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Computational Analysis of Amine−Borane Adducts as Potential Hydrogen Storage Materials with Reversible Hydrogen Uptake

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Amine−borane adducts are promising compounds for use in hydrogen storage applications, and the efficient catalytic release of hydrogen from these systems has been recently demonstrated. However, if hydrogen storage is to be of practical use, it is necessary that, once hydrogen has been removed from the material, it can be put back into the system to recharge the appliance. In order to develop such systems, we computationally screened a range of amine−borane adducts for their thermodynamic dehydrogenation properties. Structural trends, which lay the foundation for the possible design of amine−borane systems that exhibit reversible dihydrogen uptake, are established. We found that it is mainly the strengths of the dative bonds in both starting materials and products that govern the thermodynamic parameters of the dehydrogenation reactions. Thus, in general, electron-donating groups on nitrogen and electron-withdrawing groups on boron lead to more favorable systems. It is also possible to design promising systems whose thermodynamic parameters are a consequence of different steric strain in starting materials and products.

Introduction

In the past few years, research into hydrogen storage materials has intensified because of an increased interest in environmentally benign fuels. In particular, amine−borane adducts have been discussed as promising materials due to the ease of catalyzed hydrogen release at ambient temperatures.[1] However, despite the rapid progress in this area, the reports in the literature focus mainly on new, more efficient catalysts[2] and reaction media[3] or the mechanism of dehydrogenation[4] but neglect the issue of reversibility of the hydrogen releasing process, which is vital for a useful storage material.

Ammonia−borane NH_3-BH_3 is the simplest amine−borane adduct and has received most of the attention because the potential active hydrogen content is very high (19.6 wt %).[5] The thermodynamic properties of the thermally induced dehydrogenation reaction were studied by Geanangel and Wendlandt[6] and by Wolf and co-workers,[7] who showed that the reaction was exothermic using differential scanning calorimetry and thermogravimetry measurements. These results formed the basis for the development of

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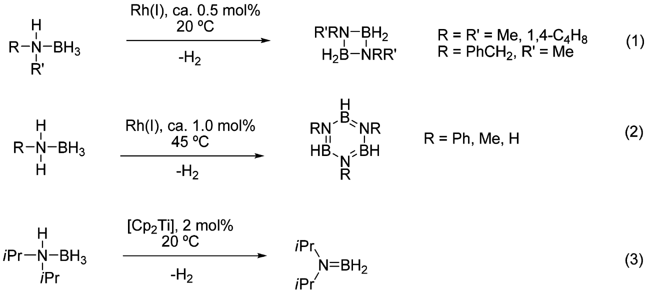
methods to calculate the thermodynamics of this and related systems of simple group 13/group 15 adducts by Dixon and co-workers.[8] They calculated that the release of 1 equiv of hydrogen at 25 °C is almost thermoneutral with an estimated $\Delta H = -5.1$ kcal/mol. Therefore, the dehydrocoupling of NH_3-BH_3 is regarded to be a potentially reversible system. However, very detailed ab initio DFT studies by Ceder and Miranda indicate that, at moderate hydrogen pressures, the ammonia−borane system is unlikely to be reversible.[9]

The only suggestion to date for a practical recyclable hydrogen storage appliance based on amine−borane adducts has been made by the DOE Chemical Hydrogen Storage Center of Excellence.[5a,10] Their concept involves transforming the dehydrogenated products with an acid to form BX_3, which then will be reduced by a hydride. This concept appears feasible, but it makes additional steps necessary. A more elegant approach would be to find a system where hydrogen can be added to the dehydrogenated compound just by pressurization with the gas.

Apart from hydrogen storage, a reversible amine−borane-based hydrogen storage material would be extremely interesting from a fundamental perspective. While hydrogen activation is commonplace using transition metal centers, main group systems, in particular metal-free systems, are extremely rare. One such main group system was a Ge_2−alkyne analog compound reported by Power and co-workers, which was hydrogenated at room temperature within 6 h.[11] It was claimed that some bacteria can activate hydrogen to generate energy with transition metal free enzymes,[12] but more recent investigations revealed that this hydrogenase is an iron-containing metalloenzyme after all.[13] The first well-characterized nonmetallic compound which was capable of reversible hydrogen addition was reported by Stephan and co-workers in 2006.[14] These workers described a phosphonium borate species which loses hydrogen in toluene above 100 °C, and the process is readily reversible at 25 °C under a hydrogen atmosphere.[15] Since then, the same group and Bertrand and co-workers have reported other systems capable of hydrogen activation, although the processes were not reversible.[16]

Scheme 1. Catalytic Dehydrocoupling of Amine−Boranes



In our laboratories, we have investigated the catalytic dehydrogenation of various amine−boranes in dehydrocoupling reactions (Scheme 1).[2a–c,4a–c] When the substituents on nitrogen were small (for example, Me), the reaction gave rings and oligomers as products (Scheme 1, eqs 1 and 2). However, when the sterically hindered $i\mathrm{Pr}_2\mathrm{NH}-\mathrm{BH}_3$ was used, the product was simply the monomeric amino−borane $i\mathrm{Pr}_2\mathrm{N}{=}\mathrm{BH}_2$ (Scheme 1, eq 3).[2b] Together with the promising thermodynamic characteristics of the closely related ammonia−borane NH_3-BH_3 and the aforementioned report of a main group based system with reversible hydrogen release, this reaction inspired us to investigate modifications to the groups on nitrogen and boron of hindered amine−boranes, to allow reversible hydrogen release. Our previous attempts to hydrogenate $i\mathrm{Pr}_2\mathrm{N}{=}\mathrm{BH}_2$ itself and analogous species under a hydrogen atmosphere were unsuccessful,[17] and to provide further insight, we decided to analyze the thermodynamics of a wide variety of amine−borane dehydrogenation reactions computationally for their reversibility (Scheme 2). The aim was to establish structural trends and, more specifically, the type of substituents likely to make reversible dihydrogen uptake a realistic possibility. In this paper, we report the results of these detailed studies.

