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On the Mechanism of $B(C_6F_5)_3$-Catalyzed Direct Hydrogenation of Imines: Inherent and Thermally Induced Frustration

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Abstract: The reaction mechanism for the transition metal free direct hydrogenation of bulky imines catalyzed by the Lewis acid $B(C_6F_5)_3$ is investigated in detail by quantum chemical calculations. A recently introduced mechanistic model of heterolytic hydrogen splitting that is based on noncovalent association of bulky Lewis acid−base pairs is shown to account for the reactivity of imine−borane as well as amine−borane systems. Possible catalytic cycles are examined, and the results provide solid support for the imine reduction pathway proposed from experimental observations. In addition, the feasibility of an autocatalytic route initiated by amine−borane hydrogen cleavage is demonstrated. Conceptual issues regarding the notion of frustration are also discussed. The observed reactivity is interpreted in terms of thermally induced frustration, which refers to thermal activation of strained dative adducts of bulky Lewis donor−acceptor pairs to populate their reactive frustrated complex forms.

1. Introduction

Catalytic hydrogenations of unsaturated organic compounds constitute an important class of chemical transformations and find broad applications both in chemical industry and laboratory organic synthesis.[1] The majority of hydrogenation reactions involve the direct use of H_2 as the hydrogen source, and they are catalyzed by transition metals (TMs). The role of metal centers and surrounding ligands in H_2 activation processes has been extensively studied for several decades, and the details of homolytic and heterolytic H_2 splitting pathways are now well understood.[2,3] However, environmental and product toxicity concerns connected with TMs have long motivated investigations directed toward achieving TM-free homogeneous catalytic hydrogenation. Most of the reactions reported hitherto required either rather drastic conditions[4,5] or the use of surrogates such as Hantzsch ester or silicon compounds instead of hydrogen.[6,7] Even direct reactions of H_2 with stable main group compounds are quite rare.[8−11] Known examples include alkali metal alkyl or aryl compounds,[8] the ArGeGeAr "digermyne" species,[9] singlet (alkyl)(amino)carbenes,[10] and the heavier group 14 element carbene analogue $SnAr_2$.[11] TM-free H_2 activation in biological systems was also considered feasible.[12,13] However, the unique hydrogenase found in methanogenic archaea, which was assumed to act as a purely organic hydrogenation catalyst, has been shown to comprise an active iron-containing cofactor and the mechanism of H_2 activation is still not resolved.[14]

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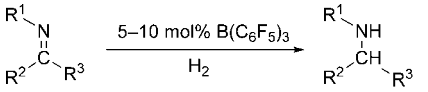
10.1021/ja809125r CCC: $40.75

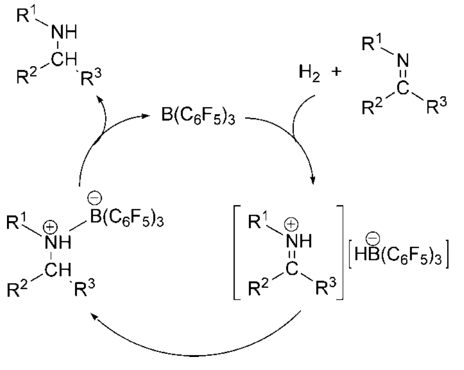
Scheme 1. Direct Hydrogenation of Imines Catalyzed by $B(C_6F_5)_3$



A major breakthrough toward direct catalytic hydrogenation by non-TMs has been achieved very recently by Stephan and co-workers discovering a reversible TM-free H_2 addition/elimination process.[15−17] The involved intramolecularly linked Lewis acid−base species, $Mes_2P–(p-C_6F_4)–B(C_6F_5)_2$ (Mes denotes mesityl (2,4,6-$Me_3C_6H_2$) group), was shown to react readily with H_2 at very mild conditions, and its reduced form ($Mes_2HP–(p-C_6F_4)–BH(C_6F_5)_2$) could liberate H_2 at 100 °C.[15] This milestone experiment has initiated a series of studies in this field leading to the development of various linked systems as well as simple Lewis acid−base pairs that are capable of heterolytic hydrogen splitting.[18−28] Easy transfer of the activated hydrogen to unsaturated substrates has been demonstrated[18−23] allowing successful catalytic applications for direct hydrogenation of imines,[18−20] nitriles,[18] and aziridines,[18] as well as enamine[19,20] and silyl enol ether[21] C═C double bonds. The key to this unprecedented reactivity, as suggested by Stephan and co-workers, is the presence of free Lewis donor and acceptor sites.[29] This is ensured by steric hindrance of the classical dative bond formation in these pairs, which have been termed frustrated Lewis pairs (FLPs).[29,30]

As a fruitful application of this concept, Stephan's[31] and Klankermayer's[32] groups have independently showed that the absence of the dative bond renders the heterolytic H_2 cleavage also in certain imine−borane pairs possible. Hydrogenation of such imines, which is a valuable transformation from a synthetic point of view,[33] can thus be accomplished using solely the Lewis acid $B(C_6F_5)_3$ as catalyst (see Scheme 1).[31,32] Experimental mechanistic studies on this reaction allowed the formulation of a catalytic cycle (Scheme 2),[31] which shares a number of features with the mechanism of the related $B(C_6F_5)_3$-catalyzed hydrosilylation reactions.[7,34] Hydrogen splitting by the frustrated imine−borane system has been proposed to yield an ion pair consisting of an activated iminium ion and a hydridoborate ion. An amine−borane dative adduct is then formed in the hydride transfer step. Thermal dissociation of this adduct delivers the amine and regenerates the free borane that can enter the cycle again.

