free NHC is therefore limited by TS1-6, and the regeneration of cat3 is limited by the elimination of H_2 from cat2. Figure 5 shows the pathway for regeneration of free NHC via C–H activation of **1** by cat3. Because AB interacts favorably with cat3,[11] **1** must displace AB from the cat3–AB adduct prior to C–H activation whenever AB is abundant. This situation raises the overall barrier for free NHC regeneration to 24.8 kcal mol^{-1} (25.3 kcal mol^{-1}), or to 28.6 kcal mol^{-1} (29.1 kcal mol^{-1}) including free energy corrections. Not only does the carbene C–H activation exhibit a deuterium KIE (TS1-6, C–H (H from AB): 3.9), but regeneration of cat3 from cat2 shows both N–H and B–H KIEs.[11] Thus, the N–H and B–H KIEs of this mechanism agree with the experimental KIEs, while AB dehydrogenation by cat1 only exhibits a N–H KIE.[10,11]

Because our results show that free NHC dehydrogenates AB, we investigated the possibility that aminoborane species containing sp^3 boron and nitrogen atoms could be activated in a similar manner to release the second equivalent of H_2 from AB. Specifically, the reactivities of $NH_3BH_2NH_2BH_3$,[22] cyclic $(NH_2BH_2)_2$,[22,23] cyclic $(NH_2BH_2)_3$,[24,25] and cyclic $(B_2N_2H_7\text{-}NH_2BH_3)$[26] are considered. Table 1 lists the barriers for dehydrogenation of these species by Enders' NHC. The TS geometries are similar to that of AB dehydrogenation by free NHC (see the Supporting Information). Dehydrogenation of $NH_3BH_2NH_2BH_3$ and cyclic $(B_2N_2H_7\text{-}NH_2BH_3)$ involve barriers similar to that of AB, whereas cyclic species are more difficult to dehydrogenate due to ring strain at the newly formed double bond.

Herein we propose a novel mechanism in which free Enders' NHC assists Ni NHC catalysts in catalytically dehydrogenating AB, parallel to direct AB dehydrogenation

Table 1: Activation of aminoborane oligomers by Enders' NHC.

Free carbene dehydrogenation of aminoborane species	Barrier [kcal mol^{-1}]
NH_3BH_3 activation	15.1 (14.7)
$NH_3BH_2NH_2BH_3$ activation at NH_3 end	16.0 (15.9)
$NH_3BH_2NH_2BH_3$ activation at BH_3 end	21.2 (22.3)
cyclic $(NH_2BH_2)_2$ activation	27.0 (28.1)
cyclic $(NH_2BH_2)_3$ activation	20.8 (21.6)
cyclic $(NH_2BH_2)_2NH_2BH_3$ activation at tail	15.4 (15.7)