Computational Details

The calculations were performed with the Macromodel[18] and Gaussian 03[19] programs. When the R groups on the amine−borane were other than H or simple halogen atoms, we initially performed a conformational search using Macromodel. Depending on the size of the molecule, the geometries of the three to five conformers lowest in energy were then reoptimized using the B3LYP[20] level of theory (Gaussian 03) with standard split-valence polarized 6-31G(d,p) basis sets on all elements except iodine.[21] For the latter,

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the Los Alamos ECP[22] was used to represent the inner core electrons, with the valence electrons described with the standard double-ζ LANL2DZ basis set,[19] supplemented with a set of d-polarization functions.[23]

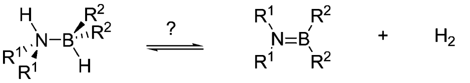
To generate the key thermochemical properties, full geometry optimization was followed by vibrational frequency calculations to confirm that true minima were obtained and to derive corrections for zero-point energy, internal energy, and free energy (at 298.15K) in the rigid-rotor harmonic oscillator limit. We also calculated the C_S transition states (TS) for the rotation around the double bond of the dehydrogenated amine−boranes. Vibrational frequency calculations confirmed that TSs were found. Additional higher-level single-point energy calculations (MP2[24]/aug-cc-pVTZ,[25] SCS-MP2[26]/aug-cc-pVTZ, and G3[27]) were carried out for four selected systems. The G3 energies presented use zero-point energy corrections obtained from B3LYP/6-31G(d,p) calculations (instead of the default for G3, HF/6-31G(d)). The ZPE corrections for the MP2/aug-cc-pVTZ and SCS-MP2/aug-cc-pVTZ calculations were calculated at the B3LYP/6-31G(d,p) level. Dipole moments and natural bond orbital (NBO) charges[28] were obtained from the B3LYP calculations. The solvent effect of tetrahydrofuran (THF) and toluene has been taken into account for selected systems by means of the polarized continuum model (PCM)[29] on the B3LYP/6-31G(d,p) optimized structures without further geometrical optimization. Calculated solvation free energies were combined with gas-phase reaction free energies to obtain dehydrogenation free energies in solution.

All energies presented in this paper were calculated at the B3LYP/6-31G(d,p) level until stated otherwise and are given in kilocalories per mole. For comparison, the potential energy differences (zero-point energy corrected) ΔE (at 0 K), enthalpies ΔH (at 298.15 K), and free energies ΔG (at 298.15 K) are given.

Results and Discussion

All of the reactions were studied at the B3LYP level of theory using 6-31G(d,p) basis sets, because this is a good compromise between accuracy and cost. Computational efficiency was very important, because our aim was to screen a relatively large range of amine−borane adducts. It has been shown that B3LYP underestimates the energy of the central N → B dative bonds in BX_3-NR_3 compounds.[30] Although our focus is on the energetics of the somewhat different dihydrogen elimination process (Scheme 2), we accordingly calibrated the accuracy of our B3LYP calculations for four examples using G3, MP2/aug-cc-pVTZ, and SCS-MP2/aug-cc-pVTZ single-point computations (for potential energies, see Table 1). All levels of theory give very similar results, with the B3LYP and the more accurate G3 calculations in very good agreement. Also, our computed enthalpy values for the dehydrogenation of H_3N-BH_3 (B3LYP/6-31G(d,p) and G3, −7.0 kcal/mol; MP2/aug-cc-pVTZ, −5.2 kcal/mol; and SCS-MP2, −6.5 kcal/mol) agree well with high accuracy values in the literature (CCSD(T), −5.1 kcal/mol).[8a] We therefore believe that B3LYP should provide useful accuracy for all species discussed below.

Scheme 2. Potentially Reversible Dehydrogenation Reaction



(4)

Table 1. Reaction Potential Energies (kcal/mol) at 0 K for Selected Dehydrogenation Processes (see Scheme 2) from Single-Point Energy Calculations on B3LYP/6-31G(d,p) Optimized Geometries at B3LYP/6-31G(d,p), G3, MP2/aug-cc-pVTZ, and SCS-MP2/aug-cc-pVTZ Levels of Theory

method/basis set	$R_1 = R_2 = H$	$R_1 = Me, R_2 = H$	$R_1 = H, R_2 = F$	$R_1 = H, R_2 = CF_3$
B3LYP/6−31G(d, p)	−8.7	−4.9	−12.3	4.3
G3	−8.0	−6.2	−11.3	6.7
MP2/aug-cc-pVTZ[a]	−6.9	−0.4	−10.1	9.1
SCS-MP2[a]	−8.2	−1.8	−11.9	7.5

[a] For these potential energies, ZPEs calculated at the B3LYP/6-31G(d,p) level were used.

For the amine−borane dehydrogenation reactions of Scheme 2, a loss of gaseous dihydrogen means that the entropy of reaction will be favorable at all temperatures.[31] Our calculations find that the entropic contribution to the free energy of reaction, $-T\Delta S$, is on the order of −8 kcal/mol at room temperature due to the formation of free dihydrogen. This means that, from the point of view of hydrogen storage, the ideal system is one that has a significantly positive, but not too large, enthalpy of reaction, ΔH. In such a case, the Gibbs free energy change, $\Delta_r G$ is positive at room temperature (leading to a favorable negative $\Delta_r G$ for the reverse hydrogenation reaction), but upon slight heating, $\Delta_r G$ will be negative, leading to a loss of hydrogen.

Our initial calculations addressed the parent NH_3-BH_3 system, together with derivatives $R_2^1NH-BHR_2^2$ with electron-donating substituents on the nitrogen of different steric hindrances (H, Me, *i*Pr) and electron-withdrawing groups on boron, as well as the dimethylborane derivatives (Table 2).

In our calculations, the differences between the potential energies, ΔE (0 K), the enthalpies, ΔH (298 K), and the free energies, ΔG (298 K), are highly consistent, so we focus the discussion on the key ΔH (298 K) data. Replacing the hydrogen on nitrogen with the more electron-donating methyl

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Table 2. Relative Energies in kcal/mol at 0 K (ΔE) and 298.15 K (ΔH and ΔG) for the Dehydrogenation $R^1{}_2NH-BHR^2{}_2 \rightarrow H_2 + R^1{}_2N{=}BR^2{}_2$[a]

on N\on B		H	F	Cl	Br	CF_3	C_6F_5	OTf	Me
H	ΔE	−8.7	−12.3	−6.1	−4.8	4.3	−5.2	0.3	−15.7
	ΔH	−7.0	−10.8	−4.5	−3.2	6.0	−3.4	2.1	−13.9
	ΔG	−15.9	−18.4	−12.4	−11.1	−2.5	−11.9	−7.1	−23.0
Me	ΔE	−4.9	−7.5	−2.3	−1.5	8.5	−2.5	5.8	13.0
	ΔH	−3.5	−6.0	−0.8	0.5	10.6	−0.5	7.6	11.5
	ΔG	−11.5	−14.1	−9.1	−8.8	0.8	−9.7	−1.9	−20.0
*i*Pr	ΔE	−9.4	−11.4	−4.6	−2.5	8.6	−4.1	2.9	−13.9
	ΔH	−7.5	−9.5	−2.7	−0.7	10.5	−1.9	5.1	−11.9
	ΔG	−16.7	−18.6	−11.9	−9.7	1.4	−12.2	−4.7	−21.4

[a] Correlation of thermodynamical data with substituents on B and N.

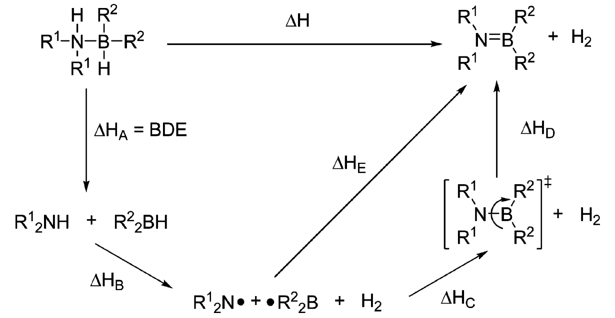
Table 3. Other Substituent Effects−Relative Energies in kcal/mol at 0 K (ΔE) and 298.15 K (ΔH and ΔG) for the Dehydrogenation $R_2{}^1NH-BHR_2{}^2 \rightarrow H_2 + R_2{}^1N{=}BR_2{}^2$

	$R_1 = F$, $R_2 = H$	$R_1 = Cl$, $R_2 = H$	$R_1 = Br$, $R_2 = H$	$R_1 = CF_3$, $R_2 = H$
ΔE	−5.4	−12.4	−10.0	−21.5
ΔH	−3.6	−10.7	−8.3	−19.5
ΔG	−11.9	−18.8	−16.4	−29.5

group leads to a general increase of ΔH by roughly 4 kcal/mol. Upon changing the methyl group into the even more electron-donating, but more bulky, *i*Pr group, ΔH slightly decreases in most cases, whereas in others, it is barely changed. We also observed a trend for the halogen substituents on boron: In the series R^2 = F, Cl, and Br, the overall dehydrogenation enthalpy becomes increasingly more positive. With CF_3 as a substituent on boron, the dehydrogenation enthalpy is even more positive, but with C_6F_5, the enthalpy value is between those for Cl and Br in all cases. We then examined how reversing the electronic properties of the substituents on boron and nitrogen would affect the dehydrogenation reaction (Table 3). In general, the enthalpies were more negative than those for the corresponding amine−boranes with the electron-donating groups on nitrogen and with electron-withdrawing groups on boron, except for the case of $F_2NH-BH_3/F_2N{=}BH_2$, which will be discussed in more detail below.

In our attempt to identify suitable molecules for hydrogen storage, it is desirable to elucidate which factors are likely to lead to a suitable thermodynamic profile. No useful correlation was found between the reaction enthalpy and parameters such as the NBO charges on H, N, and B of both species; changes in the NBO charges upon dehydrogenation; the N−H, N−B, B−H, and N=B bond lengths and the changes in bond lengths; the dipole moments and changes in the dipole moments; or the energies of the π and π^* orbitals in the dehydrogenated molecules.[32] We then decided to scrutinize the process further by splitting the factors that influence the overall enthalpy of the reaction into contributions originating from the different types of bonds. Thus, for the overall dehydrogenation reaction (ΔH), we conceived a thermodynamic cycle (Scheme 3 and Table 4), where the amine−borane dissociates into the amine and the borane (bond dissociation enthalpy, BDE = ΔH_A). Then, the dihydrogen molecule and the radical fragments $R_2{}^1N\bullet$ and $R_2{}^2B\bullet$ are formed (ΔH_B), and after that, the σ bond between these fragments is formed (ΔH_C).

Scheme 3. Thermodynamic Cycle for the Dehydrogenation Reactions



The enthalpy of the π bond is then described by ΔH_D. All enthalpies were calculated from optimized fragments/molecules and transition states. While ΔH, ΔH_A, and ΔH_B could be computed directly from the optimized amine−boranes, amines, boranes, and dehydrogenated amine−boranes, the σ-bond enthalpy, ΔH_C, was computed indirectly by calculating the overall σ- and π-bond enthalpy, ΔH_E (from the optimized radical fragments $R_2{}^1N\bullet$ and $R^2{}_2B\bullet$ and the dehydrogenated amine-borane), and then simply subtracting the π-bond enthalpy (ΔH_D). The evaluation of the formation enthalpy of the π bond, ΔH_D, presents a problem that has been addressed in different ways in the literature, mainly for olefins[33] and main group olefin analogs.[34] One approach is to calculate this value from the enthalpies of a disproportionation reaction of the product of hydrogen radical addition to the double bond. Another approach is to evaluate the rotation barrier around the double bond, which has the advantage that there is no concern on which end of the double bond a H• radical adds (N or B), which would lead to very different radical intermediates. The latter conceptual method has been employed by Dixon and Grant for simple hydrogen-substituted group 13 to group 15 adducts.[35]

Using this method, the $R^1-N-B-R^2$ dihedral angle was rotated by 90°, which disrupts the interaction of the lone pair of nitrogen with the empty orbital on boron. From this geometry, the TS was optimized, and the adiabatic rotation barriers were calculated as the difference between the TS

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(32) For tables and figures of these quantities, see the Supporting Information.

(33) (a) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976; pp 63−65. (b) Carter, E. A.; Goddard, W. A., III *J. Am. Chem. Soc.* **1988**, *110*, 4077. (c) Wang, S. Y.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 7282. (d) Nicolaides, A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 6750.

(34) Dobbs, K. D.; Hehre, W. J. *Organometallics* **1986**, *5*, 2057.

(35) Grant, D. J.; Dixon, D. A. *J. Phys. Chem. A* **2006**, *110*, 12955.

Table 4. Calculated Enthalpies for the Thermodynamic Cycle Depicted in Scheme 3 for Different Substituents on Boron and Nitrogen[a]

entry	R on N	R on B	ΔH	ΔH_A	ΔH_B	ΔH_C	ΔH_D	ΔH_E
1	H	CF_3	6.0	47.9	105.9	−115.6	−32.2	−147.8
2	H	H	−7.0	28.4	103.6	−108.8	−30.2	−139.0
3	H	Br	−3.2	26.3	101.0	−109.3	−21.2	−130.5
4	H	Cl	−4.5	24.5	102.6	−110.9	−20.8	−131.7
5	H	F	−10.8	15.1	107.7	−117.1	−16.5	−133.6
6	Cl	H	−10.7	16.9	76.4	−84.3	−19.7	−104.0
7	Br	H	−8.3	20.0	79.4	−91.1	−16.6	−107.7
8	F	H	−3.6	21.3	68.9	−75.5	−18.3	−93.8
9	CF_3	H	−19.5	7.1	107.5	−112.9	−21.2	−134.1
10	F	CF_3	9.0	29.7	71.2	−74.1	−17.8	−92.0
11	Me	H	−3.5	32.1	90.0	−94.4	−31.2	−125.6
12	Me	F	−6.0	19.9	94.1	−102.0	−17.9	−119.9
13	Me	Cl	−0.8	27.3	89.0	−96.4	−20.6	−117.1
14	Me	Br	0.5	31.4	87.3	−95.8	−22.4	−118.2
15	Me	CF_3	10.6	50.7	92.3	−100.9	−31.4	−132.4
16	H	Me	−13.9	16.3	104.2	−107.5	−24.6	−132.1
17	H	OTf	2.1	30.9	106.8	−116.4	−19.2	−135.6
18	*i*Pr	Br	−0.7	29.8	85.3	−96.0	−19.8	−115.8
19	*i*Pr	H	−7.5	31.0	88.0	−91.9	−34.7	−126.6
20	*i*Pr	F	−9.5	19.9	92.1	−102.2	−19.2	−121.4
21	*i*Pr	Cl	−2.7	24.4	87.0	−95.4	−18.7	−114.1
22	*i*Pr	CF_3	10.5	49.1	90.3	−102.2	−26.8	−129.0
23	*i*Pr	Me	−11.9	13.6	86.2	−88.4	−23.3	−111.7

[a] All enthalpies are at 298.15 K in kcal/mol.

and the optimized ground-state geometry.[36] The amino−boranes are roughly planar, and one might thereby expect the torsional transition state to have roughly C_{2v} symmetry, with planar B and N atoms. In practice, however, the transition states have lower C_S symmetry, due to pyramidalization at N, as described by Allen and Fink.[37] This means that the N → B σ bond at the transition state is somewhat different than that at the minimum of the amino−borane, which introduces some error into the decomposition into π- and σ-bond energies.

We noted that the bond dissociation enthalpies (ΔH_A) of the starting materials are spread over a much broader range than the relative stabilities of the products ($-\Delta H_A + \Delta H$; for a figure, see the Supporting Information), which led us to believe that, generally speaking, the bond dissociation enthalpy, ΔH_A, and thus the strength of the dative σ bond in the starting material was the dominant factor determining the thermodynamic profile of the reaction. However, when we plotted ΔH_A against the overall dehydrogenation enthalpy, ΔH, we found that, even though there was indeed a trend, the correlation was relatively poor ($R^2 = 0.80$). Likewise, when we examined whether there was a trend arising from the newly formed π bonds (ΔH_D), we found only a minimal correlation ($R^2 = 0.06$). However, when we combined both enthalpies to describe the change in the dative bond from the starting materials to the products ($\Delta H_A + \Delta H_D$), we found a strong correlation ($R^2 = 0.91$) with the overall dehydrogenation reaction (ΔH; Figure 1). If we observe a roughly linear correlation between $\Delta H_A + \Delta H_D$ versus ΔH, then, according to the thermodynamic cycle described above, the formation of the σ bond in the product combined with hydrogen formation ($\Delta H_B + \Delta H_C$) must have a constant enthalpy (for a discussion, see below). Therefore, it must be the difference in the dative bond strengths in A−B (dative σ bond) and A═B (dative π-bond) which governs the overall enthalpy of the reaction. This means that, in order to achieve a more positive overall enthalpy (ΔH), the bond dissociation enthalpy (ΔH_A) should be large, combined with a small π-bond enthalpy (ΔH_D). Such a systematic relationship was unexpected, particularly because we were comparing such a wide range of compounds with all possible combinations of electron-donating groups and electron-withdrawing groups on nitrogen and boron. Furthermore, the steric demand varied over a wide range from almost unhindered (H) to relatively bulky (*i*Pr).[38]

We set out to understand the factors influencing the magnitude of the two enthalpies ΔH_A and ΔH_D, as this understanding might guide the search for amine−borane systems suitable for reversible hydrogen uptake. Analyzing the relationship between ΔH_A and the structure of the corresponding amine−borane, we found as expected that the bond enthalpy (ΔH_A) increased with increasing σ-withdrawing character and decreasing π-donating character of the R^2 substituent on boron. Thus, ΔH_A becomes increasingly positive for the series R^2 = F, Cl, Br, H, and CF_3 with a given Lewis base, reflecting the Lewis acidity of the borane moiety.[39] Likewise, it will be increasingly positive with the increased electron-donating characteristics of R^1 (H < Me). However, with the bulkier *i*Pr group, the bond dissociation enthalpy is not as positive as would be expected on the basis of electronic arguments only. In the case of a small R^2 (H or F), it is approximately the same as for R^1 = Me, whereas

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(36) For the calculation of the energy of the species involved, these authors use a process where the atomization energies are calculated and implemented together with known heats of formation of the relevant atoms to obtain the heats of formation at 0 K.

(37) Allen, T. L.; Fink, W. H. *Inorg. Chem.* **1993**, *32*, 4230.

(38) C_6F_5-containing compounds were not calculated due to their expense.

(39) For another computational study on bond dissociation enthalpies including some amine−boranes, see: (a) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 8741. The actual cause for the stronger Lewis acidity of BCl_3 versus BF_3 is under debate. While a commonly used explanation is that the Lewis acidity is a trade off between σ-withdrawing and π-donating effects, this has been contested by Frenking: (b) Bessac, F; Frenking, G. *Inorg. Chem.* **2003**, *42*, 7990.

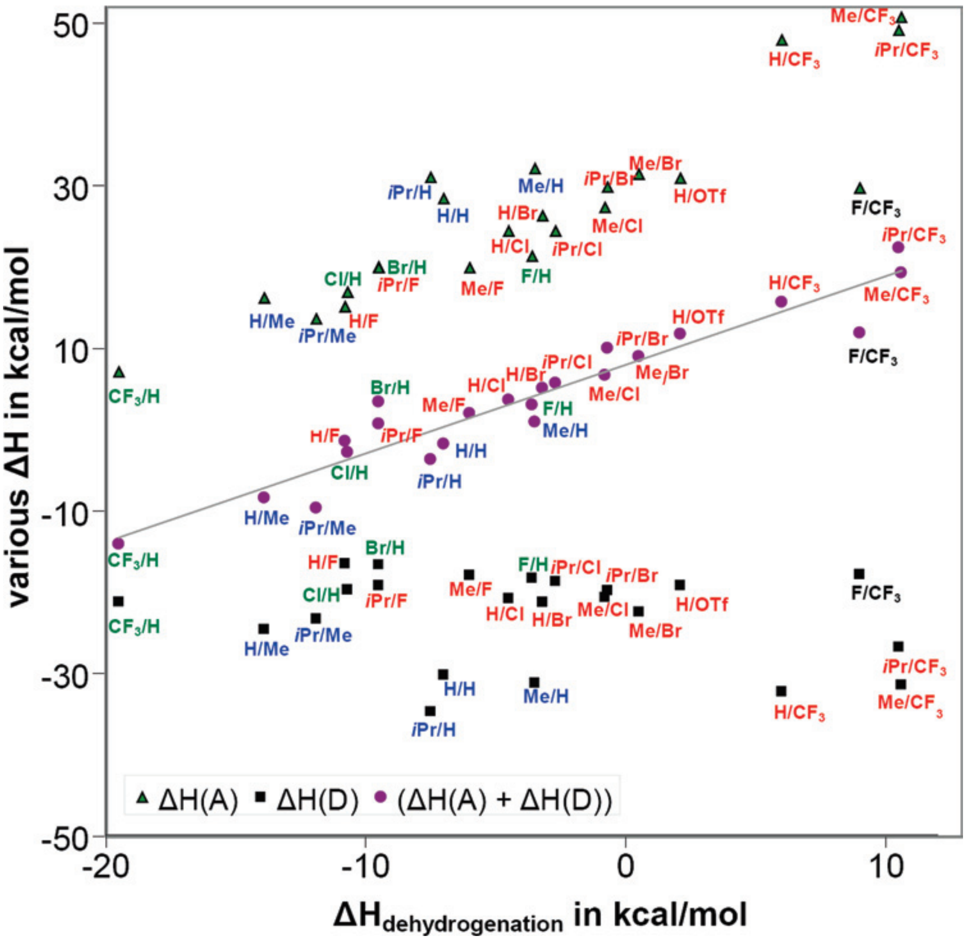


Figure 1. Correlation between ΔH_A, ΔH_D, and $\Delta H_A + \Delta H_D$ versus ΔH for the dehydrogenation.

for a larger R^2 (Cl, Br, or CF_3), it is less negative. We attribute this latter fact to steric factors, where the bulky *i*Pr groups on nitrogen may weaken the dative σ bond. The influence of the substituents on boron and nitrogen on the enthalpy of the π bond, ΔH_D, is less obvious. For a given R^1 (H or Me), we found that the strength of the dative π bond showed inverse dependencies on the R^2 substituents versus those found for ΔH_A; that is, ΔH_D became increasingly negative in the series F, Cl, Br, H, and CF_3. However, for $R_1 = i$Pr, we observed a disruption of this sequence (Cl, F, Br, CF_3, and H), presumably again for overriding steric factors. The strength of the dative σ bond in the starting material and the dative π bond in the product are thus influenced by R^2 in qualitatively the same direction. However, the influence of R^2 on the dative π bond is generally weaker than on the dative σ bond (as can be seen in the more narrow range of values for ΔH_D versus ΔH). Additionally, the π-bond enthalpy has a smaller magnitude than the enthalpy of the dative σ bond in almost all cases. The exceptions to this trend tend to be comprised of an amine moiety of moderate Lewis basicity and a borane moiety of moderate Lewis acidity. Despite the fact that, for these compounds, the π-bond enthalpy, ΔH_D, is generally considerably lower than to be expected from the general trend, this is then compensated for by ΔH_A, so that taken together ($\Delta H_A + \Delta H_D$) they fit into the overall trend. With this in mind, we concluded that, in order to achieve a more positive overall enthalpy, ΔH, one should consider electron-withdrawing groups on boron.

For R^1 = halogens and other electron-withdrawing groups and R^2 = H or Me, there was no clear trend for ΔH_A or ΔH_D (Figure 1). There may be a delicate balance between σ-withdrawing and π-donating effects and also different inversion barriers on nitrogen for these species.

Comparing a compound with electron-donating groups on nitrogen and electron-withdrawing groups on boron ($H_3N{-}BHF_2$) with compounds where the electronics have been switched ($F_2NH{-}BH_3$/$F_2N{=}BH_2$) gave us further useful understanding of these compounds. The couple $F_2NH{-}BH_3$/$F_2N{=}BH_2$ gives a relatively promising enthalpy of reaction of only −3.6 kcal/mol (Table 3), less negative than that found for $H_3N{-}BHF_2$ (−10.8 kcal/mol; Table 2). The analysis of ΔH_A and ΔH_D for these compounds showed that, while $F_2NH{-}BH_3$ displays a more positive ΔH_A (21.3 kcal/mol) than $H_3N{-}BHF_2$ (15.1 kcal/mol), the π-bond formation enthalpy (ΔH_D) for the corresponding dehydrogenated amine−borane is more negative (−18.3 kcal/mol for $F_2N{=}BH_2$ and −16.5 kcal/mol for $H_2N{=}BF_2$). Thus, the stronger Lewis acidity of the BH_3 moiety as opposed to the BHF_2 moiety seemed to be of greater consequence for the respective dehydrogenation enthalpies, ΔH. However, the strength of the dative π bond is also highly dependent on

Table 5. Further Substituent Effects—Relative Energies in kcal/mol at 0 K (ΔE) and 298.15 K (ΔH and ΔG) for the Dehydrogenation $R_2{}^1NH-BHR_2{}^2 \rightarrow H_2 + R_2{}^1N{=}BR_2{}^2$

	$R_1 = F$, $R_2 = CF_3$	$R_1 = TMS$, $R_2 = H$	$R_1 = H$, $R_2 = CF(CF_3)_2$
ΔE	7.4	−10.3	0.4
ΔH	9.0	−9.2	1.8
ΔG	0.6	−16.3	−6.5

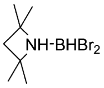
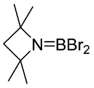
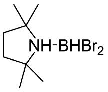
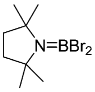
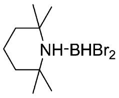
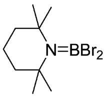
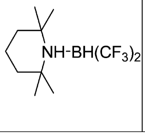
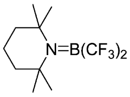
the substituents on nitrogen. Electron-withdrawing groups on nitrogen make this part of the molecule a poorer π donor, thus accounting for the lower enthalpy of the dative π-bond strength in $F_2N{=}BH_2$ with respect to $H_2N{=}BH_2$ ($\Delta H_D = -30.2$ kcal/mol). However, it has been proposed that this effect could be related to the inversion barrier at nitrogen.[35,40] In NX_3, electronegative groups on nitrogen raise the inversion barrier as compared to NH_3,[41] which will lead to a lower rotation barrier.

A related compound with even more favorable thermodynamic parameters is obtained by replacing the hydrogen atoms on boron with CF_3 groups, $F_2NH-BH(CF_3)_2$ ($\Delta H = 9.0$ kcal/mol) (Table 5). As shown earlier (Table 2), replacing hydrogen on boron by CF_3 groups leads to a more endothermic dehydrogenation reaction in all cases. The π-bond formation enthalpy, ΔH_D, is very similar for the two compounds (−18.3 kcal/mol for $F_2N{=}BH_2$ and −17.8 kcal/mol for $F_2N{=}B(CF_3)_2$), presumably primarily governed by the substituents on the nitrogen. However, the bond dissociation enthalpies (ΔH_A) vary considerably (21.3 kcal/mol for F_2NH-BH_3 and 29.7 kcal/mol for $F_2NH-BH(CF_3)_2$), which is consistent with the fact that CF_3 is strongly σ-electron-withdrawing and should render $BH(CF_3)_2$ a stronger Lewis acid than BH_3. This is also reflected in the different dipole moments for these amine−borane adducts (3.51 debye for F_2NH-BH_3 and 3.84 debye for $F_2NH-BH(CF_3)_2$) and the difference in the combined NBO charges between the amine moiety and the borane moiety (0.4 for F_2NH-BH_3 and 0.7 for $F_2NH-BH(CF_3)_2$).

We then tested other groups on nitrogen and boron to explore more substituents (Table 5). Compared to *i*Pr on nitrogen, the TMS groups should be even more electron-donating. However, we found an increasingly exothermic reaction enthalpy, perhaps due to steric congestion in the starting amine borane. The $CF(CF_3)_2$ group on boron was also tested, because it may be synthetically easier to introduce than the CF_3 substituent (Table 2). However, it gave a somewhat less endothermic reaction enthalpy than the CF_3 group, possibly because the bulky $CF(CF_3)_2$ groups lead to a relative destabilization of the sterically more congested starting material, similar to the cases of the substrates with *i*Pr groups on nitrogen, as discussed earlier.

From the previous discussion of the thermodynamic cycle, we concluded that the sum of ΔH_B and ΔH_C has to be approximately a constant. When we examined these values more closely, we found another almost linear correlation ($R^2 = 0.95$) between ΔH_B and ΔH_C, (Figure 1, Supporting Information). This correlation means that the higher the enthalpy for hydrogen abstraction for a given couple of amine and borane (ΔH_B), the more negative the σ-bond enthalpy (ΔH_C).

Table 6. Influence of Cyclic Substituents on Nitrogen—Relative Energies in kcal/mol at 0 K (ΔE) and 298.15 K (ΔH and ΔG) for the Dehydrogenation $R_2{}^1NH-BHR_2{}^2 \rightarrow H_2 + R_2{}^1N{=}BR_2{}^2$

Entry	**A-B**	**A=B**	α / ° a)	ΔE	ΔH	ΔG
1	 NH-BHBr2	 N=BBr2	0	-3.0	-1.1	-10.1
2	 NH-BHBr2	 N=BBr2	13	-4.0	-2.2	-10.8
3	 NH-BHBr2	 N=BBr2	5	1.6	3.5	-5.5
4	 NH-BH(CF3)2	 N=B(CF3)2	22	17.8	19.7	11.1

a) Dihedral angle C-N-B-R of the double bond.