Scheme 2. Catalytic Cycle for Imine Hydrogenation As Formulated by Stephan and Co-workers[31]



Inspired by these new developments, we have initiated theoretical studies to uncover the origin of these remarkable reactions.[35] In an effort to understand the facile activation of dihydrogen, we explored various reaction pathways for the heterolytic cleavage of H_2 by the prototypical frustrated Lewis pair $P(t\text{-}Bu)_3 + B(C_6F_5)_3$.[35] In line with experimental observations,[24] we found no evidence for dative P−B bond formation; however, we identified a weakly bound noncovalent $[(t\text{-}Bu)_3P]\cdots[B(C_6F_5)_3]$ complex as a possible reactive intermediate in the hydrogen activation process. We suggested that this structurally flexible adduct, also referred to as a "frustrated complex", provides preorganized active centers for bifunctional H−H bond activation and it represents an energetically strained species that enables the lowering of the activation barrier. This new mechanistic model has been shown to account for the reactivity of a carbene−borane frustrated pair toward H_2,[26] as well as for the addition reactions of FLPs with olefins.[36−38] The first member of this family of compounds, the linked phosphine−borane system $Mes_2P–(p-C_6F_4)–B(C_6F_5)_2$, has also been suggested to follow this hydrogen splitting pathway.[39]

Although the cleavage of the hydrogen molecule with FLPs has been investigated in detail, no theoretical works have so far addressed its subsequent fate in reduction processes. We now present a detailed computational study on the full mechanism of the direct imine hydrogenation mediated by $B(C_6F_5)_3$. To the best of our knowledge, this is the first attempt to completely characterize a catalytic hydrogenation process based on frustrated Lewis pairs by quantum chemical calculations. Herein, we examine the elementary steps and intermediates of

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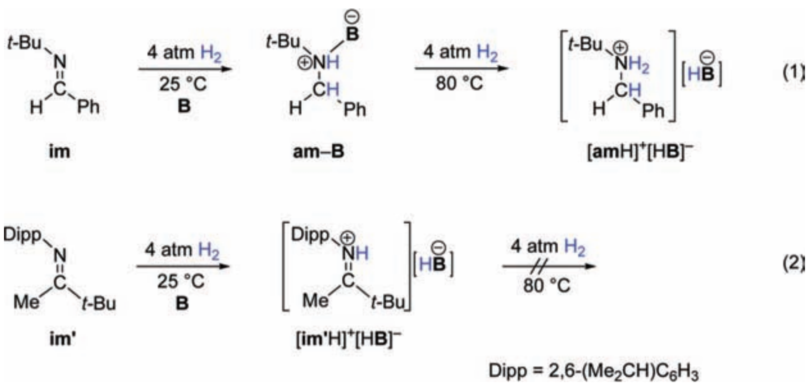
Scheme 3. Stoichiometric Reactions of Imines and Borane $B(C_6F_5)_3$ (**B**) with H_2[31]



the catalytic cycle suggested by Stephan and co-workers,[31] but an additional, autocatalytic pathway,[32] which has emerged from our calculations, will also be described. Application of our recent mechanistic model[35] to imine−borane and amine−borane frustrated pairs sheds light on conceptual novelties that broaden our understanding of frustration.

2. Computational Details

In the present work, geometries of all stationary points were fully optimized at the M05-2X/6-31G(d) level of density functional theory.[40,41] We used an ultrafine integration grid in all DFT calculations to reduce numerical uncertainty in flat regions of the potential energy surface (PES). The located stationary points were characterized as minima or first-order saddle points according to the calculated harmonic vibrational frequencies. Transition states were checked to connect the respective minima by optimizations following initial intrinsic reaction coordinate calculations.[42]

For each optimized structure, we carried out single-point spin-component scaled (SCS) MP2/cc-pVTZ calculations[43,44] using the resolution-of-identity (RI) integral approximation[45] with core orbitals kept frozen, and without correction for the basis set superposition error (BSSE). We chose this approach as it has been found that the BSSE is well compensated by the effect of the one-electron basis set deficiencies in the case of weakly bound complexes yielding accurate interaction energies.[46] The energy data presented in the paper refer to gas-phase SCS-MP2 electronic energies, unless indicated otherwise in the text.

Zero-point and thermal corrections to the energies as well as entropic contributions to the gas phase free energy were estimated using the ideal gas−rigid rotor−harmonic oscillator model at the M05-2X/6-31G(d) level. Calculated Gibbs free energy data refer to $T = 353$ K and 1 mol/L concentration. Solvation free energies were determined by single-point IEFPCM/M05-2X/6-31G(d)[47] calculations with the UA0 radii and toluene as solvent for the gas-phase optimized geometries. Explicit spheres onto unbound hydrogen atoms were added where needed, whereas all remaining parameters were left at their default values.

The density functional calculations were carried out with the Gaussian 03 software, while for the RI-SCS-MP2 calculations, the Turbomole package was employed.[48] Molecular graphics were drawn using Molekel.[49]

3. Results and Discussion

Stoichiometric Reactions. Although our main goal in the present work was to provide a sound theoretical basis for the mechanism of the catalytic hydrogenation processes described by Stephan and Klankermayer,[31,32] we first examine the stoichiometric reactions of imines with $B(C_6F_5)_3$ and H_2 (see Scheme 3). These processes have been investigated experimentally by the Stephan group,[31] and this has provided important mechanistic information for the catalytic procedures. We shall, therefore, start our discussion with analyzing the potential energy surface (PES) related to these reactions.

Results of NMR measurements indicate that imine t-BuN═CHPh (hereafter referred to as **im**) does not form a dative bond with $B(C_6F_5)_3$ (**B**);[7] consequently this Lewis acid−base pair can be classified as an FLP. When their solution is exposed to 4 atm of H_2 at room temperature, the imine is reduced to the corresponding amine t-BuNH–CH_2Ph (**am**), which then combines with the Lewis acid to an amine−borane dative adduct **am – B** (see Scheme 3, eq 1).[31] Interestingly, subsequent heating to 80 °C induces the cleavage of another H_2 molecule yielding the ammonium hydridoborate salt $[\mathbf{am}H]^+[H\mathbf{B}]^-$. A quite different behavior was experienced for the more crowded ketimine DippN═C(t-Bu)Me (**im′**), which afforded the iminium hydridoborate compound $[\mathbf{im'}H]^+[H\mathbf{B}]^-$ in the stoichiometric reaction (Scheme 3, eq 2). In this case, steric bulk has been suggested to preclude the hydride transfer to the carbon atom, thereby allowing the isolation of an important intermediate.[31]

In order to identify the elementary steps and to characterize the PES of the stoichiometric reaction, we located possible reaction intermediates and connecting transition states along the

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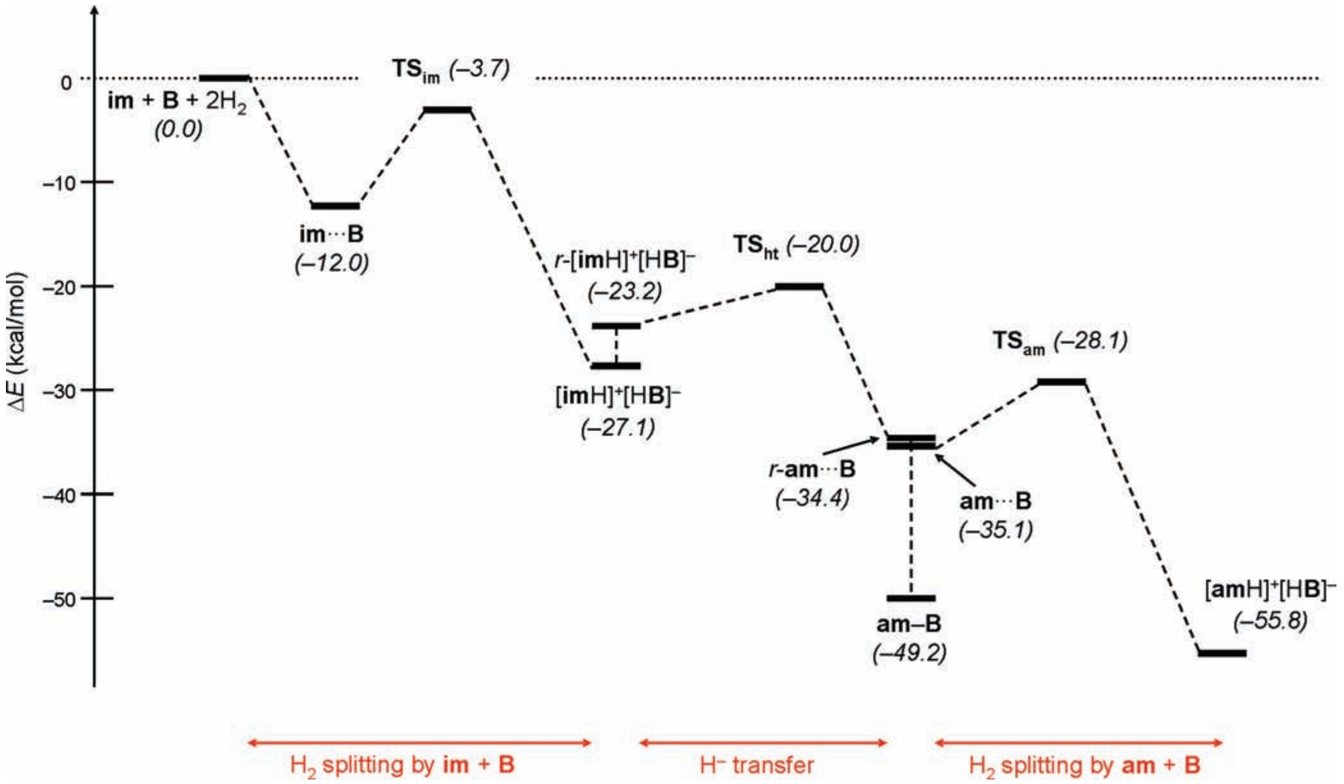

Figure 1. Electronic energy profile for the stoichiometric reaction of **im** + **B** + $2H_2$. For certain species, the *r* prefix refers to a less stable (rearranged) isomeric structure.