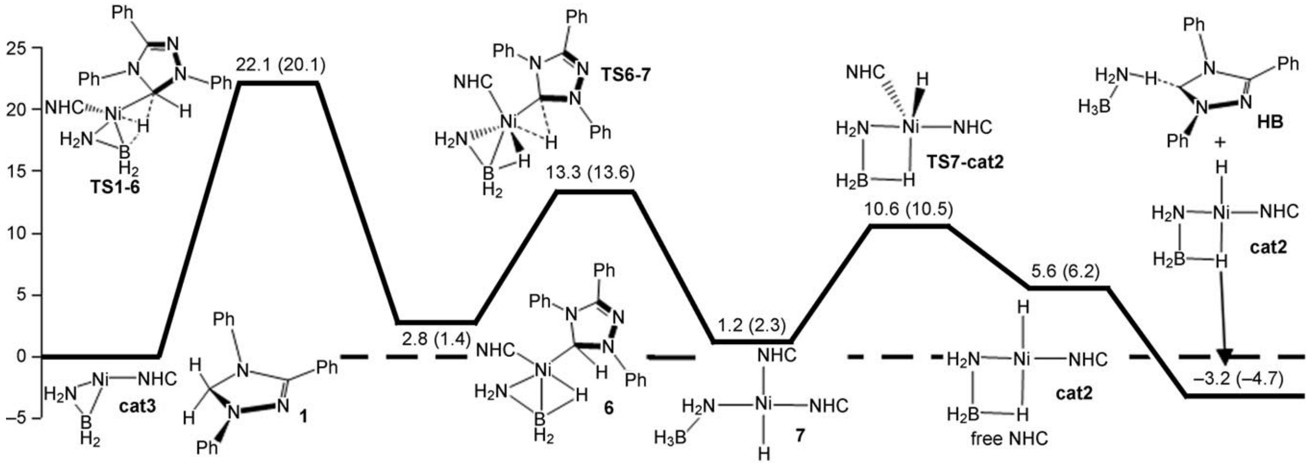


Figure 5. Full energetic profile for C–H activation of **1** at cat3 to regenerate free NHC (see lower loop of Scheme 1). Cat2 can release H_2 to reform cat3 and complete the catalytic cycle with a barrier of 25.4 kcal mol^{-1} (25.1 kcal mol^{-1}) [Eq. (2)].[11]

© 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

by Ni catalysts. NHC dehydrogenates AB to form NHC–$(H)_2$ via TSHB-1 with a relatively low barrier of 15.1 kcal$\,$mol^{-1} (14.7 kcal$\,$mol^{-1}). Although reductive elimination of H_2 from **1** has high barrier, **1** can be dehydrogenated by sequential C–H activations by the Ni monocarbene species cat3 (via TS1-6 and TS6-7) with an overall barrier of 24.8 kcal$\,$mol^{-1} (25.3 kcal$\,$mol^{-1}). These C–H activations of **1** by cat3 complete the free NHC/cat3 catalytic cycle and allow for the regeneration of the active free carbene.

The overall barriers for AB activation by free NHC and NHC regeneration (limited by TS1-6) are similar to the overall barriers for AB dehydrogenation at Ni NHC catalysts, which are 25.4 kcal$\,$mol^{-1} (25.1 kcal$\,$mol^{-1}) and 23.3 kcal$\,$mol^{-1} (22.1 kcal$\,$mol^{-1}) for AB reacting at cat1 and cat3, respectively.[11] These similar overall barriers suggest that multiple mechanisms for AB dehydrogenation are likely to be active in the Ni NHC catalytic system. In addition, the pathways considered herein show KIE for both N–H and B–H hydrogen in AB (TSHB-1: ND_3BH_3: 1.7, NH_3BD_3: 1.4, ND_3BD_3: 2.4; TS1-6 C–H (H from AB): 3.9), which contribute to the experimentally observed KIE (ND_3BH_3: 2.3, NH_3BD_3: 1.7, ND_3BD_3: 3.0).[7] The pathways presented here show both N–H and B–H KIE, whereas a less complete mechanism contains only N–H KIE (Supporting Information of Ref. [10]).

Although barriers for dehydrogenation of AB oligomers are unknown at cat1 and cat3, free NHC allows for dehydrogenation of AB oligomers with barriers below 25 kcal mol^{-1} (except of cyclic-$(NH_2BH_2)_2$). The ability of the Ni NHC system to generate more than two equivalents of H_2 from AB[7] is partly accounted for by the assistance of free NHC in breaking down AB oligomers that may not react quickly with the Ni catalysts owing to steric hindrance. This mechanism should be considered as an important aspect of Ni NHC catalytic AB dehydrogenation chemistry because: it accounts for the release of more than two equivalents of H_2,[7] it exhibits both N–H and B–H KIEs,[7] it involves rate-limiting barriers that are competitive with direct dehydrogenation by $[Ni(NHC)_2]$ [11] and which are consistent with the experimental observation that heating to 60 °C was required to achieve reasonable rates,[7] it is verified by a variety of ab initio methods (Supporting Information), and it agrees with the experimentally observed chemical reactivity of carbenes.[19,20]

Received: July 3, 2008
Revised: October 13, 2008
Published online: February 9, 2009

Keywords: ammonia · borane · density functional calculations · homogeneous catalysis · N-heterocyclic carbenes