We also find that, for R^1 = H or Me and R^2 = halogens or other electron-withdrawing groups, a more electronegative substituent on the nitrogen leads to a more endothermic H• radical abstraction, combined with a more exothermic σ-bond formation. For the series of R^1 = halogens or other electron-withdrawing groups and R^2 = H or Me, the situation is reversed, and a more electronegative element on nitrogen leads to a less endothermic H• radical abstraction and a less exothermic σ-bond formation. However, despite following the almost linear correlation (shown in Figure 1, Supporting Information), $R^1 = CF_3/R^2 = H$ has a surprisingly large positive ΔH_B and a correspondingly large negative ΔH_C. The stability of nitrogen-centered radicals dependent on the substituents on nitrogen has been studied by Li and Cheng.[42] These authors investigated the dependence of the N−H bond dissociation enthalpies for $X-C_6H_4-NH-Y$ for various substituents X and Y and found that an electron-withdrawing group for Y (Ac) or for X (Ac, CN, CF_3, CHO, or NO_2) increases this bond dissociation enthalpy. Qualitatively, we found the same trend for N-substituted amines (ΔH_B).

We also tested the influence of cyclic substituents on the nitrogen (Table 6). The amine−boranes with the four- and five-membered rings give approximately the same values for the thermodynamic parameters as the corresponding noncyclic *N*-methyl derivatives. The six-membered ring, however, gave a significantly more endothermic reaction. Since all of these cyclic amine−boranes should be electronically very similar, we suspected that the key to understanding this marked difference in the thermodynamic parameters of their dehydrogenation behavior might be found by analyzing structural differences. In the case of the five-membered ring,

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(40) This effect is less visible with the B3LYP calculations. Therefore, we repeated the calculations on the MP2/6-31G(d,p) level of theory for all compounds of the type X_2NH-BH_3 and H_3N-BHX_2 with X = H, F, Cl, and Br and the corresponding dehydrogenated products. The results are given in the Supporting Information.

(41) Clotet, A.; Rubio, J.; Illas, F. *THEOCHEM* **1988**, *164*, 351.

(42) Li, Z.; Cheng, J.-P. *J. Org. Chem.* **2003**, *68*, 7350.

Table 7. Effect of the Solvent on the Relative Free Energies in kcal/mol at 298.15 K for the Dehydrogenation $R_2^1NH{-}BHR_2^2 \rightarrow H_2 + R_2^1N{=}BR_2^2$

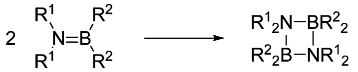
	$R_1 = R_2 = H$	$R_1 = Me, R_2 = Br$	$R_1 = H, R_2 = CF_3$	$R_1 = Me, R_2 = CF_3$	$R_1 = H, R_2 = OTf$	$R_1 = iPr, R_2 = CF_3$
ΔG (gas phase)	−15.9	−8.8	−2.5	0.8	−7.1	1.4
ΔG (THF)[a]	−5.5	0.0	5.0	5.1	−1.8	6.1
ΔG (toluene)[a]	−9.1	−3.3	2.5	3.3	−3.9	4.4

[a] For the ZPE correction, gas phase values were used.

we found a substantial distortion from the expected 180° dihedral angle of the double bond of 13° (Table 6, entry 2), presumably due to steric effects. For the six-membered ring analog, this distortion is still present, but to a lesser extent (see Figure 2). When the bromine atoms on the boron are replaced by the bulkier CF_3 groups in the case of the six-membered ring, the distortion is 22° (Table 6, entry 4). Calculations for the model system $H_2N{=}BF_2$ show that this magnitude of distortion requires only a fairly modest energy, with 1.3 kcal/mol needed to change the dihedral angle by 20° from the preferred 180°. This is in agreement with the fact that the π-bond formation enthalpy for this type of compound is remarkably low. The distortion energies of the double-bonded species are therefore not sufficient to explain why some of the calculated ΔH and ΔG values in Table 5 are larger than expected.

We then scrutinized these structures more closely and found that this trend could be explained by differences in the degree of strain of the amine rings between the starting and final products. In all cases, the angles in the ring deviated from the ideal tetrahedral angle of 109.5°. For the four- and five-membered ring compounds, the average differences were of 19.7° and 5.8°, respectively, for the hydrogenated amine and 20.5° and 5.7° for the dehydrogenated amine−borane. Therefore, the destabilization arising through this distortion is roughly the same for the starting material and the product. However, in the case of the six-membered ring, the average discrepancy from the ideal tetrahedral angle is 2.2° for the starting material, but 4.7° for the product, thus potentially accounting for the relative destabilization of the latter (Table 6, entry 4).

Scheme 4. Potential Dimerization of Dehydrogenated Amine−Borane Adducts



(5)

All of the energies discussed so far were calculated in the gas phase. However, we expected that the solvent would influence the equilibrium constant considerably because, in all cases, the dipole moment decreases substantially upon dehydrogenation. We therefore performed PCM calculations for selected amine−boranes in THF and toluene (Table 7). The effect of a polar solvent such as THF is substantial; the dehydrogenation reaction free energies were on average 7 kcal/mol higher than the gas-phase free energies. The effect is less significant in toluene, being on average only 4 kcal/mol higher. In general, the solvent influence is stronger for less-polar amine−boranes, but the overall structural trends described earlier are robust.

From these studies, the CF_3 group and the OTf group as substituents on boron emerged as the most promising candidates. When solvent effects are taken into account as well, the most promising compounds were $H_3N{-}BH(CF_3)_2$, $Me_2NH{-}BH(CF_3)_2$, $H_3N{-}BH(OTf)_2$, and $Me_2NH{-}BH(OTf)_2$.[43] However, we suspected that sterically unhindered compounds with only H on nitrogen might easily dimerize, as was observed for $H_2N{=}BH_2$, thus making the overall reaction considerably more exothermic and therefore irreversible (Scheme 4, eq 5).

We therefore probed the thermochemistry of the dimerization process (Table 8) and found that it is indeed necessary to include at least a methyl group on nitrogen to prevent

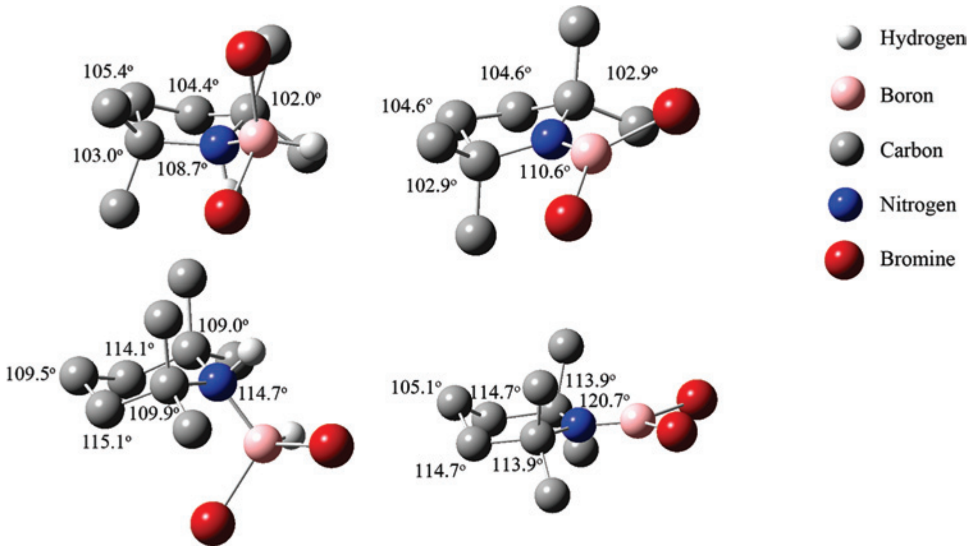


Figure 2. Internal angles of the hydrogenated and dehydrogenated five- and six-membered cyclic amine−boranes. Hydrogen atoms were removed for clarity, except for the ones bonded to boron and nitrogen.

Table 8. Potential Energies, Enthalpies and Free Energies for the Dimerization Reactions at 0 K (ΔE) and 298.15 K (ΔH and ΔG) in kcal/mol in Scheme 4

	$R_1 = H$, $R_2 = H$	$R_1 = H$, $R_2 = CF_3$	$R_1 = Me$, $R_2 = CF_3$	$R_1 = H$, $R_2 = OTf$
ΔE	−11.9	−26.2	−13.4	−12.3
ΔH	−13.6[a]	−27.0	−15.0	−12.8
ΔG	−0.8	−11.7	5.0	2.5
ΔG (THF)	−4.7	−12.6	1.3	5.8
ΔG (toluene)	−4.0	−12.7	1.5	6.3

[a] This enthalpy compares well with a high accuracy calculation by Dixon ($\Delta H = -16.4$ kcal/mol at 298 K).

this process from being thermodynamically favorable.[44] When we then took solvent effects into account as well, we found that there was only a small difference between THF and toluene. In most cases, the dimerization is predicted to be more exothermic than in the gas phase. However, the solvent influence appeared to be very substrate-dependent, and it is not possible to generalize its effect.

Conclusions

Computational screening of the thermochemistry for a range of amine−borane adducts suggests that a reversible removal of hydrogen may be possible for some of these compounds. For this type of reaction, the change in entropy will always be positive; therefore, amine−borane adducts which show a slightly positive free energy for the dehydrogenation at room temperature were considered the most promising compounds for potentially reversible systems. We found that the enthalpy for the reaction depends on the relative strengths of the dative bonds in the starting material and the product. In most cases, the dative π-bond is weaker than the dative σ bond in the starting material, and the influence of the substituents is less pronounced. In order to obtain more-positive overall reaction enthalpies, a strong dative σ bond in the starting material should be combined with a weaker π bond in the product. Thus, in general, we found that the dehydrogenation reactions tend to be more endothermic if the substituents on nitrogen are electron-donating and the substituents on the boron are electron-withdrawing. We also found a strong correlation between the homolytic N−H and B−H cleavage enthalpies of the amine and the borane fragments versus the covalent σ-bond enthalpy in the dehydrogenated amine−borane. Added together, these two enthalpies are constant. We also showed that, if the nitrogen is part of a six-membered ring, slightly increased ring strain of the dehydrogenated amine−borane leads to a relative destabilization of the product and thereby to a more endothermic reaction than is observed for smaller rings. Solvent effects are expected to increase the gas-phase enthalpies for both THF and toluene, but less so for the latter. The possibility of product dimerization was addressed. If the substituents are small, dimerization is expected, which would make such materials unsuitable as a reversible hydrogen storage material. On the basis of these results and the structural trends that have been established, compounds such as $Me_2NH{-}BH(CF_3)_2$, $H_3N{-}BH(OTf)_2$, $Me_2NH{-}BH(OTf)_2$, and $F_2NH{-}BH(CF_3)_2$ are of particular interest for further investigations.

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Note Added after ASAP Publication. There was an error in reference 31 in the version published ASAP May 24, 2008; the corrected version published ASAP May 30, 2008.

Supporting Information Available: Full citation for ref 19; coordinates and energies for all presented structures; PCM energies for selected compounds in THF and toluene; tables showing dipole moments and NBO charges of some of the calculated molecules; bond dissociation enthalpies calculated on both the B3LYP/6-31G(d,p) and MP2/6-31G(d,p) level together with relative stabilities of the dehydrogenation products of these reactions; and a figure depicting the correlation between ΔH_B and ΔH_C. This material is available free of charge via the Internet at http://pubs.acs.org.

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(43) We tested the possibility that HOTf may be preferentially released rather than hydrogen. We found that, thermodynamically, this is not expected.

(44) It has been suggested that B3LYP may predict less exothermic reactions for dimerizations such as the ones described: Bissett, K. M.; Gilbert, T. M. *Organometallics* **2004**, *23*, 850. However, this was shown for only one example.

(45) Matus, M. H.; Anderson, K. D.; Camaioni, D. M.; Autry, S. T.; Dixon, D. A. *J. Phys. Chem. A.* **2007**, *111*, 4411.