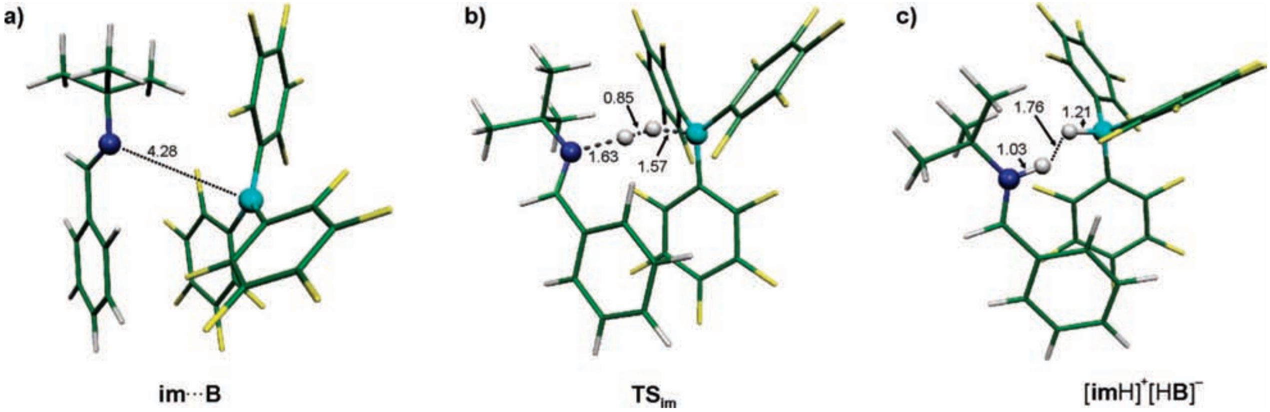

Figure 2. Optimized structures of the stationary points for the imine−borane hydrogen splitting reaction step: (a) imine−borane frustrated complex, (b) transition state of hydrogen splitting, (c) iminium hydridoborate product ion pair. Selected atomic distances are given in Å.

reaction pathway from **im** + **B** + $2H_2$ toward the $[\mathbf{am}H]^+[H\mathbf{B}]^-$ ion pair (Scheme 3, eq 1). Our results are summarized in Figure 1 in the form of an energy diagram obtained for the explored reaction route. The structures of the identified stationary points are depicted in Figures 2−5.

The process is thought to commence with the activation of dihydrogen by the imine−borane FLP. The absence of the imine−borane dative bond and the facile hydrogen splitting reaction observed experimentally is quite analogous to the $(t\text{-Bu})_3P$ + **B** system investigated earlier.[24,35] We therefore assumed similar noncovalent association of the imine−borane frustrated Lewis pair, and we indeed identified computationally the frustrated complex **im···B** (see Figure 2a). The structure of this complex reveals that $\pi-\pi$ stacking, C−H···π, and C−H···F interactions are responsible for the association and give rise to an appreciable binding energy of −12.0 kcal/mol. Although formed in an entropically unfavored process, this intermediate reacts rapidly with H_2 via the transition state $\mathbf{TS_{im}}$ (Figure 2b), which represents only a small energy barrier for this elementary step, lying 8.3 kcal/mol above **im···B** + H_2. The heterolytic cleavage of the H−H bond is an exothermic process and yields the iminium hydridoborate ion pair $[\mathbf{im}H]^+[H\mathbf{B}]^-$ (Figure 2c).[50]

All these features bear close resemblance to those obtained for the $(t\text{-Bu})_3P$ + **B** + H_2 reaction[35] indicating that the H−H splitting processes occur via similar mechanisms. In both reactions, the hydrogen activation is initiated by simultaneous

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(50) On the reactant side of the TSs associated with H_2 splitting, shallow minima can be identified corresponding to very weak ternary complexes; however, the reactions are suggested to be essentially bimolecular occurring upon the encounter of the frustrated complex and H_2.

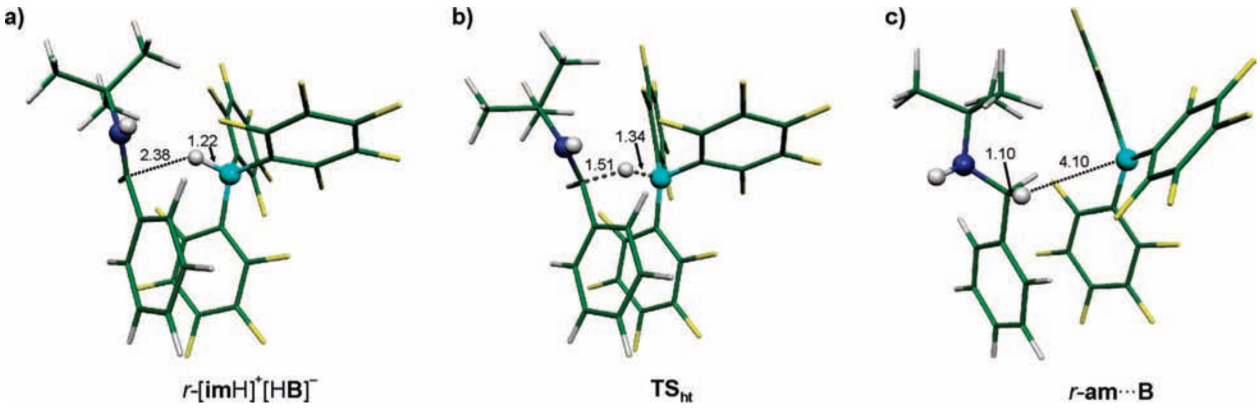

Figure 3. Optimized structures of the stationary points for the hydride transfer step: (a) rearranged iminium hydridoborate ion pair, (b) transition state of hydride transfer, (c) weakly bound amine−borane product complex.

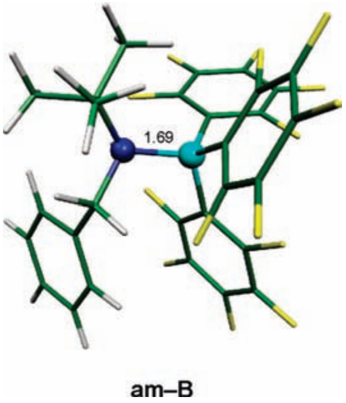

Figure 4. Optimized structure of the amine−borane dative adduct.

donor → $\sigma^*(H_2)$ and $\sigma(H_2)$ → *acceptor* electron donations leading to the polarization and the final cleavage of H_2. Our results indicate that this low-barrier, exothermic reaction can take place easily at room temperature, which is in line with experimental observations.

Activated hydrogen being available in [**im**H]$^+$[H**B**]$^-$, subsequent reduction of the iminium by the hydridoborate can easily occur. An internal rearrangement of the [**im**H]$^+$[H**B**]$^-$ ion pair gives an isomer (*r*-[**im**H]$^+$[H**B**]$^-$) wherein the B−H bond points toward the unsaturated carbon atom of iminium (Figure 3a). The hydride transfer in *r*-[**im**H]$^+$[H**B**]$^-$ occurs via **TS$_{ht}$** (Figure 3b) with a rather low overall activation energy (7.2 kcal/mol).[51] This step is exothermic as well and yields the neutral amine–borane adduct *r*-**am···B** (Figure 3c) bound by secondary interactions. The formation of a dative bond between **am** and **B** leads to a significantly more stable classical adduct (**am** – **B**, see Figure 4), which is the observed product of the reaction at room temperature.

As shown by experiments, elevated temperature is sufficient to dissociate the N−B dative bond and an additional H_2 splitting process takes place. In analogy with the imine−borane pair, a preorganized amine−borane frustrated complex can be identified on the PES (**am···B**, see Figure 5a). This species has a binding energy of −12.7 kcal/mol with respect to **am** + **B**, and it is slightly more stable than the *r*-**am···B** form. As expected, **am···B** features similar reactivity with H_2 as the **im···B** complex in that the H−H cleavage proceeds in a low-barrier exothermic reaction step.[50] Our calculations show that the located transition state **TS$_{am}$** (Figure 5b) lies only 7.1 kcal/mol above the **am···B** + H_2 level. However, given that the amine−borane system has a notably deeper energy minimum at its datively bound **am** – **B** form, higher activation energy is needed to reach the transition state. These results are in full agreement with the experimental finding that the formation of the [**am**H]$^+$[H**B**]$^-$ ion pair product occurs only at 80 °C. It is also reassuring to see that the optimized geometry of [**am**H]$^+$[H**B**]$^-$ is in good accordance with the structure determined from X-ray diffraction measurements.[31,52]

Catalytic Process. Our computational results described up to this point provided us with a firmly established picture of the key steps of the imine hydrogenation reaction. We shall now discuss how these elementary steps are combined in a catalytic process. Experimentally, hydrogenation of **im** readily proceeds at 80 °C and 1 atm of H_2 pressure in the presence of 5 mol% **B**, although somewhat more forcing conditions were employed for other imines.[31,32] To monitor the kinetic and thermodynamic feasibility of the reaction steps involved in the catalytic reduction of **im**,[31] we present solvent phase Gibbs free energy data (calculated for $T = 80$ °C) in this section.

The main steps and the free energy profile of the catalytic cycle suggested by Stephan and co-workers[31] (hereafter referred to as cycle 1) are depicted in Figure 6. It is apparent that the hydrogen splitting represents the rate-limiting step in this cycle with an estimated activation free energy of 16.5 kcal/mol. The **im···B** species is predicted to lie 2.0 kcal/mol above the reactants indicating that this reactive intermediate is present only in rather low concentrations in the solution. The [**im**H]$^+$[H**B**]$^-$ ion pair forms in an exergonic step and gives the weakly bound *r*-**am···B** species in a low-barrier hydride transfer process. In the last step, this complex releases the amine product and the borane catalyst via dissociation. It should be pointed out that as the reaction proceeds and **am** develops in considerable amount, the free **B** catalyst is quenched in the stable amine−borane dative adduct.[53] This implies that the free energy required to dissociate the **am** – **B** dative bond (7.0 kcal/mol) must be included in the barrier of the rate-determining step. Thus, the overall barrier of the H_2 splitting is estimated to be 23.5 kcal/mol.

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(51) The barrier of hydride transfer for the sterically more crowded **im′** (see Scheme 3, eq 2) is predicted to be significantly higher (24.7 kcal/mol), which is in agreement with experiments showing that the hydrogenation reaction stops at the [**im′**H]$^+$[H**B**]$^-$ species.

(52) See the Supporting Information for details.

(53) Sterically more crowded amines might not be able to quench the catalyst effectively.

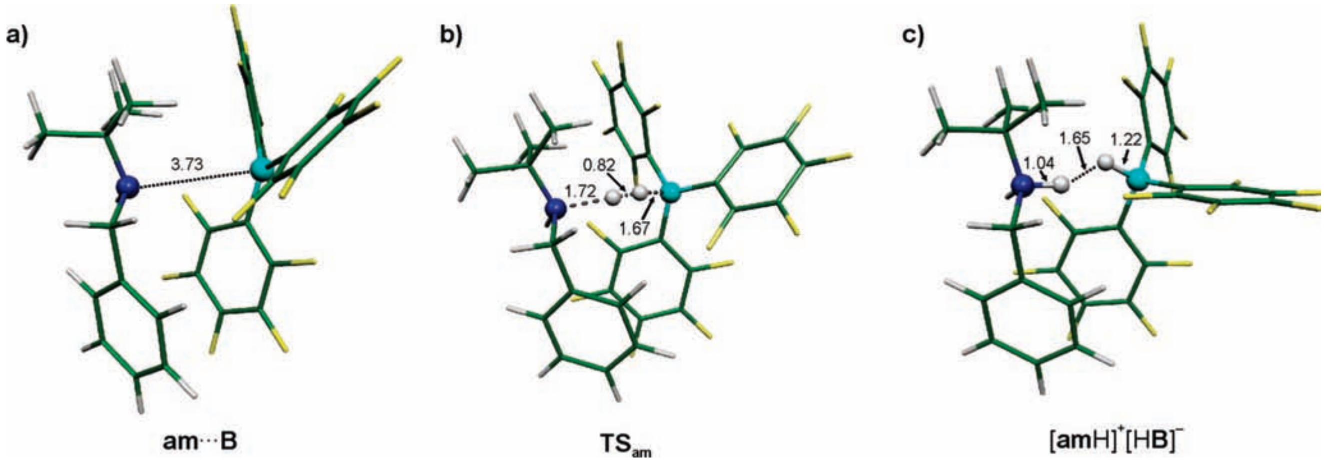


Figure 5. Optimized structures of the stationary points for the amine–borane hydrogen splitting reaction step: (a) amine–borane frustrated complex, (b) transition state of hydrogen splitting, (c) ammonium hydridoborate product ion pair.

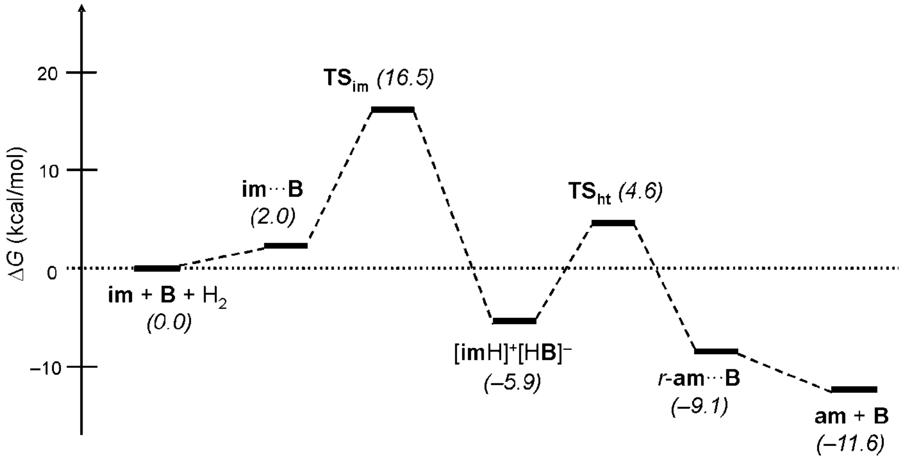


Figure 6. Solvent-phase Gibbs free energy profile at $T = 80$ °C for catalytic cycle 1.

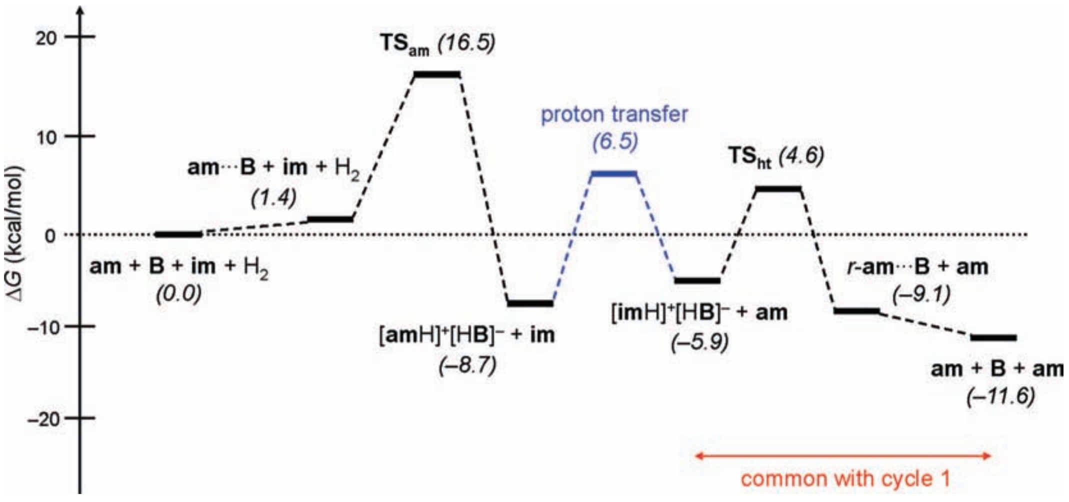
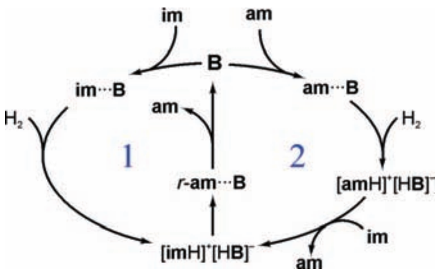


Figure 7. Solvent-phase Gibbs free energy profile at $T = 80$ °C for catalytic cycle 2. The barrier for the proton exchange step (shown in blue) was estimated from a PES scan calculation.[52]

The results for the stoichiometric reaction have pointed out that the amine–borane pair **am** + **B** is able to cleave dihydrogen at elevated temperatures. We envisioned that this process may also play a role in the catalytic hydrogenation of **im**. In Figure 7, we present the calculated free energy profile for a catalytic pathway that can be associated with the amine–borane H_2 cleavage (cycle 2).

The first stable intermediate in this cycle is the ammonium hydridoborate compound [**am**H]$^+$[H**B**]$^-$, which is formed via **TS$_{am}$**. The activation free energy of this step is almost identical

Scheme 4. Interconnected Catalytic Cycles for Imine Hydrogenation



to that predicted for the imine−borane pair pointing to competing reaction channels in H_2 activation. We then considered proton exchange between the ammonium ion and the imine molecule, as experimental observations for a number of related systems[18,54,55] indicate that catalytic imine reduction is usually initiated by imine protonation. Our calculations confirm that the present protonation reaction, producing the free amine and the iminium hydridoborate ion pair $[\mathbf{im}\mathrm{H}]^+[\mathrm{H}\mathbf{B}]^-$, is feasible.[56] The amine−imine proton transfer can take place in a ternary $\mathbf{im}\cdots[\mathbf{am}\mathrm{H}]^+[\mathrm{H}\mathbf{B}]^-$ complex, and the barrier estimated from a PES scan calculation shows that the reaction is kinetically allowed.[52] Although the proton activation of imine in terms of the $[\mathbf{am}\mathrm{H}]^+[\mathrm{H}\mathbf{B}]^- + \mathbf{im} \rightarrow [\mathbf{im}\mathrm{H}]^+[\mathrm{H}\mathbf{B}]^- + \mathbf{am}$ reaction is slightly endergonic, the subsequent hydride transfer (via $\mathbf{TS_{ht}}$) and the dissociation of the *r*-**am···B** species (already described for cycle 1) provide significant stabilization along the reaction pathway and render the overall reduction process thermodynamically feasible as well.

These considerations suggest that cycle 1 proposed by Stephan et al.[31] can be extended by cycle 2 involving the cleavage of hydrogen via the amine−borane pair, which is followed by its transfer to the imine. The two catalytic routes form interconnecting cycles as illustrated in Scheme 4. The catalytic process starts necessarily with cycle 1, which is based on imine-mediated heterolytic H_2 splitting, but as soon as the amine product appears in notable amount in the reaction mixture, cycle 2 represents a competing reaction pathway.[57] This second cycle is in fact an autocatalytic route, the possibility of which has been mentioned by Klankermayer et al., but no details have been reported in their paper.[32] Cycle 2 can also be regarded as a transfer hydrogenation pathway, wherein the $[\mathbf{am}\mathrm{H}]^+[\mathrm{H}\mathbf{B}]^-$ species serves as the hydrogen donor and reduces **im** to **am**. A similar transfer mechanism (without autocatalysis) has also been suggested by Stephan and co-workers[18] to operate in reactions where the substrate to be reduced does not readily participate in hydrogen cleavage requiring the presence of both bulky Lewis base and acid components.[18,31]

Conceptual Issues. We think it is worth pointing out that the amine−borane pair **am** + **B** represents an intermediate case between the classical (sterically unhindered) and frustrated Lewis pairs. While the previously investigated P(*t*-Bu)$_3$ + **B** pair[35] can be regarded as an *inherently frustrated* system in the sense that its energy minimum corresponds to the frustrated complex, the present **am** + **B** pair exhibits a datively bound global minimum lying well below its frustrated complex form (see Figure 8). However, the optimized structure of **am** – **B** suggests a notable degree of strain in this adduct, which is also borne out by its relatively small binding energy of −26.8 kcal/mol. For a comparison, the binding energy of the essentially strain-free $(CH_3)_2NH$ – **B** adduct is predicted to be −39.3 kcal/mol. Nevertheless, the active sites in **am** – **B** are still quenched, and thermal activation is required to reach the reactive frustrated state. This pair thus shows *thermally induced frustration.*

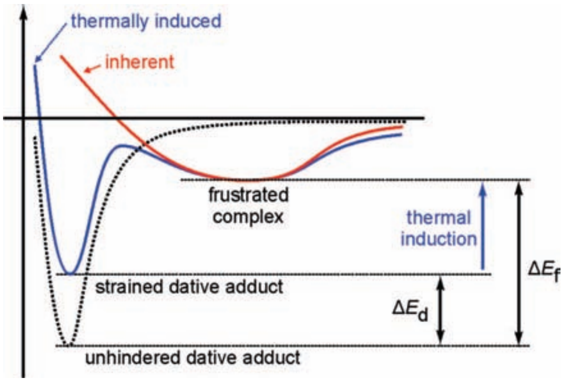


Figure 8. Systems showing inherent and thermally induced frustration. Strain energies related to the dative adduct and to the frustrated complex are denoted by ΔE_d and ΔE_f, respectively. ΔE_f was termed earlier[35] as the frustration energy.

Thermally induced frustration, presumably a consequence of “intermediate” steric bulk, is not uncommon among the recently investigated systems. However, temperatures required to induce FLP-type reactivity may vary significantly depending on the amount of strain involved in the dative adduct (ΔE_d) and in the frustrated complex (ΔE_f, see Figure 8). For example, our calculations indicate that the imine−borane pair **im** + **B** may also form a weak dative bond,[52] but it is almost as strained as the frustrated complex as indicated by the computed binding energy (−12.9 kcal/mol). A notably smaller strain has been calculated by Tamm and co-workers for a frustrated carbene−borane pair.[26] These authors also derived a potential energy curve displaying the two minima associated with the datively and weakly bound structures, which nicely fits into the qualitative picture presented in Figure 8. Nevertheless, experiments still showed no evidence for the presence of the carbene−borane dative adduct in significant amounts in equilibrium,[25] and the H_2 activation was found to occur at room temperature[26] and even at −78 °C.[25] The present amine−borane pair **am** + **B** is closer to the classical extreme possessing an isolable dative adduct and requiring high temperatures to reach the frustrated state.

The concept of thermal induction may also cover situations where the FLP-type reactivity is quenched reversibly but in a different way than simple covalent adduct formation. An example has been provided by Repo, Rieger and co-workers, who studied the diisopropyl amine + **B** system.[23] This pair forms an equimolar mixture of an ammonium hydridoborate salt and a carbon−boron datively bound compound at room temperature, but the reaction can be reversed at 110 °C to regenerate the free Lewis acid and base, which readily cleave H_2 (see Scheme 5).[23]

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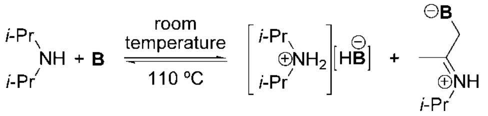
(56) We have also considered the possibility of hydride attack to the unactivated imine and found this process to be thermodynamically unfavored. For instance, hydride transfer from $[\mathrm{H}\mathbf{B}]^-$ to **im** is calculated to be endergonic by 73.8 kcal mol^{-1}.

(57) Due to the flexibility of the noncovalent complexes, *r*-**am···B** is supposed to easily isomerize to **am···B** without dissociation, thereby providing a shortcut from cycle 1 to cycle 2.

Scheme 5. Reversible Reaction of Diisopropyl Amine and **B**



Thermally induced frustration can also be observed for intramolecularly linked FLPs, e.g., in the ethylene-brigded phosphine−borane species $Mes_2P-CH_2CH_2-B(C_6F_5)_2$. This compound has been found experimentally to exist as a four-membered heterocycle (an intramolecular dative adduct), but room temperature is sufficient to induce hydrogen splitting reactivity.[22] The strength of the dative bond in similar ambiphilic molecules has been studied in recent works,[58−62] and in some cases, evidence has been presented for an equilibrium between the bonded and nonbonded forms.[58,59] As pointed out by these contributions, consideration of such equilibria may be expedient in the design of reactions based on cooperativity of Lewis acidic and basic moieties.[63]

4. Summary and Conclusions

In the present work, we investigated the direct hydrogenation of bulky imines catalyzed by the Lewis acid $B(C_6F_5)_3$.[31,32] We carried out accurate quantum chemical calculations and provided detailed energetics for the elementary steps involved in the underlying mechanism. The main conclusions drawn from our computational results can be summarized as follows.

(a) The mechanism of heterolytic H_2 splitting described for the $P(t\text{-}Bu)_3 + B(C_6F_5)_3$ pair,[35] and applied for the $Mes_2P-C_6F_4-B(C_6F_5)_2$ system[39] as well as an N-heterocyclic carbene + $B(C_6F_5)_3$ pair,[26] also accounts for the observed reactivity of frustrated imine−borane and amine−borane pairs.

(b) In the borane-catalyzed imine hydrogenation, the reduced product amine can participate in the hydrogen activation process and, therefore, opens up an autocatalytic pathway.[32] This pathway is suggested to be competitive to the imine−borane hydrogen activation route. Generally speaking, such alternatives may be important in all cases where more than a single frustrated pair is present in the reaction mixture.

(c) The model of FLP-type reactivity can be refined to involve intermediate case Lewis pairs that do not exhibit inherent but only thermally induced frustration. The temperature-dependent equilibria between the dative structure, the frustrated complex, and the dissociated components might serve as an additional possibility of fine-tuning or switching their chemical behavior.

The present findings provide additional insight into FLP-type reactivity and may assist the development of new, advanced transition metal free catalytic systems. Further theoretical studies aimed at characterizing the chemistry of frustrated pairs is underway in our laboratory.

Acknowledgment. This work was supported by the Hungarian Research Foundation (Grants K-60549 and K-68360).

Supporting Information Available: Comparison of calculated and experimental geometry of the ammonium hydridoborate salt, details of the proton exchange step, structure of the imine−borane dative adduct, complete ref 48, total energies, and Cartesian coordinates of all stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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