---

[1] T. B. Marder, *Angew. Chem.* **2007**, *119*, 8262 – 8264; *Angew. Chem. Int. Ed.* **2007**, *46*, 8116 – 8118.
[2] F. H. Stephens, V. Pons, R. T. Baker, *Dalton Trans.* **2007**, 2613 – 2626, and references therein.
[3] M. C. Denney, V. Pons, T. J. Hebden, D. M. Heinekey, K. I. Goldberg, *J. Am. Chem. Soc.* **2006**, *128*, 12048 – 12049.
[4] T. J. Clark, C. A. Russell, I. Manners, *J. Am. Chem. Soc.* **2006**, *128*, 9582 – 9583.
[5] T. J. Clark, G. R. Whittell, I. Manners, *Inorg. Chem.* **2007**, *46*, 7522 – 7527.
[6] D. Pun, E. Lobkovsky, P. J. Chirik, *Chem. Commun.* **2007**, 3297 – 3299.
[7] R. J. Keaton, J. M. Blacquiere, R. T. Baker, *J. Am. Chem. Soc.* **2007**, *129*, 1844 – 1845.
[8] A. Paul, C. B. Musgrave, *Angew. Chem.* **2007**, *119*, 8301 – 8304; *Angew. Chem. Int. Ed.* **2007**, *46*, 8153 – 8156.
[9] Y. Luo, K. Ohno, *Organometallics* **2007**, *26*, 3597 – 3600.
[10] X. Yang, M. B. Hall, *J. Am. Chem. Soc.* **2008**, *130*, 1798 – 1799.
[11] P. Zimmerman, A. Paul, C. B. Musgrave, unpublished results.
[12] (Ed.: P. Kocovsky, A. Malkov), *Tetrahedron* **2006**, *62*(2–3).
[13] D. Enders, T. Balensiefer, *Acc. Chem. Res.* **2004**, *37*, 534 – 541.
[14] V. Nair, S. Bindu, V. Sreekumar, *Angew. Chem.* **2004**, *116*, 5240 – 5245; *Angew. Chem. Int. Ed.* **2004**, *43*, 5130 – 5135.
[15] K. Zeitler, *Angew. Chem.* **2005**, *117*, 7674 – 7678; *Angew. Chem. Int. Ed.* **2005**, *44*, 7506 – 7510.
[16] A. P. Dove, R. C. Pratt, B. G. G. Lohmeijer, H. Li, E. C. Hagberg, R. M. Waymouth, J. L. Hedrick in *N-Heterocyclic Carbenes in Synthesis* (Ed.: S. P. Nolan), Wiley-VCH, Weinheim, **2006**, pp. 275 – 296.
[17] Gaussian 03 (Revision E.01): M. J. Frisch et al., see the Supporting Information.
[18] M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* **2003**, *24*, 669 – 681.
[19] G. D. Frey, V. Lavallo, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Science* **2007**, *316*, 439 – 441.
[20] M. K. Denk, J. M. Rodezno, S. Gupta, A. J. Lough, *J. Organomet. Chem.* **2001**, *617–618*, 242 – 253.
[21] W. A. Herrmann, M. Elison, J. Fischer, C. Kocher, G. R. J. Artus, *Chem. Eur. J.* **1996**, *2*, 772 – 780.
[22] A. C. Stowe, W. J. Shaw, J. C. Linehan, B. Schmid, T. Autrey, *Phys. Chem. Chem. Phys.* **2007**, *9*, 1831 – 1836.
[23] V. S. Nguyen, M. H. Matus, D. J. Grant, M. T. Nguyen, D. A. Dixon, *J. Phys. Chem. A* **2007**, *111*, 8844 – 8856.
[24] K. W. Boddeker, S. G. Shore, R. K. Bunting, *J. Am. Chem. Soc.* **1966**, *88*, 4396 – 4401.
[25] J. S. Wang, R. A. Geanangel, *Inorg. Chim. Acta* **1988**, *148*, 185 – 190.
[26] a) W. J. Shaw, J. C. Linehan, N. K. Szymczak, D. J. Heldebrant, C. Yonker, D. M. Camioni, R. T. Baker, T. Autrey, *Angew. Chem.* **2008**, *120*, 7603 – 7606; *Angew. Chem. Int. Ed.* **2008**, *47*, 7493 – 7496; b) P. M. Zimmerman, A. Paul, Z. Zhang, C. B. Musgrave, *Inorg. Chem.* **2009**, *48*, 1069 – 1081.

© 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim